

# VALUE Adding THROUGH SOLVENT EXTRACTION

VOLUME 1

THE UNIVERSITY OF MELBOURNE  
Department of Chemical Engineering  
Parkville, Victoria 3052 Australia

ISBN 0 7325 1250 6 (Set of 2 volumes)

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Printed in Australia

# VALUE Adding THROUGH SOLVENT EXTRACTION

VOLUME 1

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Papers presented at ISEC'96 - Value Adding Through Solvent Extraction, held at the Carlton Radisson Hotel, Melbourne, Australia, 19 - 23 March 1996.

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## FOREWORD

Solvent Extraction as a separating and purification technique has grown over the last century to a most powerful technique that has found application over a broad range of chemical processing industries, including metallurgy, nuclear, chemical, petrochemical, food, pharmaceutical and environmental waste management. It has drawn expertise from a broad spectrum of disciplines resulting in a literature that ranges from the more fundamental works on co-ordination chemistry, chemical kinetics, hydrodynamics of two phase systems, interfacial phenomena through to process development, equipment design and control.

In the Australian context solvent extraction has found most applications in the hydrometallurgy area with Uranium, Copper, Nickel and Cobalt primarily producing products worth in excess of \$500 million dollars in 1994. The use is expanding significantly with pilot plants for Nickel, Vanadium and Rare Earths in operation, as well as a number of major expansions and new developments under discussion.

There are also plants for lube oil and propane deasphalting in the petrochemicals area, for hop extraction using supercritical CO<sub>2</sub> in the food area and morphine extraction in the pharmaceuticals area amongst others.

A conference such as the International Solvent Extraction Conference brings expertise from around the world but also across a broad range of disciplines, resulting in a significant degree of cross-fertilisation.

One of the strengths of solvent extraction is its selectivity and so it is not surprising to see the development of many new extractants continuing with the aid of molecular modelling, in some cases helping in the screening of alternative structures. Also there is a continuing effort to incorporate the selective chemistry of these extractants into membrane devices, although the application of such devices is still limited. It seems that the pharmaceutical and waste treatment areas are the most fruitful for this technology.

An understanding of the hydrodynamics and mass transfer rates in a two phase liquid-liquid system is still far from complete and so there is a proliferation of different types of contactors to try to find the best performance for a given situation. The modelling of these devices has moved from the one dimensional axial dispersion model to population balance models but with the introduction of more empirical parameters resulting in loss of generality. So the search is on for a deeper understanding of the coalescence and breakage mechanisms and droplet hydrodynamics in these columns. Also the variety of contactors now present the process designer with a range of residence times in which the phases are in contact so that differences in kinetics of extraction can be exploited to even further enhance the separation achieved. This, however, requires a knowledge of the kinetics which is

another area that is currently receiving much attention. Thus Solvent Extraction research is going from strength to strength with the applications expanding into a range of new areas such as food, waste treatment, etc. and the synergism that comes from having a diverse group of people across a range of disciplines is always exciting.

I would like to express my sincere thanks to all the members of the Organising Committee for their hard work, without which this Conference would not have been possible. I would also like to thank the sponsors of the Conference, and the members of the International Solvent Extraction Committee for their advice and support.

The Organising Committee wishes to express their appreciation to all the authors for their contribution and to all the attendees, without whom there would be no Conference. We welcome you to Melbourne and hope you have a stimulating and enjoyable Conference.

Geoff Stevens,  
Chairman, Organising Committee

## PREFACE

The ISEC'96 proceedings have been written and compiled as a result of significant efforts from a number of people. We would like to take this opportunity to thank all those involved and in particular recognise the contributions made by the authors, reviewers and Dr John P. Kisler, who finalised all the manuscripts for publication.

All authors were requested to present their work within six pages. We recognise that this does constrain the amount of information which can be presented and were pleased to find that almost all authors met these requirements. Overall the willingness of authors to meet the guidelines or make adjustments to manuscripts based on the reviews has assisted us in presenting you with a very professional final publication.

We would especially like to thank authors whose first language is not English. In many parts of the world researchers still do not have easy access to word processors and we acknowledge the extra efforts required by them to meet the guidelines.

The technical standard of the conference has been assured by the many reviewers who read and commented on the manuscripts. A list of these is provided on the next page. All reviews were undertaken on a volunteer basis and included many from overseas locations. We thank them for their efforts and in particular their willingness to undertake a thorough assessment of the manuscripts they were responsible for, thereby ensuring that the ISEC'96 conference meets the standard set by the many ISEC conferences that have preceded it.

Finally it is the time and patience contributed by Dr Kisler that took the authors contributions and prepared them for our publishers. His effort enabled us to add that extra finishing touch to each paper, displaying the ISEC'96 logo.

We hope you find the information you seek within our publication and that they are well referenced over the years to come.

David C. Shallcross  
Rohani Paimin  
Leanne M. Prvcic

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## ISEC'96 is supported by

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## RECOMMENDED NOMENCLATURE

### SI UNITS

a	specific interfacial area
$a_p$	specific area of a drop
A	column cross-sectional area
$A_p$	amplitude of pulse or oscillation (stroke= $2A_p$ for reciprocating plates)
b	exponent
c	concentrations
C	coefficients ( $C_1, C_2, \dots$ )
$C_o$	orifice discharge coefficient
$C_d$	drag coefficient
d	drop size
$d_p$	packing size
$d_h$	horizontal diameter
$d_v$	vertical diameter
D	distribution ratio or diameter
$D_N$	nozzle diameter
$D_o$	orifice diameter in plate
$D$	diffusion coefficient
e	voidage or free area
E	axial mixing coefficient
$E$	degree of extraction (fraction extracted)
f	frequency
$f_n$	natural frequency
$f_v$	volume fraction
F	flow rate (volumetric)
$F_s$	shaft force
g	gravitational coefficient
h	height
H	compartment, stage or dispersion height
i	class number
I	intensity of agitation
J	flux
$k_B$	Boltzmann constant
K	equilibrium constant
$K_{oc}$	overall rate coefficient
L	length
$l_s$	shaft displacement

$L$	total column length or fluid thickness
$m$	equilibrium line slope, (solvent/aqueous or continuous/dispersed) or exponent
$M$	molecular weight
$n$	number of drops or exponent
$n_p$	number of plates or stages
$N$	agitator speed or number of transfer units or total number of stages
$p$	drop breakage probability
$P_s$	power per disc or turbine or stage
$\Delta P$	pressure drop
$r$	distance in radial direction
$r_o$	radius
$R$	flow ratio, dispersed/continuous
$R$	internal enhancement factor for mass transfer
$s$	Laplace variable
$t$	time
$T$	temperature
$U$	velocity other than superficial phase velocity (in drops, circulation, turbulent etc.)
$U_s$	shaft displacement velocity
$v$	volume
$V$	superficial phase velocity
$V_T$	terminal velocity
$V_o$	characteristic velocity
$V_k$	characteristic velocity
$V_{slip}$	slip velocity
$w$	mass or width
$x$	dimensionless aqueous concentration or distance in x direction
$X$	dimensionless distance x
$y$	dimensionless solvent concentration, or distance in y direction
$Y$	dimensionless distance y
$z$	fraction length
$z$	valency

## GREEK

$\alpha$	backflow ratio
$\delta$	film or plate thickness
$\lambda$	interfacial tension
$\sigma$	surface tension or second moment
$\tau$	a specific time
$\theta$	reduced time or angle from drop front
$\phi$	fraction or hold-up of dispersed phase
$\rho$	density
$\Delta\rho$	density difference
$\vartheta$	specific energy or power ( $\text{W}/\text{m}^3$ )
$\varepsilon_m$	viscosity or first moment
$\mu$	viscosity or first moment
$\lambda$	extraction factor $mF_{\text{solv}}/F_{\text{aq}}$ or coefficient
$\psi$	function
$\kappa$	viscosity ratio (dispersed/continuous)
$\eta$	efficiency
$\Gamma$	surface concentration of contaminant
$\nu$	number of daughter drops

## GROUPS

Ar	Archimedes	$\Delta\rho \rho_c d^3 g / \mu_c^2$
Bi	Biot	$d k m / D$
Bo	Bond	$g d^2 \Delta\rho / \gamma$
Eö	Eötvös	$g d^2 \Delta\rho / \gamma$
Fr	Froude	$U^2 g d$ or $N^2 D r / g$
Mo	Morton	$g \mu_c^4 \rho / \rho_c^2 \gamma^3$
Pe	Peclet	$Pe_d (dV/E)$ or $Pe_L (LV/E)$ or $d U/D$
Re	Reynolds (drop)	$\rho_c d^3 V_r / \mu_c$
Sc	Schmidt	$\mu / \rho D$
Sh	Sherwood	$kd/D$
We	Weber	$\rho_c d U^2 / \gamma$ or $\rho_c N^2 D_R^3 / \gamma$

## SUBSCRIPTS

a	aqueous
c	continuous phase
cr	critical
d	dispersed phase
e	effective value
f	flooding or formation

i	interface or <i>i</i> th value
j	jet
m	mean value
max	maximum
o	original (initial) value
p	plate
s	solvent
$\infty$	bulk value or at infinite distance
C	column
I	inlet
M	molecular
N	nozzle
R	rotor
S	stator
T	tank (for mixer or terminal)

**SUPERSCRIPT**

*	equilibrium value
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## SOLVENT EXTRACTION - A HISTORICAL REVIEW

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Trying to go back in history is like stepping on to unsteady ground. For we have to use our imagination to interpret the meaning of what the archaeologists have discovered. The result can't be a reliable scientific statement of engineering precision and reliability. Going back in history also means to interpret the object under study - in our case extraction - in its political, social and cultural setting. So half an hour's lecture won't provide more than a vague outline.

We can assume that the production of perfumes and medicines by extraction from flowers and leaves with the help of water is one of mankind's oldest technologies. Perhaps our ancestors succeeded in doing this while they were still hunters and gatherers, for even then they needed to learn how to observe cause and effect in natural processes. Or perhaps it was not until after that most decisive step in human history, the transition to agriculture and animal husbandry that required solid dwellings and settlements. Tilling the soil and breeding animals could only be successful once the regularity and constancy of natural phenomena had been recognized. The process of becoming settled took place about 7000 years ago in Neolithic times, a mere batting of an eyelid in terms of the earth's history, which comprises several billion years.

The cradle of human civilization may have been in Asia Minor, today's Turkey, and in Mesopotamia, the land between the Euphrates and Tigris rivers, today's Iraq, and also in Syria and Egypt. This is where the most ancient known advanced civilizations arose, with sophisticated state structures, monarchies, scriptures and worship of the dead. The oldest bronze finds of the Bronze Age that followed from Neolithic times come from Mesopotamia. The Babylonians may have mined the copper and tin needed to make bronze in the foothills of the Caucasus. The Egyptians had their own resources.<sup>1</sup>

As mentioned already, the development of extraction is closely linked with the search for medicines and perfumes. One of the most important crafts in Mesopotamia and Egypt was the making of ointments and perfumes. The products were mainly used for medical, religious and cosmetic purposes. There is said to have been tremendous extravagance in the use of ointments, incense and perfumes. For the rich the most important item in a daughter's dowry was an adequate selection of perfumes. Conversely an ancient Assyrian law states: "A man who casts out his wife gives her (...) neither oil, nor wool, nor garments." /LEV 59/. In ancient Egypt even the statues in the temples were salved three times a day. The fashion of the day required the oiling of people's heads and clothes. The ancient Egyptians must have been literally dripping with fats and oils.

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<sup>1</sup> In 213 BC ancient Chinese writings were destroyed by the Emperor Shi Hoang Ti to prevent innovations. Therefore we can't be sure whether alchemy and special chemical technologies were developed in his time or even earlier in ancient China /FIE 52/.

During ancient Egyptian feasts people carried perfumed cones on their heads. Body heat caused these to melt gradually and give off perfumes as the oils flowed down their bodies. What do we know about the earliest extraction processes and equipment?

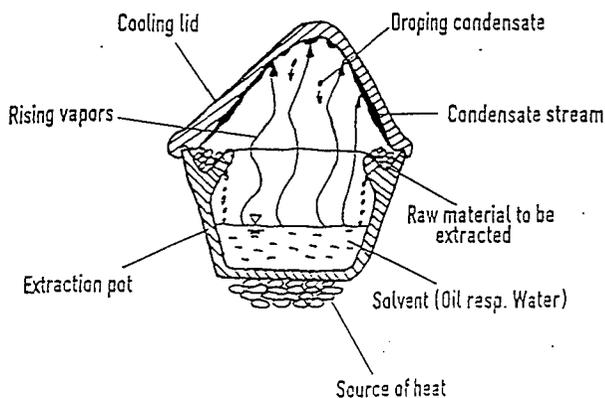


Fig. 3: Prehistoric extraction pot<sup>2</sup>

Excavations about 250 km north of Baghdad in Iraq yielded pots like these made of hard, sandy material, perhaps air-dried clay. They are estimated to date from about 3500 BC /LEV 59/. We assume that chopped vegetable or animal raw material was put into the surrounding groove and the bottom was filled with water or oil as a solvent. The whole pot was perhaps placed on a source of gentle heat such as fresh animal dung, which will have caused some of the solvent to evaporate. The rising vapours condensed on the lid through heat loss to the outside air, or on damp cloths. The condensate, which flowed down the sloping lid into the surrounding groove, extracted certain components from the raw material and with these dripped back into the bottom of the vessel through holes. This is termed a batch process. Other vessels had larger surrounding grooves with no drainage holes. So we can presume that a kind of extractive distillation method had already been invented. The biological raw material was put into the bottom of the vessel together with the solvent. The extract was evaporated by heating and the precipitated condensate was collected in the groove free of any solid impurities.

The discovery of ancient texts brought proof that a highly-developed pharmaceutical-chemical technology already existed in ancient Mesopotamia. The oldest preserved clay tablets which prove the application of extraction date from around 2100 BC. They were excavated about 400 km south of Baghdad /LEV 59/. Let's look at one of these texts showing how to make a medicine:

"Purify and pulverize the skin of a water snake; pour water over the AMASHDUBKASAL plant, the root of myrtle, pulverized alkali, barley and powdered fir resin; boil; let its (the extract) water be decanted; wash it (the ailing organ) with the liquid; rub tree oil upon it; let SAKI be added." /HOL 57/

<sup>2</sup> The majority of figures will first be shown during the lecture

Boiling water was used here as a solvent to extract the substances, as in many other recipes. The frequent use of alkali or common salt (NaCl) is interesting. These substances enriched the rising vapours with solutes by decreasing the water's steam pressure.

The raw materials used are from vegetable and animal sources. Here we read of pulverized snake skin, root of myrtle, etc., and we note that the process was intensified by mechanical and thermal means such as chopping and heating. In other texts we read that certain materials such as potassium nitrate were prepared before the extraction, and this indicates considerable knowledge of chemical technology. Since alkali is also mentioned, presumably obtained by steeping wood ash, we can presume an early knowledge of unrefined soaps and their uses.

Our full knowledge of extraction in those days is obtained from clay tablets from the time of the Assyrian king Tukulti-Ninurta I, who subjugated the whole of Mesopotamia around 1220 BC within an Assyrian empire. These describe extraction processes for the manufacture of perfumes. Perfumes were fragrant mixtures based on fats or oils, and thus also included ointments and salves. The authors of perfume texts were women. Other crafts involving chemical technology can also be traced back to the kitchen, the women's realm. All the pots made of glass, clay or metal, all the dishes, bottles, stirrers and stoves were at the same time also kitchen utensils.

**What procedures did they follow? /EBE 49/** They washed and dried the raw materials such as blossoms, roots, leaves, etc. Then they pounded them in a mortar. A part was left to steep for a day in boiled well water. The rest was slowly added to the suspension and once again left to steep. This principle made it possible to enrich the aromatic substances considerably in only a few stages. The mashes were probably strained, or else slowly heated as a suspension while oil was stirred in. This made the aromas merge into the oil which separated off as upper phase after covering and cooling. What we have here is a sequence of solid-liquid and liquid-liquid extraction just like that still used in laboratories today. They had also already discovered that oil can be made to absorb fragrances better by the addition of gum resins, for instance from Cyprus grass. Even then they improved the separation of fine dispersed emulsions by lining the clay sieves with wool or hair, like today's technical fibre filters, which are set in front of gravity separators to cause droplet coagulation.

Creating fragrant perfumed waters was much more complicated than producing ointments because it is difficult or even impossible to dissolve most essential oils in water. The various operations had to be repeated as many as forty times to get high yields. Not until 100 or 200 AD did Alexandrine alchemists start using distillation. This provided an elegant answer to the problem of how to separate a homogeneous phase into its volatile and less volatile components, so that the production of perfume based on alcohol became faster and easier.

**What do we know about the raw materials? /PAS 90/** The most important source of oil in Mesopotamia was sesame seed, since olive trees didn't flourish there. Sesame seeds contain up to a third of their weight in oil. Even today this is used in foods and as a preferred primary product for ointments. It was produced by mechanical and extractive processes. The abundance of plant varieties in the Near East provided a wide range of fragrant waters and salves without any dependence on imports. The earliest written proof of extraction being used in ancient Egypt is to be found in the oldest medical papyrus dated about 1600 BC. This was bought from an Egyptian by a German, Georg Ebers, in Luxor in 1872 or 1873. It became world-famous under the name of the "Ebers Papyrus" /JOA 73/. Beside fats and oils, alcoholic solvents such as beer

and wine are mentioned for the first time. These were only used because of their medical effectiveness and not because of any physical advantages. The similarity of the extraction procedures used by both the Babylonians and the Egyptians is remarkable and throws light on the varied connections between the two cultures. We have to note that neither the procedures nor the equipment of extraction were developed any further in either culture. It is assumed that a strong sense of tradition made people cling to old methods. They didn't investigate the physical and chemical phenomena even though mathematics and astronomy were highly developed in Mesopotamia by around 1000 BC.

The sophisticated cultures of Mesopotamia and Egypt began to be replaced by those of Antiquity, that is the great cultures of the Greeks and Romans, from about the 6th century BC onwards. The Greeks in particular, with their art, architecture, philosophy and democratic constitutions, laid the foundations of European civilization and history. The Macedonian king Alexander the Great created an enormous empire by his successful campaigns between 336 and 323 BC.

This empire stretched from Greece via Egypt and the whole of the Near East to India. I mention this in order to emphasize the possibilities that existed within it for reciprocal influences between the various cultures, especially since the Alexandrine age was very keen on science. After all, Aristotle, the greatest and most learned philosopher of the time, was the young Alexander's tutor and mentor. Aristotle occupies a special place in the history of alchemy, the forerunner of scientific chemistry, because he developed early theories, a theory of mixture and a theory of elements /STR 76/. These were exceedingly influential in western science for two thousand years. I will return to them briefly later. Nevertheless, neither alchemy nor procedures of chemical technology, such as extraction, made any worthwhile progress in Antiquity, apart from the invention of distillation around 100 to 200 AD. Skills of chemical technology were taken over virtually wholesale from the earlier cultures of Mesopotamia and Egypt in their use for producing medicines, salves and perfumes /SHE 85/. This is documented in many works by Theophrastus, a pupil of both Plato and Aristotle, from around 300 BC, as well as in those of Dioscorides from Anazarbas, today's Ainvarza near Ankara, as around 50 AD. It is now thought that the Greek philosophers so much disdained crafts of any description that the connection between theory and practice failed to be noticed and therefore no scientific experiments were made. Social conditions also stood in the way of progress. The ruling classes were anxious to retain the status quo while the suppressed classes were too weak to change things. Nothing changed when the Romans came to the fore in later Antiquity either, because the Roman Empire developed a martial culture that devoted all its intellectual potential to the arts of state and war and not to the craft of extraction.

There are some Roman texts showing systematically and in detail the various stages of extraction, for example in the writings of Dioscorides. He had travelled widely as a Roman military physician early in the first century AD and compiled a general pharmacopeia for physicians in his "Materia medica" /FES 67/. There was no appreciable change in extraction equipment.

Fig. 6 shows a closed outer cylinder as insulation against the environment. Inside it is another closed cylinder which could be taken apart into three pieces. In the inner vessel raw materials were extracted by means of solvents at temperatures that could be regulated. The heat caused the solvent to evaporate. This then condensed in the upper part and flowed down to the bottom. It remained within the extractor and could be considerably enriched with extracted substances. The outer cylinder had an insulating function.

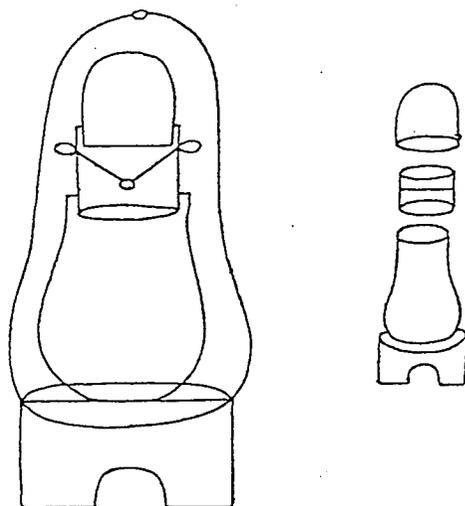


Fig. 6: Vessel for digestion /BER 67/

We mustn't forget the Arabic period that followed on from Antiquity. It began in the 7th century when waves of migration away from the Arabian peninsula took place which culminated in the conquest of Syria (in 636), Egypt (in 641) and finally Spain (in 718). The Arabians took over and cultivated the sciences of Antiquity. The scientific and medical texts of Antiquity were translated into Arabic on a grand scale, as a result of which they survive today /GAR 48/. Pharmacology reached heights hitherto unknown and the first pharmacies were founded. The experimental and functional techniques these required were above all extraction and distillation, and these were taken over from those used in Alexander's time. In other words there were no new developments, only further development of traditional methods. The Arabs benefitted from the fact that, in contrast to Greek philosophy, alchemy concentrated on experiment and craftsmanship, so that experimental chemistry came into being. However, this was chiefly engaged in the vain search for a substance, a quintessence, that would turn base substances into precious metals such as gold. For the first time there is a description of liquid-liquid extraction for removing pigment from oil using water as the solvent. However, it is likely that this procedure, too, was taken over from the Mesopotamian cultural region /ENG 86/. A new development was the use of liquid-liquid extraction for the purification of sugar with the help of milk and lime water as solvents, although the equipment used was traditional /FES 67/. The sugar-cane, grown chiefly in Egypt and the coastlands of the eastern Mediterranean, was squashed by large stone rollers. The resulting juice was thickened by evaporation. This viscous liquid was re-diluted several times with milk. Scum containing impurities formed on top of the milk and could be skimmed off: a flotation process. A solution of unrefined sugar resulted. From the 12th or 13th century onwards this unrefined sugar solution was refined by the use of lime water as the solvent. The sugar was then taken extractively from the syrup into water by pouring water over it, which freed it of any impurities.

We have now arrived at the Middle Ages, the thousand years stretching from 500 to 1500 AD between Antiquity and modern times, a period of enormous political, social and intellectual upheavals. The emperor Charlemagne dominates the early Middle Ages. Under him the Carolingian, Franconian Empire took the place of the former western Roman Empire. Influential towns grew up in Europe between 900 and 1300. Urban culture developed with its trades, its crafts and their guilds, its free citizens, its market rights and its currency laws. Intellectual life flourished and a great number of law schools and universities were founded. Translations from Greek and Arabic led to a revival of the works of Aristotle after more than 1500 years. Together with the works of Arabian authors these led to the first scientific discussions of natural phenomena. Finally, the late Middle Ages up to 1500 experienced an abrupt downfall in Europe unleashed by terrible plagues that wiped out more than a quarter of the population, famines, peasant uprisings and revolts in many larger towns, and devastation of the countryside by wars. Only when the Renaissance began to spread across Europe from Italy around 1500 did joie de vivre and hope return. Leonardo da Vinci, painter, architect, scientist and engineer, gave expression to this period. The sciences began to break away from theology while the invention of printing, gunpowder and the pocket watch, modern forms of money economy and the discovery of America provisioned a new era.

**What about extraction in the Middle Ages and the Renaissance?** With a great number of new methods it extended to all the crafts. No longer the alchemist's laboratory but the technology of chemistry now spurred its development. The sugar industry, which until the 17th century had served mainly medicinal purposes, flourished, although refining techniques didn't differ from those of the ancient Egyptians. The same went for essential oils and salves. Ethanol, discovered during the Middle Ages around 900 AD, was the only innovation. It was obtained by distilling wine and served as a solvent in perfume production for which it increased extraction yield and the purity of the product.

The most important innovation were the metal extraction methods used in the metallurgy. Descriptions from as early as 1100 give the first indications of the separation and purification of various metals, particularly precious ones such as gold and silver, using additional substances /FES 67/. The first addition used was mercury, that had already been known to the Egyptians, and thus also the Greeks and Romans, as an amalgam with copper and tin. In the Middle Ages it was evaporated from the ores by the application of heat, after which the pure liquid was obtained by cooling. The toxicity of its vapour was already known, but nobody cared about the lives of the workers. Mercury was used as a chemical solvent to extract gold from pulverized gold ore. The resulting gold amalgam flowed as a liquid from the ore and was pressed through deerskin to be cleaned: an early diaphragm technique. Salts were added to the gold amalgam so that remaining metallic impurities could be bound to high boiling chlorides. Then the mercury was evaporated by heating, leaving behind the gold with the chlorides, which were easily removed.

To separate gold from silver the mixture was melted with sulphur as the solvent for as many times as were needed to change all the silver into black silver sulphide ( $\text{Ag}_2\text{S}$ ), after which the pure gold remained. The mineral acids, sulphuric acid, nitric acid and hydrochloric acid, were mentioned for the first time by an unidentified author at the end of the 13th century. These were obtained by means of several recipes from vitriol, saltpetre, alum and common salt that had in turn been won by steeping stones or loams, followed by crystallization as shown in the famous work "De re metallica" by the German Georgius Agricola who, in detail and with an abundance of detailed illustrations, described the mining and foundry techniques of the late Middle Ages.

**The mineral acids paved the way for metal extraction /FES 67/.** By solid-liquid extraction the metals were extracted from the crushed ores with the help of mineral acids as chemical solvents, in the same way as the process already described for mercury. Thereafter the solvent was removed by distillation. The various processes took place in temperatures ranging from that of the surroundings to 900 degrees C., which shows that smelting technology was already quite sophisticated. It can be said that the Middle Ages saw the most creative stage of the older metallurgy. By the beginning of the 16th century a proper metallurgical industry comprising many different methods but still using the old familiar equipment had grown up in Central Europe. From the middle of the 16th century onwards the more productive mining centres in Mexico, Peru and Bolivia had begun to outstrip the European ones.

Four hundred years ago the all-round scholar Andreas Libavius (1550-1616) wrote the first extant systematic textbook on chemical technology /FES 67/. In it he described more than 60 unit operations for the treatment of substances and gave systematic descriptions of all the corresponding equipment. The progress shown is mainly in the use of new solvents that enabled a wider application of the procedures while also making them more profitable. An "Almanac for Separation Experts" from the year 1780 mentions 17 solvents for about 120 applications. Pharmacology was prominent in transmitting and further developing knowledge about extraction /GÖT 80/. But otherwise traditional, one-stage extraction equipment dominated, which did not exactly enhance the efficiency of the process.

Finally, with a description of the Industrial Revolution in Europe that took place between 1750 and 1850, we come to the transition to modern times. Industrialization brought changes in the sciences, in production techniques, technology, energy sources, the transport system, markets, population and social structures. Here, however, we are concerned with the fate of alchemy and extraction techniques. By the late Middle Ages Aristotle's 2000-year-old theory about earth, water, air and fire as the four basic elements in all substances no longer provided sufficient explanation. At the end of the 18th century the Frenchman Lavoisier opened up the path to modern quantitative chemistry after his discovery of oxygen. And in 1869 the periodic system of elements finally overcame Aristotle's theoretical system /FIE 52/. Physical chemistry began to develop rapidly in the second half of the 18th century. I could mention the theorem of classical thermodynamics, the formulation of the law of mass action and of chemical equilibria, the introduction of the phase law and of chemical potential, not to mention Walter Nernst's distribution law that has become in our century the calculation basis for physical equilibria in connection with physical liquid-liquid extraction. As early as 1880, MIT in the USA inaugurated courses leading to qualification as a Chemical Engineer. The leading founders of these courses were scientists in physical chemistry. The older individuals among these worked for their Ph.D. at German universities and used their physical-chemical grounding to bring chemistry and engineering together under the heading of Chemical Engineering. Both the physical calculation of extraction processes and the engineering design of extractors profited as a result. In solid-liquid extraction considerable progress resulted from the continuous operation of bucket-conveyor extractors /FIS 83/ and from the use of screw conveyors for the transport of solid materials through the extractor. In liquid-liquid extraction the extraction patent obtained by the German engineer Paul Pfleiderer marked the start of a new era in 1898 /PFL 98/. This is the first stirred column that points to a capacity to think in terms of both physics and chemistry. Continuous counter-current phases, dispersion of one phase to intensify mass transfer, stirrers to redisperse and produce turbulences. Today we have a great variety of continuous counter-current extractors. Nowadays the processes of multiphase flow and of physical and chemical mass transfer are almost entirely understood, and usable calculation models have been developed. The equilibrium of many of the still increasing number of solvents can be predicted.

There is no need here to follow the further development of extraction by Chemical Engineering in the 20th century, for it is described in detail in current textbooks, in particular the "Handbook of Solvent Extraction" edited in 1972 by Lo, Baird and Hanson, and "Principles and Practices of Solvent Extraction" edited by Rydberg et al. in 1992, or "Liquid-Liquid Extraction" edited by Godfrey and Slater in 1994. As the papers for ISEC 96 promise, the main focus in the future will be on the application of chemical extraction for the reprocessing of sewage, for the chemical industry, for biotechnology, and for the extraction of metal salts. Research will continue to be concerned with equilibria, to grapple with the influence and calculation of surfactants and to align fluid-dynamic and mass-transfer calculations with first principles. Extraction has a long past and looks set for a great future.

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## NEW TOOLS FOR OLD QUESTIONS IN SOLVENT EXTRACTION CHEMISTRY

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### INTRODUCTION

For at least the last half century fundamental questions about the solvent extraction process have occupied the attention of chemists, chemical engineers, and hydrometallurgists. Understanding the underlying factors can be of vital significance in learning how to improve selectivity and sensitivity of extractions of metal ions. Kolthoff & Sandell(1941) were the first to investigate chelate extraction equilibria on the dithizone system. Systematic examination of thermodynamics of extraction arose in the 40's when factors affecting chelate stability began to emerge from formation equilibrium studies that started with J. Bjerrum(1941) and Calvin(1945) and soon thereafter taken up by analytical chemists Mellor(1947, 1948), Freiser(1952), and Irving (1952) as well as by inorganic coordination chemists. This resulted in the realization that most 'specific' reagents merited that designation by virtue of special physical properties or reaction conditions rather than by unusual chelation stability sequences. In fact, the dream of the early workers of developing a set of specific reagents that would react with only one metal ion each, gave way finally to the realization that one could not have specific reagents, but only a set of reaction conditions which could maximize the selectivity of the reagent. The search for specific metal reagents was understood to be more difficult when the finding that most reagents exhibited the same stability sequence for metal ions found by Mellor and Maley(1947, 1948): Pd > Cu > Ni > Zn > Co > Mn > Fe > Ca > Mg. These studies uncovered structural factors affecting the course of chelation reactions, such as the effects of electronegativity, steric hindrance, and  $\pi$ -bonding on the thermodynamic parameters associated with the formation of metal chelates. These, in turn, provided a basis for clarifying and elucidating the molecular structural factors that govern extraction equilibria and in turn, a basis for predicting selectivity Morrison and Freiser(1957). During this period, significant contributions to the understanding of the structures of metal chelates were also achieved with the aid of studies involving UV-VIS, IR, PES, and paramagnetic spectra, as well as X-ray crystallographic structure determinations.

Starting in the early 60s, our group, recognizing the vital role of kinetic aspects of extraction processes the understanding and control of practical separations, pioneered in systematic studies in extraction kinetics and in the utilization of the experimental findings to both fundamental and practical questions. In single stage kinetic studies, employing high-speed stirring extraction apparatus McClellan(1964), we were able to demonstrate that, for almost all metal chelate extraction systems, the rate-determining step(s)(rds) involve chemical reactions, rather than mass transfer and diffusion processes. The second order rate constants were found to be proportional to the rates of dehydration of the aquated metal ions. Other studies in this period include the

finding that simple aqueous phase metal complexes(e.g.,acetate, thiocyanate) can enhance metal extraction rates Subbaraman(1969) and Colovos(1975). The rates of back extraction of metal chelates were limited by the rates chelate dissociation Ohashi(1980) but were also enhanced by the presence of simple aqueous complexing agents. Hence, we were able to determine mechanistic pathways of chelate formation and dissociation as well as to devise selective methods based on time-resolved extractions.

This paper describes the results of a number of relatively new approaches(ATMES, MM, ATR, and CPC) to the study of the extraction process in general and the characterization of the L-L interface in particular. We began our study of the role of the interface in extraction processes Watarai(1982) by utilizing an Automated, microporous Teflon phase separator-equipped high speed stirring Extraction System(ATMES) and were able to differentiate between rds occurring in the bulk aqueous phase and those at the interface Watari(1983). This approach reaches a limit, however, imposed by the minimum droplet size of the organic phase obtainable( ca. 100 micron) and hence a maximum interfacial area. To study the effect of still larger interfacial areas, we adopted micelles as models(MM) of L-L phase pairs. Micelles possess structures analogous to the highly dispersed two-phase system are therefore suitable models with which to address the influence of high interfacial areas on metal complexation and decomposition reactions that are important in solvent extraction experiments. We have examined the kinetics of metal chelate formation in the presence of micelles produced by surfactants of various charge types with a stopped-flow apparatus, Chen(1994). The results bear out the validity of the model and are significant in the understanding of extraction processes.

Another novel method for determination of solvent extraction equilibria and kinetics using infrared attenuated total reflectance spectroscopy (ATR) was developed which allows complete, quantitative determination of equilibrium and kinetic parameters of metal chelate extraction systems using a total of one gram of extractant, Sperline(1992). Furthermore, as a spectroscopic tool, ATR offered the possibility of studying speciation as well as stoichiometry of the reactants and products at the interface.

Finally, we have adapted the recently developed technique called Centrifugal Partition Chromatography(CPC), Muralidharan(1994), originally developed for separations of organic and biochemical substances of interest in biotechnology, to the separation of metal ions, Muralidharan(1990), Surakitbarnharn(1991). We have found CPC to be eminently suitable for testing strategies for micro and macro scale separations of metal ion mixtures as well as for examining hypotheses for mechanisms of L-L transfer processes.

## NEW TOOLS FOR DEFINING EXTRACTION SYSTEMS

### **The Automated Teflon Membrane Extraction System(ATMES)**

In the 70s, the newly developed hydrometallurgical chelating extractants, long chain alkylated derivatives of classical laboratory chelating agents, brought to the fore questions concerning the surface activities of these extractants, their possible adsorption at the liquid-liquid(L-L) interface, and the consequent effect on the equilibrium and kinetic aspects of metal ion extractions. Previous workers, Flett(1977), focussing on the low aqueous solubility of such reagents, e.g., 2-hydroxy-5-nonylbenzophenoneoxime (LX65N), simply assumed that their aqueous

solubilities could be ignored and that chelate formation in the L-L interface was the site of the rate-determining step. Our own work with the high speed stirring extraction apparatus demonstrated that the rate constants obtained in the extraction of  $\text{Cu}^{2+}$  by LIX 65N could be well represented by an aqueous phase-located rate-determining step, Carter(1980). Such differences led to countless stimulating discussions at various meetings and conferences, and were finally resolved by the work of H. Watarai(1983a, 1983b) who, using a microporous teflon phase separator-based extraction system, Watarai(1982), found that there are several mechanisms operating in chelate extraction, differentiated by the location of the rds: a) bulk aqueous phase, b) interface, and c) concurrent reactions in both sites. The use of ATMES provides us with the ability to separate the bulk organic phase from both aqueous phase and interface, enabling us to distinguish readily and unequivocally, reactions whose rate-determining steps(RDS) occur in either (a), (b), and (c). Unequivocal evidence of the role of the interface even with relatively low molecular weight extractants as 8-hydroxyquinoline, Aprahamian(1985), when we learned that there was a limit to the extent of interfacial area produced by vigorous stirring, Aprahamian(1987), producing the plateau in rate constants previously attributed to the absence of interfacial effects on kinetics.

Kinetic measurements. With ATMES, a circulating sample(~1%) of the clear bulk organic phase is removed from the reaction flask continuously by means of a selective microporous teflon membrane, its absorbance, A, is recorded as A(t), and the results are fitted to pseudo first order kinetics. Metal complexation reactions are inherently rapid, with second order rate constants varying from  $10^3 \text{ M}^{-1}\text{s}^{-1}$  for  $\text{Ni}^{2+}$  to  $10^9 \text{ M}^{-1}\text{s}^{-1}$ , but by using the distribution of the ligand between an organic and aqueous phase, relatively large half-lives which are, therefore, easily measured are achieved. ATMES can be used to measure half lives as low as ~20s.

Equilibrium Adsorption experiments consist of measuring the  $\Delta A$ (absorbance) of the 'filtered'(through the microporous teflon membrane) organic phase observed over a range of stirring speeds for a series of increasing concentrations of reagent and extracted chelates. The  $\Delta A$  values are used to calculate a Langmuir isotherm for each of the interfacially active components. As a matter of course, absorbance values are also employed to measure extraction equilibrium constants. Recently, we interfaced the FT/IR to this system in order to monitor systems involving aliphatic reagents, Majdan(1989). The introduction of infrared spectroscopic measurements in the ATMES opens up a whole new dimension of eligible systems accessible to both equilibrium and kinetic studies which give us greater freedom in our selection of interesting systems to examine.

In addition to the information concerning interfacial processes, reaction mechanisms for interesting metal chelate formation and dissociation reactions in the bulk phases are also determined. As an example, an interesting comparison and contrast between the extraction behavior of 8-quinolinol(QOH) and its S-analog, quinoline-8-thiol(QSH) reveals that while only the anion of QOH,  $\text{QO}^-$ , is interfacially active, both QSH and  $\text{QS}^-$  exhibit interfacial activity, Chen(1993). The rate constants in the bulk aqueous phase of the formation of the 1:1 Ni complexes for both QSH and  $\text{QS}^-$  are similar to those of the 8-quinolinol. The interfacial rate constant for the  $\text{QS}^-$  was only twice that of that in the bulk phase, in marked contrast to the  $\text{QO}^-$  which was over tenfold larger.

### **Micelle Models(MM) of Solvent Extraction Systems**

ATMES experiments suffer from two major limitations. First, the smallest drop sizes attained by high speed stirring are 150 - 200  $\mu$ , making it impossible to achieve the desired higher range of interfacial areas needed to fully study the role of the interface. Second, when the reaction half-life,  $t_{1/2}$  is below ~20s, reliable kinetic data are not achieved, putting many interesting systems beyond our reach. These limitations are overcome by (a) using micelles, which we have demonstrated, Muralidharan(1990), Chen(1995), are valid models for solvent extraction systems, having an exceptionally high interfacial area to volume ratio, together with (b) **stopped flow kinetics** apparatus capable of reliably monitoring reactions whose  $t_{1/2} \geq 0.4$  milliseconds. This provides a method of describing metal complex formation and dissociation reactions in micellar systems which has led us to application of the approach to examine a wide variety of metal chelate extraction systems of analytical significance, Inaba(1993, 1995). Study of the temperature dependence of the kinetic behavior in a variety of micellar systems is rewarding; e.g., we found that, while activation parameters for the dissociation of the Ni complex of 2-methyl-quinolin-8-ol are identical in water and in the neutral micelles, they are significantly different in anionic and cationic micellar systems, indicative of special interactions in these cases, Cai(1995).

The greatly enhanced range of formation and dissociation half-lives accessible to stopped flow measurements and the successful validation of micelles as models of extraction systems will enable us to characterize the kinetics and mechanisms of many interesting extractions and back extractions of metal ions that react too quickly to be observed reliably in the ATMES system. This has proven especially useful already in aiding our understanding of CPC(v.i.).

### **FT/IR Attenuated Total Reflectance(ATR) Studies of L-L Processes.**

A novel spectroscopic method, combining conventional bulk transmission and attenuated total reflectance(ATR) IR measurements in a known geometry was developed, Sperline(1986), at the University of Arizona, enabling us to calculate from the enhanced absorbance in ATR, values of  $\Gamma$ , surface excesses, at aqueous - organic liquid interfaces as well as at liquid - solid interfaces.

Using Apiezon M(ApM) as a representative of an aliphatic hydrocarbon solvent (in which chelate agents and metal chelates can be dissolved) and an aqueous phase at controlled pH and metal ion content, we have been able to distinguish between components dissolved in the bulk organic film and those which are adsorbed at the interface in addition to determining the extent of adsorption at the organic-aqueous film interface, Sperline(1987, 1990).

We developed a novel method for study of solvent extraction equilibria and kinetics using ATR which allows complete, quantitative investigation of an entire system using a total of one gram of extractant, making this an economical method for evaluation of new, commonly unavailable and/or possibly expensive reagents, Sperline(1992).

### **Centrifugal Partition Chromatography(CPC).**

We have recently adapted to metal ions separations, the relatively new multistage separation apparatus referred to as Centrifugal Partition Chromatograph(CPC), a compact, multistage countercurrent distribution device depending on centrifugal force rather than gravity to move one liquid(mobile) phase through the other(immobile) phase, Muralidharan(1990), Surakitbarnharn(-1991). Originally developed for application to biotechnological separations, we have found CPC

to be eminently suitable for testing strategies for micro and macro scale separations as well as for examining hypotheses for kinetics of L-L transfer processes, Surakitbarnharn(1991), Chen(1994). For example, even with the most selective extractants, results obtained in single stage experiments are not good enough to obtain complete separation. CPC allows us to achieve complete separations of adjacent trivalent lanthanide metals, Muralidharan(1994). Our studies revealed that the CPC chromatographic band width was sensitive to the nature of the lanthanide metal (light vs. heavy), the flow rate of the aqueous mobile phase, and its pH. In fact, one of the most important findings of our studies is that, while chelate formation and dissociation kinetics are a contributing factor in determining the utility of single stage extraction procedures, such considerations are **vital** in multistage operations. It is of relatively little importance whether an extraction reaction takes two to three minutes before achieving equilibrium in a single stage procedure; one can hardly work fast enough to be concerned. In CPC and other multistage separations, however, reactions whose half-lives are as low as 1 second, seriously compromise chromatographic efficiency. We have compared the kinetics of back extraction by means of stopped-flow kinetic studies in Triton X-100 micelles, which we found to function as model systems for the corresponding two phase CPC system, and found linear correlations between the half-life of the back-extraction reaction and the chromatographic inefficiency(CETP -defined in an analogous manner to the HETP).

Not only do such studies point clearly to the applicability of kinetics principles to the improvement of chromatographic efficiency, but also also provides a novel and simple method of studying relatively fast reaction kinetics( half-lives of under 100msec), Chen(1994).

While this review of several new approaches to the still fascinating problems of L-L separation processes is far from complete, I think it speaks of a renewed interest of a broad and growing segment of separation scientists that guarantees further advances in this critically important area of science and technology well into the 21st century.

#### ACKNOWLEDGEMENTS

The author is deeply indebted to and grateful for the inspiration provided largely by his graduate students and postdoctoral research associates without whom this work could never have been accomplished. The generous assistance of the National Science Foundation through the years is gratefully acknowledged.

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## SOLVENT EXTRACTION PROCESSING PLANTS - PROBLEMS, ASSESSMENTS, SOLUTIONS

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### ABSTRACT

Solvent extraction plants should be reasonably trouble-free, for the process has (or should have) been designed on the basis of: sound chemistry; reagents selection; mass transfer characteristics relative to the kinetics, equilibrium, stages; the influence of the continuous phase and the influence of the amount and type of shear required for mass transfer; possibility for the formation of stable emulsions, precipitates, and cruds; selection of the appropriate contactor for the process, and its proper operation; automation and control; and the engineering scale-up.

However, it is rather surprising that, after almost 50 years of commercial solvent extraction plants that the above fundamental criteria for design are, to a large extent, ignored. The result has been that almost without exception there are problems in the solvent extraction operations. These "problems" are often not understood, for the plant operators recognize that something is not performing to design and so the "symptom" is treated and not the cause. The problems or "symptoms" noted by the operators include the following:

- low solvent loading
- poor quality product (loading to saturation, scrubbing, selective scrub, wrong extractant, co-extraction vs selective extraction)
- degradation of solvent (in process and in Cu tankhouse)
- cruds and emulsions
- precipitates
- excessive solids in the feed (reduction to less than 20 ppm)

Very rarely is the fact that the choice of equipment and its operation could be the problem, and in fact, is usually not considered or tested during the plant design.

Of course the above have been the cause of high operating costs in the several plants because the source of the problem has not been determined, nor corrective actions taken. Instead, very expensive ancillary processes and/or equipment are employed to "reduce the impact on the process economics".

This discussion will cite a number of plant situations encountered by the author, using examples of Cu, U, Cd/Ni, Co/Ni, Zr, and Rare Earth operations, to demonstrate the various problems that were encountered and the steps suggested or taken to improve the operation.

### INTRODUCTION

Solvent extraction as one of several unit operations in hydrometallurgy processing and refining has now been operative for over 45 years. The development started with the nuclear industry, first with

the refining of uranium using ether as the extractant in the late 1940's, soon followed by TBP as the safer extractant. Then the extraction process was taken to the uranium mills in the mid 1950's to provide an up-graded uranium product. Plants and refineries to that date were not large. Then with the copper industry recognizing the potential benefits of the solvent extraction process, the first large copper SX plant went on-stream in 1969. Thus from that time the SX process became generally accepted and larger copper plants were to be placed in operation.

Since that time there have been a considerable number of SX operations, of all sizes in the mining/metallurgical industry from the very small precious metals circuits and the radionuclide and reprocessing circuits, the medium size rare and less common base metals, and to the larger base metal plants. Now there are processes developed for virtually every metal in the periodic table of elements. Some of the processes are in operation, some have reached the pilot plant stage, while others are still in the development and optimization stages.

In addition to the mining/metallurgical industry, which of course accounts for the greater tonnage of solution treated and products produced, there have been the developments and plants for the production of inorganic salts, production of pharmaceuticals, petrochemicals, and the application to the food industry.

Thus there have been considerable technologies and process applications already developed for the extraction, separation and refining of metals and other constituents by solvent extraction processing. As my background is in metals separation, this paper will address that area.

There are many aspects to be considered in the design of the solvent extraction process, and include the following important areas:

- Chemistry - Extractants, Modifiers, Diluents
- Mass transfer - Dispersion and Coalescence
- Equipment - Selection and Operation
- Economics
- Environmental and Solvent Losses

All impact on the possibility of the successful design, and if some are partially ignored then problems in the plant operation can be anticipated.

In this paper several plants experiencing problems in the operation were examined and solutions were proposed and implemented to increase the overall efficiency and thereby reduce the operating costs. Also included are aspects of extractants, diluents and contacting equipment. Specific deficiencies are noted, as well as areas where modifications could result in substantial improvements in plant operations.

The "key" in all situations was to first determine, logically, the possible cause of the "problem" by:

- a) characterizing the "problem" by various analyses
- b) verifying "suspected cause" in bench tests
- c) subsequent testing on a continuous circuit
- d) determining, by tests, possible solutions to the problem
- e) testing options in a continuous circuit
- f) evaluation of the relative economics of the treatment procedures
- g) selection of the best option and application to the plant

## PLANT PROBLEMS AND ASSESSMENT

Several plants were assessed as regards plant performance, samples tested, analyzed, cruds characterized (Ritcey, G.M., 1988), and recommendations made to improve the total performance and thus reduce costs. Because of the constraints in length of the paper, only summaries are presented.

The plant assessments have indicated that there are numerous causes of plant inefficiency. However one of the common causes that has been demonstrated is that of the solvent being fouled resulting in decreasing rates of coalescence, decreased loading, and ultimately reduced throughput. The high shear of most of the contactors (high shear mixer settlers), together with colloids of Si, Al, and ore slimes and fines enhances the problems. More attention has to be paid during the process design, piloting and ultimate plant scale-up to ensure that such possible costly problems will not occur. Each plant will be site-specific, and therefore a good interface between the metallurgists involved in the process design and the engineers involved in the plant design is necessary.

### Some Problems Due to Silica

It was evident in many examples that Si, in its various forms, could provide a problem, and enhance the possibility for the formation of cruds. Following are some conclusions (Ritcey & Wong, 1988; Ritcey, 1982, 1985, 1986).

- 1) The presence of Si can cause or enhance the formation of cruds and emulsions.
- 2) Most cruds are composed of Si as the major constituent, together with Fe Mg Ca Al and the metal being extracted.
- 3) Unless there is a scrub stage between extraction and stripping, Si and other impurities may carry-over and appear in the strip product.
- 4) Organic continuous operation appears to minimize emulsion formation in the presence of Si.
- 5) The presence of humic acids together with Si enhances emulsions and cruds, as does high shear.
- 6) Solutions containing colloidal silica, in the aqueous continuous system, are severely retarded in phase separation rates and tend to form stable emulsions. Noticed in amines, alkylphosphates and oximes systems.
- 7) Colloidal silica and low molecular weight amines result in slower phase disengagement than higher molecular weight amines.
- 8) Most emulsions are produced by a third phase emulsifier consisting of a colloidal substance (such as silica-alumina, hydrosols or clays, ferric or aluminum hydroxide or colloidal phosphate).
- 9) Each emulsion or crud has its own characteristics and require laboratory identification. Methods of identification include microscopic, X-ray diffraction, infrared and emission spectrographic techniques.
- 10) TBP emulsions are stabilized by silicic acid.
- 11) Temperature, acidity and nature of the aqueous phase have considerable influence on the stability of the TBP emulsion in the presence of silicic acid.
- 12) Possible methods of prevention include:
  - changes in pH;
  - addition of flocculating agents to remove the emulsifier;

- addition of dispersion agents to disperse the emulsifying phase;
- change plant practice to avoid formation of the surface active materials;
- addition of fluoride or other complex to solubilize the silica colloid.

## EXTRACTANTS AND DILUENTS

### Extractants

The extractants used in the development of metals separation and refining processes have been, for the most part, the common extractants including the following: TBP, tertiary and quaternary amines, various oximes, DEHPA and other newer alkylphosphorus extractants, and carboxylic acids.

Other extractants that are or have been used to a lesser extent include the primary and secondary amines, MIBK, substituted quinolines, dinonylnaphthylsulfonic acid, phosphine oxides, and phosphine sulphides.

There are also many other excellent possible reagents such as crown ethers, eg., n-octanol in solution of ditertiarybutyldicyclohexano-18-crown-6 ( $\text{DtBuCH}_{18}\text{C}_6$ ); and bifunctional organophosphorus compounds (including the diphosphonates, diphosphinates, and diphosphine oxides), which have a demonstrated capability and use in the treatment of radionuclides and other constituents in the reprocessing of nuclear wastes (Musikas and Schulz, 1992). Two carboamoyl organophosphorus extractants that have proven useful for such waste solutions are dihexyl-N,N-diethylcarbamoylmethyl-phosphonate  $[(\text{C}_6\text{H}_{13}\text{O})_2\text{POCH}_2\text{CON}(\text{C}_2\text{H}_5)_2]$  and octyl (phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide, [CMPO;  $\text{C}_8\text{H}_7(\text{C}_6\text{H}_5)\text{POCH}_2\text{CON}(\text{CH}_2\text{CH}-(\text{CH}_3)_2)$ ]. However these compounds, and many others noted at this ISEC and previous conferences and in the literatures, are still expensive and therefore perhaps most useful for the treatment of small flows. Therefore the "non-industrial" reagents are not considered here.

In addition to the metal recovery systems there is also the opportunity for the use of SX in the application to the recovery of by-products, acids, and also in effluent control. All the above reagents would be considered, depending upon the specific problem and application.

Extraction has been primarily from  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{H}_3\text{PO}_4$  solutions. To provide information as to the particular extractant or extractants of possible application to the recovery and separation of specific metals or components is beyond the scope of this presentation. Rather, the aim is to show where, in spite of the large number of extractants presently available, there are deficiencies in aspects of extraction, scrubbing and stripping. These factors, together with the rates of reaction, will thus affect the selection of the contactor and its operation in a particular system.

### Problems and Opportunities

Already there are a number of available commercial extractants. Why does the industry require new extractants?

Most extractants and their performance depends on several parameters, singly or together, including: acidity or basic properties, anion concentration, oxidation state/valency of metals to be separated, and relative extraction kinetics, usually enhanced as a function of increase in temperature. In the evaluation of possible extractants, not only does extraction have to be considered, but also the

scrubbing and stripping characteristics. That is, an extractant may exhibit excellent extraction performance, but may be difficult to scrub or remove contaminants, or to recover the desired metal without difficulty in stripping.

Some extractants are more easily degraded than others, and most extractants may contain unreacted products of the manufacture. Because some will co-extract undesirable metals or organic acids readily and therefore act as a "poison", the chemical properties are effected (loading, extraction efficiency, and scrubbing and stripping) as well as the physical operation (emulsions, high entrainment, poor coalescence and cruds).

To consider whether there is, or should be, a demand for new and better extractants, we must consider the extractants we have at present and determine their deficiencies. These will be considered under the following 3 headings: solvating, anionic (ion association), and cationic (includes chelating).

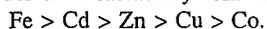
### **Solvating Extractants**

The performance of the solvating agents depends on the acidity and/or anion concentration, oxidation state/valency of metals to be separated, and relative extraction kinetics. Under specific conditions, TBP has the capability for the treatment and recovery of most of the metals in the periodic table, depending on the anion and its concentration, free acidity, valency, etc. TBP has had its major use in the nuclear industry for U, Zr, and various radionuclides, and for base metals such as Fe, Zn and others.

TBP can have many uses where the metal in the aqueous phase has formed an anionic species strong enough to form a solvate with the organic phase. Although there are many metal species that do form extractable anions, there are also some that are not extracted. Such metals include Ni, Mg, Pb. Thus other similar metals such as Co or impurities may be extracted selectively and separated from the Ni.

This phenomena provides for unique separation characteristics using that extractant.

The order of extractability some base metals from chloride solutions with TBP follows closely:



One major advantage of the solvating reagents is that water or slightly ionized water is all that is required for stripping, because of the extraction as a solvate.

Perhaps the negative side of the solvating extractants is that of solubility loss of the extractant, as well as the degradation to mono- and dibutyl-phosphates during use and recycle. These degradation products have to be periodically washed from the solvent, otherwise they will provide surfactant properties which can adversely affect the phase separation properties. Also with TBP is the usual requirement for a large number of stages, as the stagewise efficiency is usually less than compared to some of the other extractants.

MIBK shows similar characteristics, and is even more soluble in the aqueous phase. Such systems, such as the Hf/Zr separation, require a solvent recovery stage. Both TBP and MIBK extractants can be used in a concentrated form in the plant.

TOPO and perhaps DBBP have greater selectivity than the other solvating reagents, but have more limited application. The stripping is also not as easy.

The more recent triisobutylphosphine sulphide (TIPS) has an application in the recovery of silver and other metals that usually form sulphides. However there have not been much operational data published, and therefore the long-term stability of such a reagent is not available.

### **Anionic Extractants**

The performance of anionic extractants depends, in many cases, on similar properties as that described for the solvating reagents. That is the anion and/or hydrogen ion concentration are the major control, and like the solvating reagents there are metals such as Ni which do not form anionic extractable species. The anion concentration, if too high for the particular system, will act as a stripping medium and thus poor extraction will result. Selectivity is often of the order of primary < secondary < tertiary. The solubility losses follow the reverse order.

The quaternary amines have not had the same use as that of the other amines, particularly the tertiary for U, but they have been extremely useful in several extraction plants particularly from alkaline solutions. These include V, Cr, W.

If the extraction has been from nitrate or chloride media, the stripping will be with water or water containing some alkali or acid or salt. Extraction from sulphuric acid usually means that the stripping will be performed with reasonably strong acidic or alkaline solutions.

### **Cationic Extractants**

There are a number of cationic extractants, for the chelating extractants are in this class together with the alkylphosphorus extractants and the carboxylic acid extractants. Extraction is pH-dependent, and the metals with the highest valency are preferentially extracted to those metals with the lower valencies. A divalent metal requires 2 moles of extractant, and the reaction releases 2 moles of acid. Thus, to maintain the required equilibrium pH during extraction, the cationic extractant systems often require the addition of a neutralizing agent to provide a buffer. The amount is equivalent to the amount of acid released, which is therefore dependent upon the total metal(s) extracted. At low pH, the extraction of Cu by chelating extractants is no problem, but much above pH 2 then extraction will be affected by acid release.

Thus extraction at weakly acidic conditions (eg pH 5) can be costly due to alkali addition requirements. Also, if a metal has to be extracted above the hydrolysis pH of iron, then the additional problem and cost of iron removal is necessary to derive maximum benefit from the cationic extractants.

### **Extractant Opportunities**

#### **General**

Adding a structure to an existing reagent to improve the selectivity, synergism, kinetics ( extraction, scrubbing and stripping) may prove extremely useful in certain processes.

### **Solvating Extractants**

A reagent with less solubility and degradability than TBP, and with better stage wise efficiency and selectivity, could be an asset.

### **Anionic Extractants**

Primary amines have potential, particularly for co-extraction systems, but have high solubility in the aqueous phase. The primary amines are also more toxic to the environment than the tertiary amines, and so the increased solubility makes their present use even less desirable. Perhaps the structure can be modified to provide for less solubility and thus result in making this class of amines more useful.

Although there are plants using the quaternary amines in alkaline systems, nevertheless the effects of high alkalinity and ion association means that the loading is low. Improved extractants capable of operating at high pH would be desirable.

### **Cationic Extractants**

It is now becoming more desirable to have the ability for extraction of common base metals such as Co, Ni, at low pH, near the acidity of the leach solution. This would eliminate the present requirement to remove iron prior to extraction. The result would also mean that acid released during the extraction at the low pH will not have the severe effect on the extraction efficiency, and therefore there will not be the same requirement to maintain neutralization during extraction in the range pH 3-7.

The ability to strip "poisoned" sites, eg  $\text{Co}^{3+}$  from chelates and  $\text{Fe}^{3+}$  from alkylphosphates would be desirable. Also, it would be advantageous to be able to easily remove loaded "organic acids" from the solvent so that extraction efficiency can be maintained without additional expensive solvent treatment.

### **Diluents**

Although there are numerous diluents produced by several oil companies throughout the world, nevertheless most of the commonly-used diluents are aliphatic, containing perhaps 10-20% aromatic as well as other constituents such as paraffins and naphthenes. There can be real effects on the performance of the process--both physically (coalescence rate, entrainment losses) and chemically (loading, metals discrimination, stages required, stripping). It is also possible that some of the diluents may extract (on their own) certain impurities such as organic acids.

Therefore a narrow range of diluents should be examined and assessed for the particular process application, considering the above. We probably have sufficient diluents, of various chemical compositions and properties such as flash point and solvency, that no further developments may be required. What is really lacking in this important area is the complete understanding and appreciation of the diluent properties as affecting the choice for the system.

## CONTACTING EQUIPMENT AND ITS OPERATION

Throughout the examination and assessment of plants and their problems there has always been the difficulty of separation or determination of the "cause and effect" due to the feed solution, the solvent reagents, and the contacting equipment and its operation. The temperature during mass transfer as well as the choice of phase continuity in any system can have a profound effect on the performance in both the physical and the chemical aspects of mass transfer.

However to provide the necessary disoersion of one phase in the other phase, energy has to be provided to the system to provide droplets of a sufficient size for optimum mass transfer. The smaller the droplets the faster, and more complete, is the reaction. The size will be an optimum for each particular system, and as the droplets become smaller then necessary, no further mass transfer occurs. However, by producing extremely fine droplets, smaller then actually required for mass transfer, the rate of coalescence is adversely affected.

Thus, in the case of mixer settlers, in which pumping is combined with agitation, the system is placed under severe shear conditions, often considerably greater than required for mass transfer. The result has been poor phase separation, emulsions and cruds. Also, where the mixer box may be designed for a specific flow and capacity for a certain contact time, increase of time in the mixer (reduced flows) will result in the droplets becoming even finer, and therefore the problems of phase disengagement in the settler are compounded.

Therefore, if the extractant has fast kinetics, and the system requires many stages of contact, it may be advisable to consider the more gentle type of multi-stage or differential contactors such as the sieve-plate pulse columns and agitated columns. Even centrifugal contactors might be considered, although producing fine droplets, any problem of phase disengagement is overcome by the centrifugal action during extraction and separation. However the presence of solids is undesirable.

The liquid-solids separation and clarification are costly plant operations, and if one or both could be eliminated, there would be a significant economic advantage. As most operations use mixer settlers with the high shear, very little solids can be tolerated. In fact, although the aim has usually been to reduce the suspended solids to <30 ppm or less, nevertheless significant crud is formed which constitutes major problems in the settlers. Although coalescing devices can be placed in the settlers, these soon become coated and have to be removed periodically for cleaning--which is expensive and labour intensive. The application of a low shear contacting devices, such as in-line mixers and the sieve-plate pulse or other columns should be considered in such situations where solids are present,

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## SOLVENT EXTRACTION IN BIOTECHNOLOGY

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### ABSTRACT

Solvent extraction in biotechnology is an established technique, and yet some of the fundamentals are still poorly understood. This paper reviews some key areas in this field such as: the influence of broth constituents on mass transfer in whole broth extraction; the use of colloidal liquid aphrons (CLAs) in pre-dispersed solvent extraction; the extraction of polar solutes using reactive extractants in CLAs, and; the extraction of proteins using reverse micelles. Certain conclusions are drawn in order to stimulate further thought on the future directions of research in this area.

### INTRODUCTION

Solvent extraction is an established technology in the chemical and process industries, and has been used for certain applications in biotechnology for a considerable period of time, eg. penicillin extraction. Hence there is a widespread perception that it is a "mature" technology in terms of its application and theoretical understanding (Baird, 1991)). Nevertheless, in reality solvent extraction applications are considerably more developed than the underlying design data, methods for scale-up and design are primitive and somewhat unreliable, and some of the fundamental mechanisms involved are only poorly understood. This applies to an even greater degree in the use of solvent extraction in biotechnology. Hence the **aim of this paper** is to briefly review some key areas in both conventional solvent extraction, and recent novel developments, in order to highlight some of the fundamental research questions that need to be addressed in the future. In accomplishing this it is hoped to stimulate thoughts on the future developments of solvent extraction in Biotechnology.

Solvent extraction of organic solutes depends very strongly on the molecular weight and polarity of the compound of interest. With low molecular weight solutes (<1000 Daltons, eg. antibiotics) which are quite non-polar, solvent extraction is fairly straightforward, and there is considerable empirical design data around. However, with large solutes (>1000 Dalton, eg proteins), or with mildly polar solutes such as the amino acids, conventional techniques are not applicable, and novel techniques such as reactive extraction and reverse micelles become necessary. Both types of extraction will be explored in the following discussion.

On a more specific note, in applying solvent extraction to biological processes there are a number of problems which can arise :-

- 1) Due to the complexity and heterogeneity of fermentation broths they can never be fully characterised, and little is known about the influence of solids (whole cells and cell debris) on mass transfer and partitioning. In addition, the influence of some of the soluble constituents at the solvent-broth interface is poorly understood, but in the main reduces overall mass transfer, and in some cases can influence the partitioning of some solutes.
- 2) In many cases phase separation becomes very difficult due to stabilisation of the dispersed phase by the adsorption of surface active components at the interface. Furthermore, increasing the power input per unit volume increases the interfacial area, and hence speeds up extraction, however, this also increases the time for phase separation. In addition, the power costs can become significant as the dispersed phase droplet size increases.
- 3) Polar solutes present in the broth are poorly extracted due to their low partition coefficients, hence any solutes of interest cannot be separated using solvent extraction.
- 4) Solvent extraction is a nonselective technique, and hence any non polar solute present in a broth will be removed according to its partition coefficient. If the technique could be made more selective then its economic viability would increase.

These specific problems will now be examined more closely in the rest of the paper.

### INTERFACIAL MASS TRANSFER AND PARTITIONING

The direct extraction of extracellular products from fermentation broths using solvent extraction has many potential advantages such as the elimination of an expensive cell removal step, and enhanced product recovery. Furthermore, if this occurs during the fermentation itself then it could enhance the product yield and rate of production due to thermodynamic considerations. It is puzzling, therefore, that so little work has been carried out on quantifying the effects of the broth constituents on extraction. Crabbe *et al.* (1986) appear to be the first researchers who have closely examined the influence of solids on mass transfer when they extracted ethanol from a yeast suspension in distilled water using n-decanol in a "Lewis cell". They found that the presence of yeast cells severely reduced the overall mass transfer coefficient from  $5 \times 10^{-6}$  to  $0.7 \times 10^{-6}$  m/s, and was independent of yeast concentration in the range 0.1-20 kg/m<sup>3</sup>, although below 0.02 kg/m<sup>3</sup> there was no effect. They calculated that the cell concentration when the mass transfer fell precipitously was equivalent to a buildup of one to five layers of yeast cells at the interface, and based on the early work of Lewis (1954) postulated that the decrease in mass transfer was due to an increase in interfacial rigidity. Interestingly, when they tried the same extraction out of fermentation broth, they noted a 70% increase in the mass transfer coefficient, although they observed gas bubbles passing through the interface, and a fragile precipitate at the interface.

Weatherley *et al.* (1993) examined the influence of both yeast and fungi in fermentation broths on the transfer of ethanol into tri-n-butyl-phosphate (30%)/heavy distillate in a Lewis cell. In contrast to the results above, they found that the overall mass transfer coefficient decreased smoothly over a cell concentration range of 0-3 g/l, and at 3g/l of yeast the overall mass transfer coefficient ( $0.8 \times 10^{-6}$  m/s) was similar to what Crabbe *et al.* had measured. They also found that at the same cell concentrations, the mycelia had a significantly greater influence on reducing mass transfer (~ 60%) than the yeast cells, and that in the absence of cell material the mycelial culture resulted in lower mass transfer. This they suggested was a result of soluble constituents in the broth, and could be due to a combination of rheological effects and the inhibition of interfacial turbulence. This observation is consistent with other work of theirs (Weatherley and Turmel, 1992) where they examined the

terminal velocity of single drops of whole and filtered broth in a solvent phase, and found that they behaved as rigid spheres due to the presence of surface active organics or mycelia, or both, at the interface. This resulted in a reduction of internal circulation and drop oscillation, and hence mass transfer, and Lye (1993) found a similar effect when extracting proteins with a reverse micelle phase containing the anionic surfactant AOT.

Absorbance of surface active compounds at the interface should lead to a lowering of the interfacial tension, and while very little work has been done in this area, Hamilton and Weatherley (1995) found that for yeast resuspended in water the surface tension only dropped from 40 to 35 mN/m as the cell concentration increased from 0 to 3 g/l. In contrast, when filtered broth containing ethanol (0-12%v/v) was tested it lowered the interfacial tension to 20 mN/m, and when broth and cells were present at the same concentrations the figure dropped to 18 mN/m, so the authors concluded that the effects of ethanol and yeast on interfacial tension were not entirely independent. In contrast to this data, the effect of an anionic surfactant on interfacial tension in a reverse micelle system was to lower the interfacial tension from 35 to 1.75 mN/m (Lye, 1993). Hence it appears that while the broth constituents are not strongly surface active, they do lead to a reduction in mass transfer, and this could be due either to hydrodynamic effects (eg. variation in stable drop size for dispersed systems, changes in circulation velocities, interface immobilisation, and the restriction of interface movement because of interfacial tension gradients), or to physico-chemical effects (eg surface blocking - "sieve effect", solute-surfactant interactions which lead to a departure from interfacial concentration equilibrium when mass exchange occurs between two phases) (Mudge and Heideger, 1970).

Nevertheless, in some instances the presence of a surfactant at the interface can result in the enhancement of mass transfer. Recent work of ours (Lye and Stuckey, 1996) in a Lewis cell extracting erythromycin from an aqueous phase at pH 10 in the presence and absence of anionic (SDS - 0.02%w/v) and non-ionic (Softanol 30- 2%w/v) surfactants showed that the overall mass transfer coefficient increased by over 50% in the presence of SDS over a range of Reynolds numbers. In contrast, the presence of a non-ionic surfactant considerably reduced mass transfer, while the presence of both led to intermediate behaviour. Experiments using laser light scattering at the interface revealed that interfacial turbulence (Marangoni instabilities) could not explain this increase. While the data reveals a dependency of mass transfer on Reynolds number, demonstrating an element of diffusional control, a preliminary explanation for the increase with SDS is an interaction between the surfactant and the solute at the interface enhancing solute transfer.

One result of the presence of interfacially active compounds at the interface is the production of stable emulsions which are difficult to break, and create major problems during direct broth extraction. Lennie et al (1990) carried out some work on the causes of emulsion formation during direct broth extraction of *Aureobasidium pullans*. They fractionated the whole broth into a clarified fraction and an ultrafiltered (< 10 K Dalton) fraction and found that while the first two created very stable emulsions, the later fraction containing low molecular weight compounds showed little more tendency to emulsify than distilled water. This may be indirect evidence that low molecular weight organics only form "mobile films" (Lewis, 1954) at the interface, while higher molecular weight organics (proteins) lower the surface tension sufficiently to form stable emulsions. What influence these categories of compounds have on overall mass transfer is not known. These authors then added low concentrations (50 ⇒ 500 mg/l) of anionic (SDS) and cationic (CPB) surfactants to the clarified broth and observed that stable emulsions no longer formed. They explained this

observation by postulating a mixed surface layer that had neither the rigidity of the pure protein film, nor the steric or electrostatic repulsion properties found with layers of pure small molecule surfactants. Obviously, the addition of small quantities of a low molecular weight surfactant increased the surface tension, and it may be that the addition of a surfactant to a fermentation broth may increase mass transfer by destabilising the interfacial film. Szabo (1992) carried out similar work both at laboratory and full scale and found that the addition of ~2.5 g/l of a fatty amine polyglycoether (NADAR 107A), and a polyalcoxilate blend (ARMOGARD D-5306) resulted in minimal emulsion formation.

Finally, while the influence of whole broth constituents on partition coefficients would appear to be extremely important from a commercial perspective, virtually no work has been carried out in this area. Weatherley *et al.* (1993) examined the influence of yeast cell concentrations up to 3 g/l on the partitioning of ethanol into n-decanol, and found that they had no effect, although they point out that far higher concentrations need to be tested for a realistic assessment of their influence. These authors (1994) also assessed the partitioning of iso-propanol into n-decanol from an *Aueobasidium pullans* broth containing both single cells and hyphae. Using various fractions they found that the partition coefficient was lowest for the filtered broth (0.94), higher for a whole broth (1.0), and highest (1.14) for a broth containing only single cells. In order to try and quantify the effect of the cells the broth was separated into single cells and hyphae, and the cells resuspended in either buffer or filtered broth. Their results were surprising since the highest value obtained was in the presence of single cells and buffer, and this demonstrates that the increase was not due to the production of soluble surface active constituents during fermentation. The authors hypothesised that this increase may have been due to the propanol extracting constituents from the cell surface, or making the cells more permeable.

The practical result of all these effects on a large scale was shown by Anderson and Lau (1955) in a series of experiments on a large scale Podbielniak centrifugal contactor. Under identical operating conditions, extraction of whole broth compared with clarified broth resulted in significantly lower (10-15%) extraction efficiency and the number of theoretical plates. In addition, despite an enhancement of performance with clarification, mass transfer performance with biological fluids is still significantly worse in these type of extractors compared to purely chemical systems.

### **PRE-DISPERSED SOLVENT EXTRACTION USING COLLOIDAL LIQUID APHRONS**

One novel technique which may ameliorate some of the problems discussed above such as ; emulsion formation, reduction of interfacial mass transfer, and low interfacial mass transfer areas is the use of colloidal liquid aphones (CLAs) in pre-dispersed solvent extraction (PDSE). CLAs are postulated to consist of a micron sized solvent droplet encapsulated in a thin aqueous film ("soapy-shell") stabilised by the presence of a mixture of non-ionic and ionic surfactants (Sebba, 1987). Aphones have been used to extract antibiotics (Lye and Stuckey, 1994,1996), and organic pollutants such as dichlorobenzene (Wallis *et al.*, 1985) and 3,4-dichloroaniline (Lye *et al.*, 1994).

CLAs are formulated by the addition of a solvent phase containing a non-ionic surfactant (eg a polyethoxylate at ~ 0.5%w/v) into an aqueous phase containing either a cationic/anionic/non-ionic surfactant at ~ 0.5-1.0%w/v. The solvent phase can be as polar as ethyl acetate, and the phase volume ratio (volume of solvent/volume of aqueous) reached can be as high as 20 while still maintaining water as the continuous phase (Matsushita *et al.*, 1992). Due to the presence of the

surfactants this process only requires very low power inputs. This formulation results in a dense polyaphron phase which can be dispersed in a solute solution in a volume ratio of 1: 100-500, and leads to individual CLAs with a Sauter mean diameter of 4-10 $\mu$ . At a dilution of 1:100, 4 $\mu$  CLAs have an interfacial mass transfer area of approximately  $15 \times 10^3 \text{ m}^2/\text{m}^3$ . The stability of the CLAs as measured by a "half-life" is quite long, varying from 20 minutes to over many days depending on pH, ionic strength, salt type and temperature (Lye and Stuckey, 1996). After extracting the solute of interest, the CLAs can either be floated and broken by colloidal gas aphrons (CGAs- Stuckey et al, 1993), or more logically separated by cross-flow microfiltration before being back extracted (Rosjidi *et al.*, 1994). Furthermore, if the solute can be back extracted, then the CLAs can be recycled and reused.

Due to their very high interfacial area per unit volume, solvent extraction of non-polar solutes such as erythromycin using CLAs (PDSE) is extremely rapid, and at this point in time is too fast to determine experimentally (Lye and Stuckey, 1994,1996), however, a theoretical calculation results in an extraction equilibrium of around  $10^{-2}$  seconds. In contrast, it was found that the stripping (back extraction) rate was at least an order of magnitude slower than the extraction rate, and measurable, while the recovery of erythromycin from the CLAs was only around 75% (Lye and Stuckey, 1996). Because of the rate of extraction and stripping, and the complex structure of the CLA interface, it is difficult to determine what caused these effects, however, an attempt was made to simulate this system in a Lewis cell. These results showed that both extraction and stripping were diffusion controlled, and since the solvent used (decanol) had a viscosity 13 times higher than water, it appears that the slower stripping rate was due to a lower diffusivity in the organic phase. The low recovery rate at this time appears to be due to a complex forming between the surfactant and the erythromycin, but more work needs to be done to confirm this.

While this extraction has not yet been attempted from real broths, this technique has the potential to reduce, or eliminate, the possibility of emulsion formation since the emulsion has been preformed, and due to the large interfacial mass transfer area per unit volume, enable small, low residence time solvent extraction contactors to be used for whole broth extraction. In addition, due to the low power input required to formulate CLAs, the use of this technique will reduce the power requirements of solvent extraction and the solvent inventory required. Despite the fact that in this case the interfacial mass transfer resistance is only marginally relevant to the commercial application of this technique due to the large interfacial area, it is interesting to speculate as to whether the type of interface found in CLAs will result in high or low resistances. It is known that with an anionic surfactant, the CLAs are strongly negatively charged ( $\sim -45 \text{ mV}$ , Matsushita *et al.*, 1992), and since much cell debris is also negatively charged it may be that the surfactant may prevent accumulation of cells at the interface. In addition, since the CLAs are preformed, it may be that high molecular weight surface active solutes such as proteins may not be able to accumulate at the interface unless their pI is considerably higher than the broth pH.

#### **SOLVENT EXTRACTION OF POLAR SOLUTES WITH CLAs**

Conventional solvent extraction is poor at extracting polar solutes such as carboxylic/amino acids and proteins since they have very low partition coefficients. However, if a reactant can be solubilised in the solvent phase then we can reactively extract these solutes (Kertes and King, 1986), and if we can incorporate this extractant into stable CLAs then we have a potentially powerful and versatile extraction system. We have recently carried out some preliminary work on

the extraction of phenylalanine with Aliquat 336 (tricaprylmethylammonium chloride) dissolved in octanol (unpublished). Aliquat was used since it has been shown to give good partition coefficients for organic acids, although it is not so anion specific as other extractants such as DEHPA, and needs a diluent due to its high viscosity. While some researchers (Yang *et al.*, 1992) have suggested that diluents have no effect on the partition coefficient of carboxylic acid-Aliquat 336 complexes, we have found that the more polar the solvent, the higher the partitioning of phenylalanine, with alcohols giving the best results.

Our results have shown that it is possible to formulate CLAs with as much as 500 g/l of Aliquat in the solvent phase, and this results in partition coefficients as high as 30 for phenylalanine. It was found that as the Aliquat concentration increases, the CLA half-life also increases, with a corresponding decrease in the size of the CLAs. Due to the surface activity of the Aliquat, it may act to lower the surface tension of the CLA interface by competing with the other surfactants present. Increasing the pH in solution lead to a reduction in half-life, but this was still around 45 minutes at pH 9.9. One intriguing result was that the stability of the CLAs increased when the extracted phenylalanine was present in the CLAs, and at this point it is not clear why this was so. Finally, in contrast to Rajec and Ngo Manh (1995), we found that there was no significant difference between the partition coefficients measured in CLAs and normal solvent extraction using mixer settlers.

#### REVERSE MICELLE EXTRACTION OF POLAR SOLUTES

Finally, another technique to extract polar solutes which has received considerable attention in the last decade are reverse micelles. These are nanometer sized droplets of an aqueous solution stabilised by the presence of a surfactant at the interface (a water in oil-w/o- microemulsion). Considerable work has been carried out on the fundamentals of protein extraction using reverse micelles, and much is now understood about the influence of pH, salt type and concentration, and protein type on extraction yield and activity. However, in order for this technique to be used commercially, a number of key questions still have to be resolved, and these include : protein selectivity; back stripping efficiency and activity recovery, and ; contactor design.

The question of **protein selectivity**, that is the ability of a reverse micelle system to selectively remove a target protein from a mixture, has only been addressed by a handful of workers, and in all cases the proteins were extracted from a buffered aqueous phase. Goklen and Hatton (Goklen, 1986; Goklen and Hatton, 1987) investigated a series of binary mixtures, and one ternary one. In the latter case they were able to quantitatively extract cytochrome c and lysozyme from ribonuclease A. Woll and Hatton (1989) separated ribonuclease A from concanvalin A, while Aires-Barros and Cabral (1991) were able to separate a crude mixture of two lipases. In each of these cases the workers found no interaction between the proteins, although in most cases the proteins had vastly different sizes and isoelectric points (pI). If there were other proteins present in a broth that had similar pI's, and were perhaps smaller, it is not known how this would affect extraction efficiency and selectivity. Wolbert *et al.* (1989) showed that there was a strong correlation between the molecular weight of a protein and it's "electrostatic driving force [ $pH_{opt} - pI$ ]" for maximal solubilisation, with larger proteins the driving force had to be greater. These authors also found a strong correlation between the "symmetry of charge distribution", ie how homogeneously charge was distributed on the surface of the protein (Barlow and Thornton, 1986), to it's degree of forward transfer ; the more asymmetric the charge, the greater the transfer. Finally, Lye *et al.* (1991) showed that the relative rates of extraction of lysozyme and ribonuclease-a from a mixture were different, and Hentsch *et al.*

(1992) showed that both the forward and back extraction rates increased with increasing temperature. It is possible that all the above factors could be used to understand, and hence manipulate the selectivity of a target protein from protein mixtures.

The **back stripping efficiency** in recovering protein activity from the reverse micelle phase is critical in the overall competitiveness of the process, and is not nearly as well understood as forward extraction. Nevertheless, there is considerable evidence in the literature that in many, but not all, cases as much as 76-95% of the initial protein activity is recovered, with concentration factors as high as 16 (Vincente *et al.*, 1990; Dekker *et al.*, 1991). Back stripping is complex since it is known that both the forward conditions (eg pH, salt type and concentration, surfactant type and concentration), and the back conditions influence both yield and activity. Conventionally, the protein is recovered by contacting the reverse micelle phase with an aqueous phase at a pH above the pI for anionic surfactants (AOT), or below it for cationics (TOMAC), and a high ionic strength (~1M KCl). This results in an enriched aqueous phase which can be further purified, and while not common, the salt can be ammonium sulphate (Eremin and Metelitsa, 1988), which could then be used to salt out the protein. Raised temperature has also been used to recover the protein, and both Marcozzi *et al.* (1991) and Dekker *et al.* (1991) increased recovery considerably up to 40<sup>o</sup> C. Although loss of activity is often observed during RM extraction, there is very little in the literature on how and why the proteins are denatured. The loss is thought to be due to interactions between the surfactant and protein charges, and results in precipitation at the phase interface.

Finally, the efficient **design of contactors** is critical if reverse micelles are to be used on an industrial scale. Again, somewhat puzzlingly there are only a handful of papers in the literature, and all of the techniques used are derived from classical liquid-liquid contactor design. Dekker *et al.* (1986) used a classic mixer-settler arrangement to extract  $\alpha$ -amylase with TOMAC/Rewopal HV5/isooctane. They found that TOMAC inactivated the enzyme, and the mass transfer rates were relatively low leading to large solvent volumes. Membrane extractors were used by Dahuron and Cussler (1988) with polypropylene hollow fibres to provide a large surface area for transfer, however, like Dekker *et al.* (1990) they found that controlling the phase interface through back pressure was very difficult, and that mass transfer of the protein was reduced by precipitation in the membrane pores. Dekker *et al.* (1990) circumvented this problem by contacting the two phases directly, and then separating them using a 0.2 micron polypropylene crossflow membrane. While their results are sparse, the separation was run over 4 hours without a decrease in efficiency. Supported liquid membranes were used by Dekker *et al.* (1990), and Armstrong and Li (1988), with a reverse micelle phase in the pores, and a stripping phase in the lumen. While the technique worked reasonably well, its main limitation was the slow diffusion of protein through the reverse micelle phase.

Further work by Dekker *et al.* (1991) involved the evaluation of a centrifugal contactor, and increasing temperature to recover a protein rich aqueous phase (2000 times concentrated). Final recoveries were good (73%), but this type of extractor is complicated, and relatively expensive. In light of this, a number of workers have evaluated spray columns which have a number of advantages such as their ease of construction, low capital cost, and ease of operation. In addition, their low energy input circumvents the problem of stable emulsion formation. Lye (1993) found that operated in semi-batch mode the spray column did not form stable emulsions, but the AOT used increased the rigidity of the interface lowering the mass transfer. Mass transfer correlations were used to predict the uptake of protein, and while they were useful, they could not account for the

variation in the electrostatic interactions between the protein and the reverse micelle interface over the range of experimental conditions used. Han *et al.* (1994a) extracted intracellular proteins from *Candida utilis* using a spray column in batch mode, and found that after back stripping only small quantities of protein were recovered. These authors (1994b) then used a column packed with glass helices to improve phase separation, and their minimal data was difficult to interpret. Finally, Carneiro-da-Cunha *et al.* (1994) used a rotating disc contactor in continuous mode to extract a cutinase. While extraction increased over time, a stable emulsion was formed after 60 minutes.

In selecting the optimum liquid-liquid contactor for both forward and back extraction with reverse micelles, it appears that while simple, spray columns suffer some significant problems like substantial backmixing which results in a performance of only 1-2 stages. Based on the criteria of low emulsion formation, high performance (number of theoretical stages per metre), low throughput, high phase flowrate ratios, and the ability to handle solids in the feed, it appears that the "raining bucket" contactor may have considerable potential (Pratt and Stevens, 1992). While some basic work on axial mixing and mass transfer has been carried out on this unit (Sheikh *et al.*, 1972; Wang *et al.*, 1977), no information is available in the literature on its use in extracting biological broths.

## CONCLUSIONS

Based on the discussion above, the following conclusions can be drawn :-

- 1) Despite the obvious importance of understanding and quantifying the influence of broth constituents on mass transfer and partitioning, there is still very little information available in the literature, and what there is is often contradictory, and does not provide enough insight in order to be able to take account of these effects in designing full scale direct broth extraction units. More work is needed on the role of surfactants, both biologically produced and externally added, on reducing or enhancing interfacial mass transfer, and the fundamental mechanisms by which this occurs.
- 2) While the use of CLAs in direct broth extraction may have considerable potential, more detailed work is needed on exploring potential problems such as the interaction of broth constituents with the interface, and their influence on mass transfer. In addition, techniques to separate the CLAs after extraction, preferably on a continuous basis, should be developed.
- 3) Preliminary results on the incorporation of a reactive extractant into CLAs to extract polar solutes are interesting, but considerably more work needs to be done on areas such as : the feasibility of back extraction; solute specificity; effect of system formulation, and; what controls the kinetics of extraction, before this technique may be suitable for use on an industrial scale.
- 4) Despite the substantial amount of research on the extraction of proteins with reverse micelles, many practical questions relating to the use of this technique in industry still remain such as : whether the system can be modified to exhibit a certain amount of selectivity towards specific proteins; how can protein activities be maximised in overall recovery, and; what is the most appropriate extractor to use for continuous whole/filtered broth extraction.

## ACKNOWLEDGEMENTS

The author would like to acknowledge the support of the BBSRC in carrying out this work, and the work of Gary Lye and Justin Scarpello.

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## Liquid-Liquid EXTRACTION EQUIPMENT: PROGRESS AND PROBLEMS

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### ABSTRACT

Progress in simulation and prediction of equipment performance is reviewed with reference to some specific problems that require further study.

### INTRODUCTION

The development of a chemical process involving liquid-liquid extraction cannot always be independent of choice of equipment to carry out the extraction step. Problems in equipment design and operation may arise from having separation factors near 1.0, extreme values of distribution coefficient giving rise to extreme phase flow ratios, slow kinetics, extreme viscosity ratio, very small density difference or very low interfacial tension. Thus the chemical process can be constrained by considerations of equipment. Processes involving rare-earth extraction, water-washing of organic streams, metal ion extraction involving slow chemical reaction, metal-loaded organic phases with densities near that of the aqueous stream and two-phase aqueous systems for recovery of products of fermentation all pose problems for the equipment designer. A parallel rather than a sequential approach to implementation of a process is therefore required with chemists and engineers working together. The design engineer will need data on equilibria and kinetics which the chemist may be expected to provide.

Those involved in liquid extraction equipment design usually have several rôles;

- development and application of calculation procedures (models)
- generation of appropriate data (laboratory, pilot plant)
- solving problems occurring with existing plant.

It is presently the case that industrial needs and problems are driving research activity although use of modern calculational procedures by industrial designers is the exception not the rule.

Provision of continuing education courses, instruction manuals and computer programmes will gradually effect improvements in technology transfer. A warning note is that the band of equipment enthusiasts is probably growing smaller as a consequence of decline in funding of research and a trend to fund emerging technologies at the expense of consolidation and development of well-established technologies - Professor Porter make this point clearly for distillation (Porter, 1995).

Since the first industrial applications of liquid-liquid extraction in the 1920's (Hampe et al, 1994) understanding of equipment performance and development of design procedures has slowly reached the point where excellent simulation of existing plant is possible but prediction

from first principles can only be made with usually unacceptably large margins of error. So why have industrial plants worked acceptably well all these years?

- some of them probably have not
- design is based on pilot plant performance
- full-scale plant is made larger than necessary
- full scale plant was not of large diameter in early years
- modifications are made to full scale plant
- experience is accumulated by equipment suppliers and operators.

Improved design procedures can reduce risk and capital cost and clearer understanding can lead to better equipment and more sophisticated control. Modern computers allow highly sophisticated calculations to be made in realistic times. The prospect of eliminating expensive pilot plant test work is the present goal of much research work.

### SIMULATION OF COLUMNS

a) The present state of simulation of columns is good (Steiner, 1994; Gourdon et. al, 1994) but insofar as models with large numbers of adjustable parameters can fit the shape of elephants some further work is required. The main topics requiring attention are;

1. Correlations for drop breakage frequencies in both laminar and turbulent environments; the effect of scale-up and change of shape of agitated compartment; the effect of dispersed phase hold-up; breakage mechanism in packed columns; the effect of counter-current flow of continuous phase.
2. The relationship between terminal and characteristic drop velocity; the effect of scale-up and change of shape of agitated compartment; the effect of continuous phase velocity.
3. Correlations for inter-drop coalescence; the effects of physical properties; the effects of flow conditions; the effect of hold-up and drop size; coalescence in the bulk phase and coalescence on surfaces.
4. Mass transfer coefficients; the effects of interfacial contamination; the effects of agitation; the effects of break-up and coalescence (drop life-times); dependence on drop size and time.
5. Continuous phase axial mixing; effect of dispersed phase hold-up; effect of low flow ratio (continuous/dispersed).
6. Multicomponent mass transfer; effects of coupling and hydrodynamics.

Work is currently being undertaken on items 1, 2, 4 and 6 by the author and colleagues and is discussed below. We study single drop behaviour in rotating disc contactors of 152, 300 and 600mm diameter, Kühni columns of 152 and 300mm diameter and packed columns of 152mm diameter. Studies of drop swarms can be made in columns of 152mm only.

- b) Studies of breakage, coalescence and mass transfer for structured packings present particular difficulties because drops cannot be observed with steel packing and wetting problems can arise when mass transfer occurs using test systems recommended by the EFCE Working Party on Distillation, Absorption and Extraction (Bart et al, 1994). Drops can break on the exposed edges of sections of structured packings (Mao et al, 1994). What happens inside packing or at perforated plates positioned between sections? Coalescence between drops in structured packing is a potentially dominant factor in determining drop life-time and hence drop-side mass transfer coefficient. We know virtually nothing about this topic; work is in progress to devise small-scale apparatus to obtain data required for design purposes.
- c) The relationship between terminal ( $V_T$ ) and characteristic drop velocity ( $V_K$ ) is commonly termed a constriction factor,  $C_R$ ,

$$C_R = V_K / V_T$$

which has been used as an adjustable parameter (Korchinsky, 1994; Gourdon et al., 1994). We have taken the view that this ratio is measurable using single drops and can be correlated with geometric and operating parameters (Godfrey, Slater, 1991; Bahmanyar et al., 1990; Fang, et al., 1995). However, characteristic velocity cannot be treated as a system constant (for each drop size) as is terminal velocity, because the continuous phase velocity profile changes as the flow rate changes and single drops take pathways favoured by lower opposing velocities. This effect is measurable and is important as emphasized by Gourdon et al., (1994); it has probably influenced the interpretation of characteristic velocities obtained by extrapolating slip velocity data to zero hold-up when continuous phase velocity has been varied. Kumar and Hartland (1994) have shown clearly that correlation of slip velocity data is subject to average absolute relative deviation of about 10 to 20% - this may not be completely random. Calculation of  $C_R$  using random walk theory (Dimitrova et. al, 1989) for turbulent conditions in a compartment needs further study.

- d) The mass transfer coefficient correlations used in the past show jumps in behaviour as drop size increases (stagnant, laminar circulation, vigorous circulation) and criteria for transitions were vague. A more realistic approach is to assume gradually increasing internal circulation with consequent increasing effective diffusivity, a process affected by any interfacial contamination creating a force opposing circulation. The quantification of the effects of interfacial contamination on mass transfer has been tackled in two practical ways, by using an effective diffusion coefficient in the drops alone expressed as a multiplier  $R$  of the molecular diffusion coefficient (Steiner, 1986; Temos et al., 1993), and secondly by invoking a notional interfacial velocity to be used to determine the effect of contamination on both coefficients, inside and outside drops, again requiring only one unknown parameter (Slater, 1995). We can determine the parameters required from data on mass transfer to drops in vertical motion but further effects of agitation, break-up and coalescence, and hold-up are unknown. While these could be obtained from simulation exercises values would be subject to any inadequacies in assumptions made about hydrodynamics and would be composite values impossible to scale-up with certainty. Mass transfer coefficients must be allowed to vary with drop size and life-time.

- e) A current programme involves determination of individual film mass transfer coefficients in two systems in which resistance in one phase is dominant. The effect of agitation in RDCs, Kühni and packed columns is being analysed so that the effect in other systems with resistance in both phases can be estimated. The effects of agitation on drop-side mass transfer coefficients have been examined, in the absence of drop breakage (Bahmanyar et al., 1990). The enhancement is generally moderate up to the point of breakage at some critical agitation condition, both for drop side and continuous phase film coefficients. The importance of agitation lies more in controlling drop sizes by virtue of breakage and coalescence frequencies. Part of any enhancement may be due to changing surface distribution of contaminants with consequent effect on internal circulation in drops - which would increase if contamination became more evenly distributed on a drop surface.
- f) Drop history is expected to have significance if time-dependent mass transfer in drops is important. Drops are created and destroyed at different heights in the column; a time-dependent diffusive model of mass transfer in a drop ideally needs to account for changing boundary conditions in the local bulk phase. The task is likely to be very demanding in terms of computational effort so simplification is needed.

Vigorous disturbance to drops (break-up, coalescence, interaction with agitators or plates) is generally assumed to mix drop contents so that a uniform internal concentration can be assumed and the drop starts a new 'life' at regular intervals. This concept has not been tested.

The problem of determining life-times in packed columns is probably important. Very few studies have been carried out since there are many experimental and modelling difficulties (Hamilton and Pratt, 1984; Stevens and Pratt, 1986). However, drop-side mass transfer coefficients are very sensitive to time in the region of a few seconds. The notional drop residence time in a column may be several hundred seconds, and the asymptotic value of the mass transfer coefficient can be an order of magnitude smaller than that at short times.

- g) The design of columns operating with low flow ratios of continuous to dispersed phase is subject to much uncertainty because of lack of experimental investigation. Such an operation is water-washing of dispersed phase organic streams to remove salts. Larger water flows are undesirable because of disposal problems: axial mixing in the slow-moving continuous water phase in the presence of normal hold-up (say 20%) of organic drops is uncertain. However, if the distribution coefficient is very much in favour of the continuous phase water, a concentration profile in the water should not influence performance.
- h) Multicomponent mass transfer has been much neglected but work has been recently stimulated by progress in the application of Stefan-Maxwell theory to distillation and gas absorption (Taylor and Krishna, 1993). Zimmermann et al. (1995) show that the population balance can be combined with binary mass transfer coefficients based on Stefan-Maxwell diffusivities to simulate pilot plant data. This type of work is much needed and a collaborative effort is under way with Universities in Europe.

## **PREDICTION OF COLUMN PERFORMANCE**

Ideally we need to be able to dispense with expensive testwork; some laboratory scale work seems inevitable for determining physical properties and the effect of contaminants on kinetics. Prediction then involves use of no adjustable parameters.

A reasoned approach to prediction or empirical correlation of all the factors involved is required and adequate, well-balanced coverage of the ranges of all variables is needed in correlations. Extrapolation is always risky, extrapolation to large diameter columns is usually of dubious validity.

We have adopted this approach with the rotating disc contactor of 152mm diameter, 23 stages, and two chemical systems of widely different interfacial tension. Detailed information on the effects of contamination on mass transfer is required if prediction is to be possible, but in the absence of mass transfer and at hold-up below 20% (inferring negligible coalescence) prediction of drop sizes and hold-up is possible with no adjustable parameters (Ghalehchian and Slater, 1996). Our correlations of parameters needed are valid for column diameters up to 600mm and both laminar and turbulent regimes of operation but we lack a usable data set for checking the validity of the calculation procedure.

Until coalescence is better understood and data acquisition techniques are validated, prediction of all aspects of large scale equipment performance will not be possible but the computer-aided procedures are in-place.

## **SIMULATION OF MIXERS AND SETTLERS**

The population balance approach to modelling of mixers has been investigated by Tavlarides (Coulaloglou and Tavlarides, 1977) and Cruz-Pinto (Ribeiro et al, 1993) and their co-workers. Some of the assumptions on which this work is based can be challenged but progress is encouraging. Information on breakage and coalescence frequency in particular is needed as a function of all operating parameters, and the influence of surface contamination is important (Kanel and Skelland, 1993). Laboratory batch tests for kinetics will be needed for the foreseeable future.

The assumption of complete uniformity of hold-up in a mixer is not a good one since operational problems of phase inversion and entrainment generation are associated with vertical drop hold-up profiles. Scaling-up of mixer performance is still not a precise matter (Godfrey, 1994) and in particular there is the problem of prediction of drop sizes in large scale mixers. Without this knowledge scale-up of the settler using small scale batch settling or flow tests is a problem. Hartland and Jeelani (1994) have provided a thorough basis for interpretation of separation rate data which represents a major step forward.

## **OTHER TYPES OF EQUIPMENT**

It is considered that consolidation of knowledge of several commonly used equipment types is necessary with positive cost-benefit. However, contemplation of other means of achieving the process is worthwhile (Slater, 1996).

The drive in recent years to intensify processes has resulted in investigation of

- centrifugal forces
- electrical forces
- emulsion membranes (supported and non supported).

Space may be at a premium (on oil rigs, in extreme climates, nuclear processing) or inventory costs may be important (precious metals, rare earths, pharmaceuticals, nuclear processing).

Multistage centrifuges are in use but their design is not well documented (Blass, 1994). Centrifugal action applied to packed columns is more amenable to design from well-known principles (Lee et al., 1996; Lockett, 1995). Electrical fields applied to aqueous drop systems can change the breakage/coalescence balance and can enhance mass transfer (Bailes and Stitt, 1987); industrial application to phase separation is now well-advanced in the oil industry (Bailes, 1995) and much research is in progress (Yamaguchi, 1994).

Although emulsion membranes can be separated by application of an electrical field, the relatively poor kinetics are a barrier to wide implementation. The slow degradation of the emulsion is also a nuisance.

### DISPERSED PHASE DISTRIBUTORS

Numerous studies have been made to determine the sizes of drops formed from nozzles and perforated plates. The hole diameters used are similar to the drop diameter which ideally should be similar along the column to avoid marked profiles in hold-up. Once a nozzle velocity is chosen the number of holes and their diameter remain to be selected (using dispersed phase flow rate). The industrial designer of a distributor will elect for a smaller number of larger holes on grounds of expense - if it is agreed to having a distributor at all. If holes of 10mm or more are used it is doubted if equations used remain valid. To obtain even distribution of flow from holes in a ring-type distributor hole size may vary. More work is perhaps needed on break-up of large diameter jets. Slits may be preferable to holes.

### INTERFACIAL TURBULENCE EFFECTS

The presence of interfacial instabilities has occasionally been inferred when unusually high mass transfer coefficients are found. It is rare for such suggestions to be checked by direct observation. Schlieren examination of single drop mass transfer may reveal interfacial disturbances with half-lives comparable to residence times in columns and at solute concentration driving forces which are not abnormal. Prediction is unreliable for single solute transfer and interaction between two solutes has been observed (von Reden et al., 1996; Zhang et al., 1990).

To depend on such enhancement in mass transfer in design is too risky to contemplate because of the adverse effects of contamination; better performance than designed for, assuming clean interface conditions, may be the preferred approach.

### CONCLUSIONS

Simulation of hydrodynamic performance of columns and mixer-settlers can now be done with satisfactory accuracy using population balance calculations; prediction appears feasible in the

absence of coalescence between drops. Further studies of the coalescence process are the key to further progress; assumptions made so far generally lack independent experimental verification.

Simulation of the mass transfer performance is also feasible but with rather gross assumptions about mass transfer coefficients being made if the population balance model is employed. Reasonable methods of describing mass transfer coefficients affected by contaminants are available now but the problem is currently one of determining drop life-times between coalescence and breakage events and incorporating life-times into calculations. Degrees of enhancement of mass transfer coefficients by agitation have been studied in a few cases to give guidance.

Multicomponent mass transfer kinetics are presently being studied and calculation procedures are being developed.

The application of centrifugal and electrical fields is showing much promise and will find increasing industrial application.

There are plenty of intellectual challenges remaining, with industrially meaningful value, but decreasing support for research in general and for topics considered to be mature in nature is threatening to leave the subject in an unsatisfactory state of development. This leads to cost burdens on industry as a result of inadequate equipment performance.

#### ACKNOWLEDGEMENTS

This account is the personal view of the author but the work of many others has contributed to formation of the opinions expressed. The funding of work on column design provided by Separation Processes Service (SPS), AEA Technology, Harwell, over many years is acknowledged.

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# KINETICS AND CATALYSIS OF THE HYDROLYSIS OF FORMATE ESTERS HELD IN A SINGLE ORGANIC DROP

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## ABSTRACT

The rising drop technique was used to study the kinetics of the alkaline hydrolysis of two formate esters; n-butylformate (NBF) and iso-amylformate (IAF) in toluene formed the organic phase, whilst aqueous sodium hydroxide formed the continuous phase. The effect of ester and alkali concentrations on the rate of the hydrolysis were studied. Cetyltrimethylammonium-bromide (CTAB) was used as a possible catalyst for this liquid-liquid hydrolysis. When CTAB was added to the aqueous phase, enhancement of reaction was observed, whilst its addition to the organic phase caused inhibition of the hydrolysis.

## INTRODUCTION

One of the main objectives of a liquid-liquid kinetic study is to investigate the effect of chemical reaction on the specific rate of mass transfer and compare its influence on the kinetics with that of the rates of diffusion. The reactions of the pure formate esters with sodium hydroxide have been studied by Sharma and his coworkers (Doruiswamy and Sharma, 1984). The reaction occurs whilst the ester is diffusing in the film of the continuous phase. Diffusion and chemical reaction occur simultaneously in parallel steps. The over all stoichiometry of the alkaline hydrolysis of the ester is illustrated as follows:



The reaction is second order but it becomes a pseudo first order when the concentration of one of the reactants is in excess and is relatively constant (Nanda and Sharma, 1967; Sharma and Nanda, 1968; Bhave and Sharma, 1981; Lele, et al, 1983).

Phase transfer catalysis (PTC) concerns conversions between chemical species situated in different phases. In hydrolysis or saponification PTC is often described as occurring through micelles that are formed in either phase (Dehmlow and Dehmlow, 1983). Since micellar catalysis is currently a rapidly expanding area of research, systematic and careful collection of data is necessary, in order to observe and possibly predict the underlying trends on the effects of micelles on organic reactions. In studying rate acceleration or inhibition of micelles a reasonable range of concentration above and below the critical micellar concentration (CMC) should be covered; where the critical micellar concentration is the narrow range of concentration at which the micelles first become detectable (Williams et al, 1955). In the present investigation two formate esters namely n-butyl and iso-amyl are hydrolyzed in a two-phase system, using the rising drop technique. The rate of the reaction was measured using the experimental data so collected. A method of regression analysis was employed using both linear and multivariate-linear regression analyses (Riggs, 1988; Nauman, 1987; Fogler, 1992; Caranhan, 1980). The orders of reaction with respect to both alkaline and organic phases' concentrations were calculated. The activation energies and frequency factors of the rate constant are also reported.

## EXPERIMENTAL

The esters (n-butylformate and iso-amylformate) were prepared in the laboratories of the Schools of Chemical engineering at Bradford University, Bradford, U. K. are hydrolyzed in an aqueous sodium hydroxide media. Toluene was used as a diluent for dissolving the esters. The organic phase drop-lets were produced through the stainless steel needle and allowed to rise at a fixed rate through the continuous alkaline phase and were then collected. The design of the collecting head is of a particular importance (Abdalla, 1986).

Different columns of various heights were used, (15, 30, 60, 90 and 120 cm); such columns would give a different residence time, as well as different drop sizes (Abdalla, 1986). Sodium hydroxide solutions of different molarties were also used. Variety of concentrations of esters in toluene at different reaction temperatures were employed. Constant temperature water bath was used to maintain the setup at constant operating temperature. Constant concentrations of esters and alkali at constant temperature were used to study the effect of the catalyst. Different concentrations of cetyltrimethylammoniumbromide (CTAB) were used. The concentrations of the CTAB were chosen to give a narrow range of concentrations above and below the CMC (CTAB CMC =  $9.9 \times 10^{-7}$  mole/cm<sup>3</sup>; Dehmlow and Dehmlow, 1983).

Unreacted ester in the drops collected at the collecting head were analyzed. Both feed and product were analyzed by Varian Aerograph model 940 Gas Chromatograph using a flame ionization detector (FID). The column used was a 10 ft x 1/8 in stainless steel tube packed with 20% DC-200 on chromosorb W. Tables 1 show the feed and operating conditions and the rates of the reaction for the n-butylformate (NBF) and iso-amylformate (IAF) esters.

### FORMULATION OF THE RATE EQUATION

The rates of the hydrolysis reaction depend on the concentrations of both the ester and the alkali. The suggested rate equation is of the form:

$$r = k C_A^\alpha C_B^\beta \quad (2)$$

It is required to find the order of the reaction with respect to components A and B i.e. to find the value of  $\alpha$  and  $\beta$ . Applying the method of excess (Fogler, 1992), equation (2) can be divided into two equations as follow:

$$r = k' C_A^\alpha \quad (3)$$

$$r = k'' C_B^\beta \quad (4)$$

Equations (3) and (4) can be linearized and the values of  $\alpha$  and  $\beta$  are calculated using the linear regression analysis (Riggs, 1988). Equations (3) and (4) are put in following forms for linearization:

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k' + \alpha \ln C_A \quad (5)$$

$$\ln\left(-\frac{dC_B}{dt}\right) = \ln k'' + \beta \ln C_B \quad (6)$$

The order of the reactions with respect to the two reactants are determined. The general rate equation of the reaction can be calculated and the values of the activation energy and frequency factor can be obtained. The rate equation is expressed as:

$$r_{eff} = A_o \exp\left(\frac{-E}{RT}\right) C_A^\alpha C_B^\beta \quad (7)$$

Equation (7) also can be linearized as:

$$\ln r_{eff} = \ln A_o - \frac{E}{RT} + \alpha \ln C_A + \beta \ln C_B \quad (8)$$

Using the multivariate-linear regression analysis (Riggs, 1988; Nauman, 1987) the values of  $A_o$  and  $E$  are obtained. In the above analysis the n-butylformate (NBF) and the iso-amylformate (IAF) esters were considered as component A and the alkali as component B.

The method of excess was applied to find the order of the reaction with respect to the catalyst concentration. The rate equation of the catalyzed liquid-liquid hydrolysis was assumed to be of this form:

$$r = k''' C_{CTAB}^{\gamma} \quad (9)$$

Equation (9) is linearized and solved using the same linear regression analysis; and the value of  $\gamma$  is obtained.

## RESULTS AND DISCUSSIONS

### KINETICS OF THE HYDROLYSIS

The method linear regression was used to obtain the orders of the reactions with respect to the organic and alkaline phases. Varying the organic phase concentration the collected data from the laboratory experiments were analyzed using the computer programs designed for this purpose. The rate of reaction with respect to the organic phase concentration was found. Values of  $\alpha$  equal to 1.22 and 1.31 were found for NBF and IAF, respectively. The same analysis, at constant organic phase concentrations ( $3.3 \times 10^{-4}$  mole NBF or IAF/cm<sup>3</sup>) the reaction was carried out using various alkaline phase concentrations; and the rate of the reaction is found with respect to the alkaline phase concentration. The regression analysis is again used and the results obtained showed that order of reaction  $\beta$  for the two formate esters were 0.78 and 0.69 for the n-butylformate and the iso-amylformate, respectively.

Knowing the values of  $\alpha$  and  $\beta$  for the two formate esters the effective rate equation can be obtained and the values of the activation energy E and the frequency factor  $A_0$  can be found. The data collected using constant organic phase concentration ( $3.3 \times 10^{-4}$  NBF or IAF/cm<sup>3</sup>) and alkaline phase (0.5M) at variable operating temperature were used for this purpose. The method of multiple-linear regression analysis was used and the values of the E and  $A_0$  for the formate esters were obtained. Values of E equal to 25.6 kJ/mole and 34.03 kJ/mole were found for NBF and IAF, respectively; while corresponding values of  $4.34 \times 10^4$  dm<sup>2</sup>/mole.s and  $1.25 \times 10^6$  dm<sup>2</sup>/mole.s of frequency factors ( $A_0$ ) for the two esters were obtained.

The rate equations of the esters can be formulated as follows:

for the n-butylformate ester (NBF)

$$r_{NBF} = 4.34 \times 10^4 \exp\left(-\frac{25.60}{RT}\right) C_{NBF}^{1.22} C_{OH^-}^{0.78} \quad (10)$$

for the iso-amylformate ester (IAF)

$$r_{IAF} = 1.25 \times 10^6 \exp\left(-\frac{34.02}{RT}\right) C_{IAF}^{1.31} C_{OH^-}^{0.69} \quad (11)$$

Tables 1 shows the results of the rates of reaction of the formate esters NBF and IAF; as calculated using the method of excess concentration and the effective rate equations obtained using the multiple-regression analysis. Results of table 1 show that the multiple regression analysis gave results which are very close to the ones obtained using the method of excess.

The reaction is approximately overall second order. Such order is an empirical quantity,  $\alpha$  and  $\beta$  are not always integer values (Fogler, 1992). This rate equation generally includes the effects of other variables such as hydrodynamic parameters since only the bulk concentrations of the reactants are considered. The effect of temperature on the ester hydrolysis is presented by the energy of activation (E) which is found to be 25.6 kJ/mole for NBF and 34.02 kJ/mole for IAF. These values of E were compared with values of 20.08 kJ/mole (Nanda and Sharma, 1966) and 33.52 kJ/mole (Leimul et al., 1964) for n-butylformate (NBF); and 21.76 kJ/mole for iso-amylformate (IAF) (Nanda and Sharma, 1967).

**TABLE 1**  
**Organic and alkaline phase concentrations, reaction temperature and calculated rates of the hydrolysis of the n-butylformate and Iso-amylformate esters**

Organic phase $\times 10^4$ mole/cc	Alkaline phase $\times 10^4$ mole/cc	Temp, K	NBF* $\times 10^7$ mole/cm <sup>2</sup> .s		IAF** $\times 10^7$ mole/cm <sup>2</sup> .s	
			Rate <sup>1</sup>	Rate <sup>2</sup>	Rate <sup>1</sup>	Rate <sup>2</sup>
6.5	5.0	298	4.78	4.88	4.50	5.04
5.5	5.0	298	3.65	3.98	3.75	4.08
3.3	5.0	298	2.13	2.13	2.21	2.21
1.7	5.0	298	0.93	0.95	1.01	0.96
0.63	5.0	298	0.35	0.28	0.40	0.41
0.43	5.0	298	0.19	0.18	0.16	0.17
3.3	8.0	298	2.3	3.08	2.39	3.06
3.3	6.5	298	2.22	2.62	2.32	2.65
3.3	3.5	298	1.67	1.61	1.71	1.73
3.3	2.0	298	1.25	1.04	1.17	1.18
3.3	1.0	298	0.61	0.61	0.65	0.73
3.3	5.0	308	2.8	2.98	3.38	3.45
3.3	5.0	318	3.98	4.08	4.28	5.24
3.3	5.0	328	5.59	5.49	7.15	7.76
3.3	5.0	338	7.7	7.24	11.31	11.23
3.3	5.0	348	8.81	9.41	15.47	15.90
3.3	5.0	358	11.92	12.04	21.62	22.08

1 Rate calculated using method of excess; 2 Rate calculated using the effective rate equation

\*Errors for NBF: Standard = 0.324; Normalized = 0.028; Correlation coefficient = 0.995

\*\*Errors for IAF: Standard= 0.422; Normalized= 0.0197; Correlation coefficient = 0.998

#### PHASE TRANSFER CATALYSIS (PTC)

The effect of the catalyst on the rate of the hydrolysis of the formate esters was studied by adding the cetyltrimethylammoniumbromide (CTAB) either to the alkaline phase or to the organic phase. The collected data are again analyzed using the method of excess and the order of the reaction with respect to CTAB concentration was obtained.

The rate equation was assumed to be as equation (9); and the regression analysis used before was applied. The order of reaction with respect to the CTAB concentration was found as well as the rate constant. Two rate equations were obtained for each ester presenting the effect of adding the catalyst to each of the two phases.

For the n-butylformate (NBF) the two equations obtained are as follows:

$$r_{cat} = 1.75 \times 10^{-6} C_{CTAB}^{0.097} \quad (12)$$

$$r_{inh} = 5.0 \times 10^{-9} C_{CTAB}^{-0.19} \quad (13)$$

While for the iso-amylformate (IAF) as follow:

$$r_{cat} = 3.3 \times 10^{-7} C_{CTAB}^{0.019} \quad (14)$$

$$r_{inh} = 4.53 \times 10^{-11} C_{CTAB}^{-0.41} \quad (15)$$

The two rate equations with the subscripts (cat) suggest catalysis of the reaction while the ones with subscripts (inh) suggest inhibition. These equations are again used to calculate the rates of the hydrolysis and the results are shown in tables 2 and 3 for the NBF and IAF respectively. Results of tables 2 and 3 show that the obtained rate equations represent the experimental data very well since small values of standard errors were found.

**TABLE 2**  
**CTAB concentration and the calculated rates of the hydrolysis**  
**of n-butylformate ester.**

CTAB concentration (mole/cc)x10 <sup>6</sup>	CTAB in aqueous phase* x10 <sup>7</sup> mole/cm <sup>2</sup> .s		CTAB in organic phase** x10 <sup>7</sup> mole/cm <sup>2</sup> .s	
	Rate <sup>1</sup>	Rate <sup>2</sup>	Rate <sup>1</sup>	Rate <sup>2</sup>
0.0	2.13	2.13	2.13	2.13
0.13	4.2	3.79	1.5	1.02
0.25	4.5	4.01	1.2	0.9
0.55	5.19	4.32	0.85	0.77
1.10	4.82	4.62	0.75	0.68
1.70	4.5	4.82	0.46	0.62
2.5	3.95	5.01	0.47	0.58

1 Rate calculated using method of excess; 2 Rate calculated using the effective rate equation

\*Standard error of the regression = 0.181

\*\*Standard error of the regression = 0.329

**TABLE 3**  
**CTAB concentration and the calculated rates of the hydrolysis**  
**of iso-amylformate ester.**

CTAB concentration (mole/cc)x10 <sup>6</sup>	CTAB in aqueous phase* x10 <sup>7</sup> mole/cm <sup>2</sup> .s		CTAB in organic phase** x10 <sup>7</sup> mole/cm <sup>2</sup> .s	
	Rate <sup>1</sup>	Rate <sup>2</sup>	Rate <sup>1</sup>	Rate <sup>2</sup>
0.0	2.21	2.21	2.21	2.21
0.13	2.26	2.44	0.40	0.30
0.25	2.33	2.47	0.20	0.23
0.55	2.90	2.51	0.12	0.17
1.10	3.22	2.54	0.13	0.13
1.70	2.55	2.56	0.108	0.11
2.50	2.04	2.58	0.103	.09

1 rate calculated using the access method; 2 rate calculated using the effective rate equation

\*Standard error of the regression = 0.188

\*\*Standard error of the regression = 0.24

It is now required to explain the catalysis and the inhibition effects of the catalyst when it was added to one of the two phases. CTAB ( $[\text{CH}_3(\text{CH}_2)_{15}\text{N}]^+[(\text{CH}_3)_3\text{Br}]^-$ ) is an amphiphatic molecule, having interacting polar head and nonpolar hydrocarbon tail. It will induce micelle formation in the aqueous phase, such micelles are formed after the critical micellar concentration (CMC) is reached. There is evidence showing that CTAB forms micelles in the aqueous phase and that these micelles catalyze reactions involving hydroxide ions (Bunton, 1979). The case of the inhibition of the reaction when CTAB was added to the organic phase is quite obvious. CTAB has the tendency to ionize to different degrees at different pH-values. For the pH-value of these experiments (13.7) CTAB will mostly ionized at the surface. CTAB, which is more surface active than the esters, will accumulate at the interface and block the reaction.

### CONCLUSION

The hydrolysis of n-butylformate and iso-amylformate esters held in toluene with an alkali in an aqueous phase is an approximately overall second order reaction. However, it becomes a pseudo first order when the concentration of one of the reactants is kept constant.

The use of the transfer catalyst, cetyltrimethylammoniumbromide (CTAB), in the alkaline phase enhanced the reaction, while its addition to the organic phase inhibited the reaction. The case of enhancement was suggested to be due to the micelles interaction in proximity with interface allowing the penetration of the esters into the alkaline phase. The inhibition was assumed to be due to the accumulation of the CTAB at the interface which blocked the mechanism whereby the esters penetrate into the alkaline phase.

#### NOMENCLATURE

$A_0$	Frequency factor of the reaction, $\text{dm}^2/\text{mole.s}$
$C_A, C_B$	Concentration of components A and B, $\text{mole}/\text{cm}^3$
E	Activation energy of the reaction, $\text{kJ}/\text{mole}$
k	Rate constant of the reaction, $\text{dm}^2/\text{mole.s}$
r	Rate of hydrolysis reaction, $\text{mole}/\text{cm}^2.\text{s}$
T	Temperature of the reaction, K
<b>Greek Letters</b>	
$\alpha, \beta, \gamma$	Order of the hydrolysis reaction with respect to organic, alkaline and CTAB concentrations, respectively

#### Subscripts

cat	Catalysis
CTAB	Cetyltrimethylammoniumbromide
IAF	iso-amylformate ester
inh	Inhibition
NBF	n-butylformate ester
PTC	Phase transfer catalysis

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# THE INFLUENCE OF THE MARANGONI-EFFECT ON MASS TRANSFER

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## ABSTRACT

The stability behavior of different liquid-liquid systems was investigated for drops and flat interfaces with a holographic interferometer. The results reveal that not only the direction of mass transfer and the concentration difference but also the velocity near the interface and the relative direction of flow of the phases have to be taken into account for the onset of interfacial instabilities and for the influence of the instabilities on the concentration profiles in the bulk phases.

## INTRODUCTION

In liquid-liquid extraction, mass transfer may result in local variations of composition and temperature particularly along an interface. Macroscopic interfacial convection will occur when these disturbances are amplified. This can lead to interfacial instabilities in the form of roll cells, eruptions or interfacial turbulences. These interfacial-tension-driven instabilities, known as Marangoni-effects, have been shown to enhance the mass transfer rate across the interface and the mixing in the bulk phases.

Since the first observations of Weber in 1854, many experimental and theoretical investigations have been carried out dealing with interfacial instability. Many had the aim of finding a set of criteria to predict the onset of Marangoni-effects and to describe the influence of the instability on mass transfer, e.g. Sternling and Scriven (1959), Golovin (1992). A comparison of theoretical predictions with experimental results reveals that the criteria found so far are not sufficient to describe the stability behavior of liquid-liquid systems. A new approach to the description of interfacial instability in thermodynamics terms was made by Hampe (1981).

A review about various analyses referring to the Marangoni-effect is given by Pertler et al. (1995).

## EXPERIMENTAL TECHNIQUE

Table 1 contains the ternary liquid-liquid systems used for the experiments at drops and at flat interfaces.

Table 1

phase 1	solute	phase 2
water	acetone <sup>1)</sup> , propionic acid acetic acid	toluene
water	acetic acid, propionic acid	n-heptane
water	acetic acid, propionic acid	n-hexane
water	acetic acid, propionic acid	trichloroethylene
water	acetone <sup>1)</sup> , MIPK <sup>1)</sup>	butyl acetate
water	acetone, acetic acid	ethyl acetate

<sup>1)</sup> recommended test systems for liquid-liquid extraction by the European Federation of Chemical Engineering Mišek et al. (1984)

The stability behavior of these systems was investigated by a holographic interferometer set up by Hampe. Holographic interferometry is an optical method based on the recording and reconstruction of the distribution of phase and amplitude of coherent lightwaves on a holographic plate.

## EXPERIMENTS AT DROPS

### Procedure

The measuring cell used for the experiments at drops is shown in Figure 1. Density instabilities did not occur during mass transfer because the cell was located in a horizontal position. At the beginning of a run, the cell was filled with continuous phase and the drop was injected by a syringe. Both phases were mutually saturated and no mass transfer took place at the start of an experiment. The continuous phase containing the solute flowed from a storage vessel into the cell and displaced the pure continuous phase. The flow rate was regulated by a valve. Mass transfer started into the drop after the enriched continuous phases had reached the drop. Interfacial instabilities occurring were observed and classified by distorted fringe patterns which were recorded continuously by a videocamera.

Figure 2 shows a typical fringe pattern at the beginning of a run. The drop is in equilibrium with the surrounding continuous phase. Equidistant lines indicate areas without any concentration gradients. In the right lower corner the concentration front of the entering enriched continuous phase can be identified by the bending of the stripes indicating a concentration gradient.

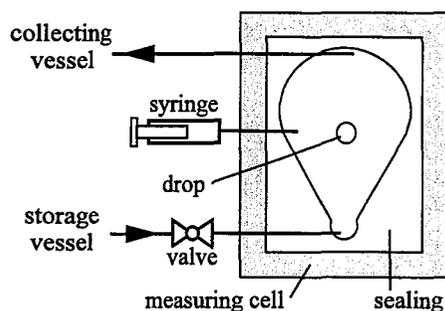


Figure 1. Top View of Measuring Cell for Drop Experiments (Hight 2 mm, Width 35 mm, Depth 50 mm)

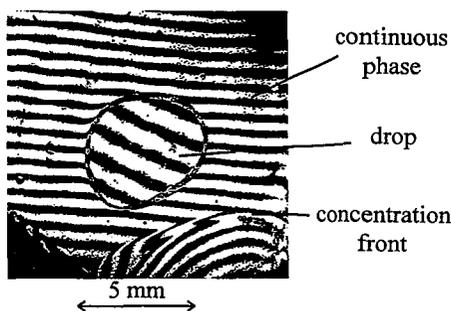


Figure 2. Typical Fringe Pattern at the Beginning of a Run

The direction of mass transfer, the concentration difference and the flow rate of the continuous phase were varied during the experiments and the influence of these parameters on interfacial instabilities was investigated. If Marangoni-effects were detected, the concentration difference was reduced in different experiments for a constant flow rate until instabilities no longer occurred. The critical concentration difference referred to the lowest concentration difference where instabilities were observed. Mass transfer was always directed from the continuous phase into the drop. The temperature was kept constant at  $20^{\circ} \pm 1^{\circ} \text{C}$  and the flow around the drop was laminar.

A classification into three different types of Marangoni-effects was made by the observed fringe patterns: Interfacial turbulences covering the entire interface (Figure 3), eruptions occurring only locally (Figure 4) and pulsations being periodically appearing eruptions.

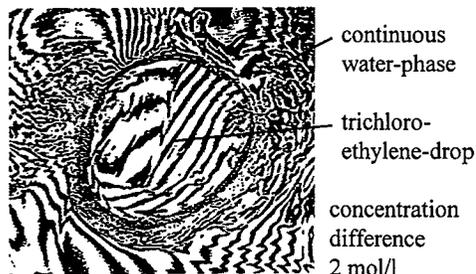


Figure 3. Interfacial Turbulences Observed in the System Water / Propionic Acid Trichloroethylene

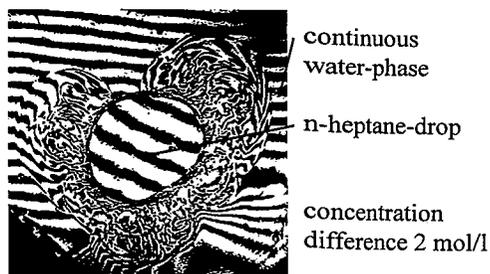


Figure 4. Eruptions Observed in the System Water / Propionic Acid / N-Heptane

### Results and discussion

Marangoni-effects were detected for all investigated systems independent of the direction of mass transfer and flow rate except for the system, water / acetic acid / n-heptane.

The instabilities were always visible in the water phase and in many cases in the organic phase, too. The values of the critical concentration difference varied from 0.05 to 4.0 mol/l even within a system dependent on the direction of mass transfer. An influence of the flow rate onto the critical concentration difference was found for eight systems. In seven of them a higher flow rate resulted in a lower critical concentration difference. The intensity of the interfacial turbulences increased with increasing concentration difference and in many cases with higher flow rates, too. With toluene or trichloroethylene as the organic phase, Marangoni-effects were detected in both phases for all solutes. With n-hexane or n-heptane interfacial instabilities were seen in the water phase only and their intensity was very weak even at high concentration differences especially during the mass transfer into the organic phase.

The concentration difference between the two phases decreased with time because the mass transfer was not stationary during the experiments at drops. For this reason, most systems showed at the beginning of a run intensive Marangoni-effects mostly in the form of interfacial turbulences which later on turned into eruptions or pulsations and finally disappeared. The time between the onset of interfacial instabilities and their disappearance increased with increasing concentration differences. At higher flow rates, the instabilities covered a greater part of the interface and the Marangoni-effects reached much further into the continuous phase. The higher transport rate of fresh bulk phases to the drop at high flow rates resulted in a shorter lifetime of the instabilities because the equilibrium was reached earlier.

## EXPERIMENTS AT FLAT INTERFACES

### Procedure

The measuring cell was located in a vertical position during the experiments at flat interfaces. The systems listed in table 1 were used for these experiments, too. Figure 5 shows the modified measuring cell. The mutually saturated phases flowed from storage vessels into the measuring cell in a cocurrent or countercurrent direction. The flow rate was regulated by two valves until the interface was positioned in the center of the cell. The flow in the cell was laminar during the runs.

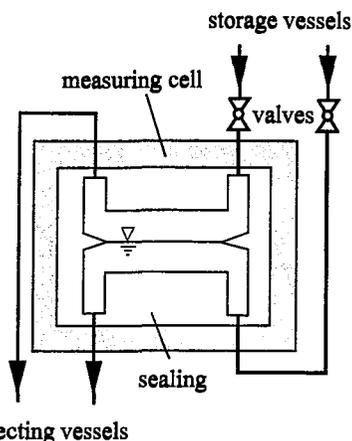


Figure 5. Side View of Measuring Cell for Experiments at Flat Interfaces (Height 35 mm, Width 50 mm, Depth 2mm)

For each system, the concentration level in the first run was chosen above the critical concentration determined in the drop experiments. If no interfacial instabilities were detected, the concentration difference was raised for the second run, otherwise it was reduced below the critical concentration difference. The direction of flow of the two phases was altered at a constant concentration difference. Interfacial turbulences and eruptions were observed during the experiments at flat interfaces only. Density effects were visible depending on the direction of mass transfer, flow rate and concentration difference.

### Results and discussion

All systems containing acetic acid as the solute showed only interfacial instabilities during the mass transfer into the water phase except the system, water / acetic acid / ethyl acetate, where instabilities were detected in both directions of mass transfer. In the system, water / MIPK / butyl acetate, interfacial instabilities were only visible during the transfer into the organic phase. In systems with propionic acid or acetone, Marangoni-effects occurred independent from the direction of mass transfer. The movement of eruptions in the system, water / acetone / butyl acetate, during cocurrent flow from the left to the right side can be seen in the left part of Figure 6. The acetone was transferred from the upper organic phase into the lower water phase at a concentration difference of 1 mol/l. The instabilities occur in both phases and were symmetric to the interface. The concentration profile along the entire interface is disturbed in both phases due to the movement of the eruptions in the same direction. In the upper phase an old concentration gradient induced by former Marangoni-effects is replaced by a new gradient near the interface. In the lower phase the eruption cannot reach the concentration gradient in the bulk phase. Thus two concentration gradients exist in the water-phase when the eruption has passed the interface. In cocurrent flow the instabilities occurred in most cases shortly after the two phases have been contacted, the location where the concentration difference is at its highest value. Due to the same direction of the instabilities in both phases, the buildup of a critical concentration gradient further along the interface is distorted and Marangoni-effects do not occur very often at any other places along the interface.

The right part of Figure 6 shows the movement of eruptions in the same system only for countercurrent flow. The eruptions, detected in the middle of the cell, are transported in different directions. The result is an asymmetric concentration profile in the phases due to the contact of a distorted and an undistorted bulk phase. Instabilities are visible in different sections of the cell because a critical concentration gradient can more easily be exceeded along the interface than in cocurrent flow.

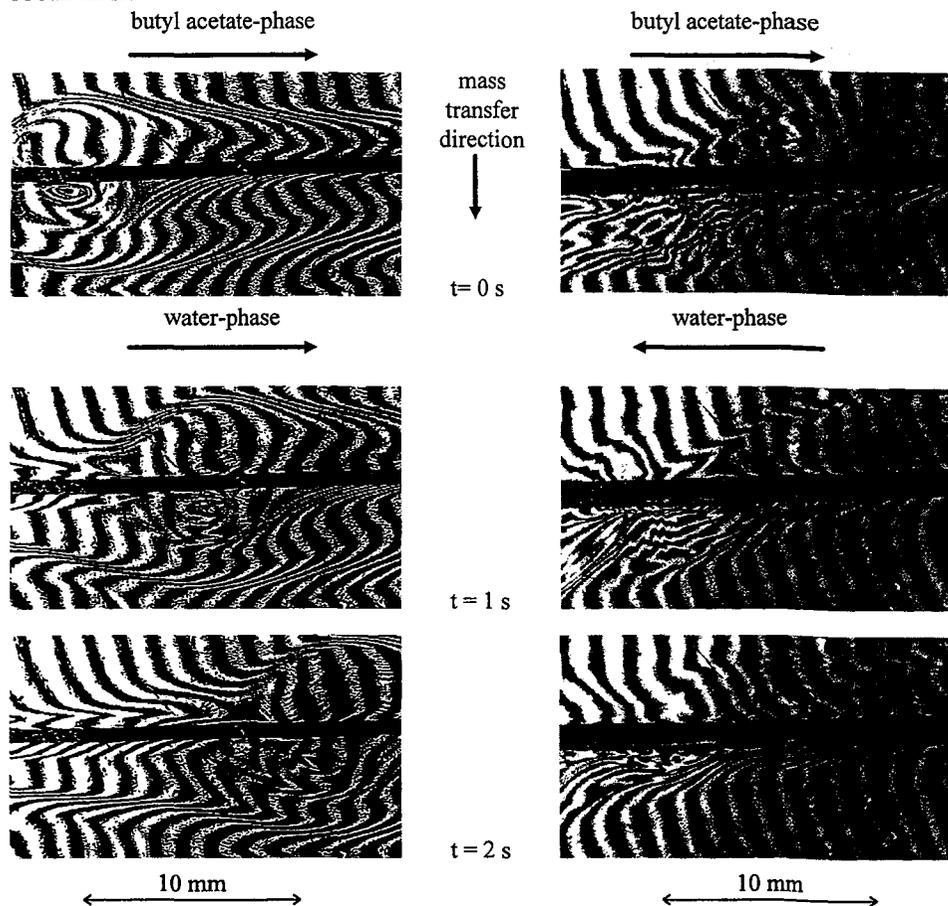


Figure. 6. Movement of Eruptions in the System Water / Acetone / Butyl Acetate at a Concentration Difference of 1 Mol/l During Co-or Countercurrent Flow

If the density profile of the system is stable, Marangoni-effects are damped and the instabilities influence the bulk phases in the vicinity of the interface only (confined convection, Figure 7). The damping effect of a stable density profile is certainly the reason why systems with acetic acid as the solute, which showed only very weak Marangoni-effects in the drop experiments during the mass transfer into the organic phase, did not show instabilities at flat interfaces. In the case of an unstable density profile, interfacial instability enhances the density instability of the bulk phases. The turbulences influence the entire bulk phases (unconfined convection) which results in chaotic

concentration profiles as shown in Figure 8. If density and interfacial instability occur together, mass transfer is very much enhanced and equilibrium is reached much earlier.

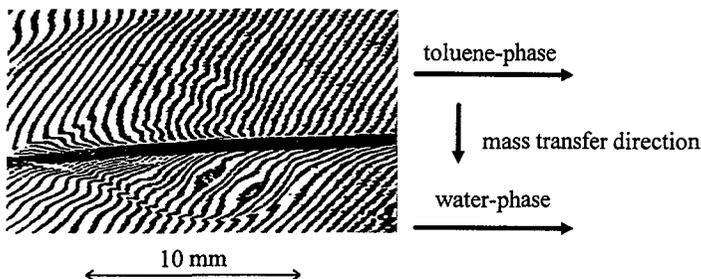


Figure 7. Confined Convection in the System Water / Acetone / Toluene at a Concentration Difference of 1 Mol/l During Cocurrent Flow

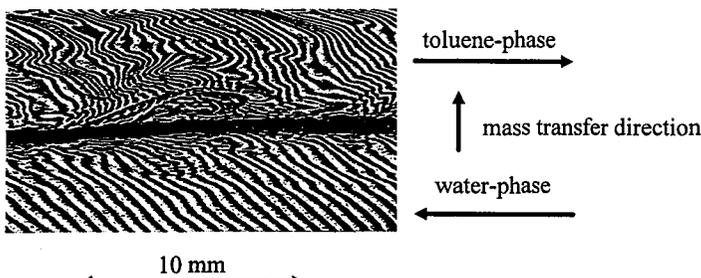


Figure 8. Unconfined Convection in the System Water / Acetone / Toluene at a Concentration Difference of 1 Mol/l During Countercurrent Flow

### CONCLUSION

The results of the drop experiments reveal that not only the direction of mass transfer but also the concentration difference and the velocity at the interface are important for the onset of Marangoni-effects. The criteria of Sternling and Scriven which predict for quiescent bulk phases instabilities for mass transfer into the organic phase, are not able to predict reliably the occurrence of interfacial instabilities for flowing bulk phases. The experiments at flat interfaces show that not only the density stability but also the direction of flow of the phases determines how instabilities affect the concentration profiles in the bulk phases.

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## EXTRACTION OF IRON(III) WITH SOME $\beta$ -DIKETONES INTO A TRITON X-100 MICELLAR PHASE: IS A MICELLAR SYSTEM SIMILAR TO A LIQUID-LIQUID SYSTEM?

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### ABSTRACT

The extraction equilibria and kinetics of iron(III) with two  $\beta$ -diketones between Triton X-100 micellar and bulk aqueous phases were measured by spectrophotometry at 298 K. The partition constant of the extractants and the extraction constant of iron(III) with the extractants in the micellar system were obtained at the same time by a successive approximation calculation. The values of these constants in the micellar system were similar to those between hexane and the aqueous solution. The rate of extraction in the micellar system was first order with respect to the metal and extractant but inverse first order with respect to the hydrogen ion, since formation of the mono complex was found to be the rate-determining step of the whole extraction reaction. By comparing the values of the rate constants obtained in this study with those in the aqueous solutions obtained previously, it was concluded that formation of the mono complex in the bulk aqueous phase controls the whole reaction and that formation at the interface is negligible. It was also found that the values of the rate constant for formation of the mono complex in the aqueous phase were decreased when the volume fraction of the micellar phase was reduced. This indicates that kinetic factors other than the rate of complex formation in the aqueous phase may affect the whole extraction rate in the micellar system.

### INTRODUCTION

It is well known that surfactant molecules in aqueous solution form micelles and that the solution can dissolve many water-insoluble solutes in the internal sphere of the aggregates. The solution can easily be handled as a single-phase solution, although the solution seems to provide a kind of solvent extraction. The use of micellar solutions instead of liquid-liquid extraction systems has been developed in many fields of chemistry. With such systems, no mechanical agitation or phase separation process is necessary, and therefore the systems appear to be suitable for extraction/spectrophotometric determination of metals using chelating reagents. Many previous studies, focusing not only on such applications -Hayashi *et al.* (1986); Watanabe *et al.* (1992); Paradkar and Williams (1994)- but also on fundamental considerations -Muralidharan *et al.* (1990); Surakitbanharn *et al.* (1991); Inaba *et al.* (1993); Saitoh *et al.* (1994)- of the extraction system, have been reported, although detailed analyses of the extraction equilibria and kinetics of the system are still limited.

In the present study, the extraction equilibria and kinetics of iron(III) with two  $\beta$ -diketones (HA) between a nonionic surfactant micellar phase and a bulk aqueous phase were investigated in order to clarify the extraction mechanisms in the micellar system. The results were compared with data for metal extraction with these two  $\beta$ -diketones in a conventional liquid-liquid extraction system to clarify the characteristics of the micellar extraction system.

### EXPERIMENTAL

**Reagents.** All the reagents were of analytical grade and used without purification. The  $\beta$ -diketones used were 1-phenyl-1,3-butanedione (benzoylacetone; BZA) and 1-phenyl-4,4-

trifluoro-1,3-butanedione (benzoyltrifluoroacetone; BFA), which were supplied by Dojindo. A nonionic surfactant, polyethylene glycol *tert*-octylphenyl ether (Triton X-100; Fluka, more than 99% pure) was used as the micelle-forming reagent.

**Procedure.** All the experiments were carried out in a thermostated room at 298 K. The micellar extraction experiments were carried out as follows. Concentrations of Triton X-100 used in the present study were within the range  $3.2 \times 10^{-3}$  - 0.16 M (0.2 - 10%). An acidic micellar solution which contained  $2 \times 10^{-5}$  -  $2 \times 10^{-4}$  M iron(III) was mixed with an acidic micellar solution of one of the  $\beta$ -diketones, and the absorbance was monitored by a Shimadzu UV-160 spectrophotometer using a quartz cell with a 1- or 5-cm light path. For determination of the extraction rate, the absorbance was measured over a certain time interval during the reaction while the value for the resulting solution after establishment of the reaction equilibrium was measured for analysis of the extraction equilibrium. The hydrogen-ion concentration of the resulting solution was measured potentiometrically by a Toa IM-40S potentiometer using a glass electrode.

In the present study, the hydrogen-ion concentration was controlled by sulfuric acid and no additional salt was added in order to avoid ion-pair extraction of charged metal species into the micellar phase.

**Data Treatment.** In the present study, the concentrations of species in the micellar phase are denoted by the subscript "m", those in the bulk aqueous phase by no subscript, and those on the basis of total volume of the micellar solution by subscript "t".

When the extraction behavior of materials in a micellar system is similar to those in a conventional liquid-liquid extraction system, the following data treatment can be performed. The partition and the dissociation of the extractant can be expressed as;

$$K_d = [HA]_m [HA]^{-1} \quad (1)$$

$$K_a = [H^+] [A^-] [HA]^{-1} \quad (2)$$

The volume fraction of the micellar phase,  $V_m$ , is defined as;

$$V_m = \Phi ([\text{Triton X-100}]_t - \text{cmc}) \quad (3)$$

here,  $\Phi$  is the molar volume of the micelle ( $1.29 \text{ M}^{-1}$ ) - Hayashi *et al.* (1986)- and cmc is the critical micelle concentration of the surfactant ( $2.4 \times 10^{-4} \text{ M}^{-1}$ ) - Kalyanasundaram and Thomas (1977)-. Using the volume fraction, the distribution of the extractant in the whole extraction system can be given by Eq. 4.

$$[HA]_t = [HA]_m V_m + [HA]V + [A^-]V = ((K_d V_m K_a^{-1} + V K_a^{-1}) [H^+] + V) [A^-] \quad (4)$$

The distribution ratio of iron(III) between the micellar and aqueous phases can be expressed as;

$$\begin{aligned} D &= [\text{Fe(III)}]_m [\text{Fe(III)}]^{-1} = [\text{FeA}_3]_m ([\text{Fe}^{3+}] + [\text{FeA}^{2+}] + [\text{FeA}_2^+] + [\text{FeA}_3])^{-1} \\ &= K_{\text{ex}} K_d^3 K_a^{-3} [A^-]^3 (1 + \sum \beta_n [A^-]^n)^{-1} \end{aligned} \quad (5)$$

where  $\beta_n$  is the stability constant of the "n-th" complex in the aqueous phase and  $K_{\text{ex}}$  is the extraction constant defined as;

$$K_{\text{ex}} = [\text{FeA}_3]_m [H^+]^3 [\text{Fe}^{3+}]^{-1} [\text{HA}]_m^{-3} \quad (6)$$

As in Eq. 5, the concentration of  $[\text{Fe(III)}]_m$  is equal to  $[\text{FeA}_3]_m$ . When concentrations and/or molar absorptivities of the complex species in the aqueous phase are small, the concentration of iron(III) in the micellar phase can be calculated from the absorbance of the solution at equilibrium,  $\text{Abs}_{\infty}$ , and the molar absorptivity of extracted  $\text{FeA}_3$  based on the total volume of the solution,  $\epsilon_{3m}$ , as;

$$[\text{Fe(III)}]_m = \text{Abs}_\infty \epsilon_{3m}^{-1} V_m^{-1} \quad (7)$$

The rate of extraction of iron(III) in the system can be expressed as the decrease of the metal in the aqueous phase as;

$$R = -d[\text{Fe(III)}] dt^{-1} = k_{\text{obsd}}[\text{Fe(III)}] \quad (8)$$

The concentration  $[\text{Fe(III)}]$  at a certain time can be calculated from the initial concentration of the metal and the concentration of iron(III) extracted at a given time.

## RESULTS AND DISCUSSION

**Partition Equilibria of  $\beta$ -Diketones and Their Iron(III) Complexes in Triton X-100 Micellar and Aqueous Phases.** The values of the dissociation constant for  $\beta$ -diketones in the aqueous phase were obtained in separate experiments using a liquid-liquid distribution method. The values of  $\log K_d$  obtained were  $-8.73$  for BZA and  $-6.07$  for BFA.

Absorption spectra of the sample solutions in the visible region were checked to obtain the molar absorptivities of the extracted species. The absorption spectra of BFA solutions showed a maximum at 445 nm and the shape was not changed by a change in the ligand anion concentration. The absorbance at 445 nm reached a plateau in the high anion concentration region, and thus the molar absorptivity of the extracted  $\text{FeA}_3$  based on the total volume,  $\epsilon_{3m}$ , was  $3950 \text{ M}^{-1} \text{ cm}^{-1}$ . In contrast, the shape of the absorption spectra for the BZA system changed in accordance with ligand anion concentration. This may have been due to the presence of complex species in the aqueous phase, and thus the absorbance could be written as;

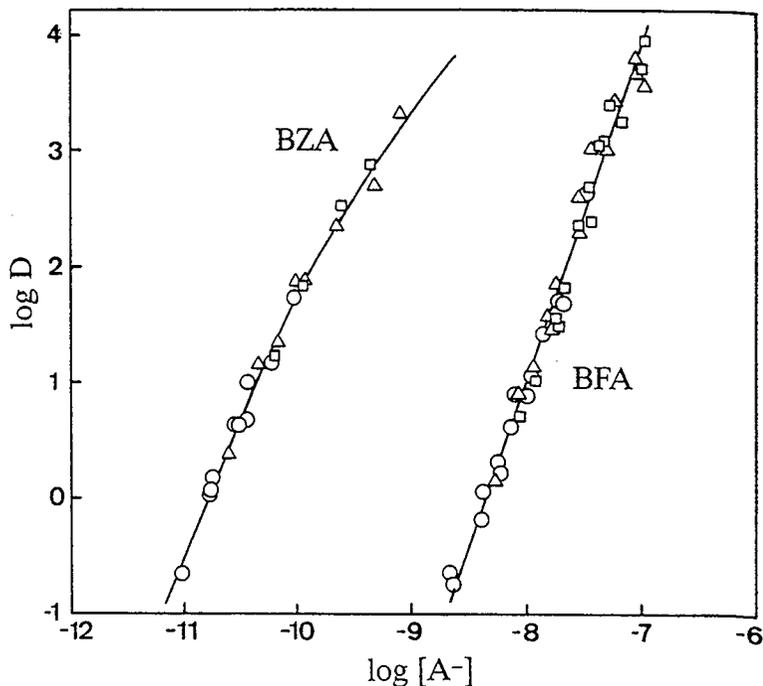
$$\text{Abs}_\infty = \epsilon_{3m}[\text{FeA}_3]_m V_m + \sum(\epsilon_n[\text{FeA}_n^{3-n}]V) \quad (9)$$

where  $\epsilon_n$  represents the molar absorptivity of the "n-th" complex in the aqueous phase. Here, the complex species in the aqueous phase can be assumed to be the mono complex,  $\text{FeA}^{2+}$ , -Sekine and Inaba (1982)-, and the concentrations of extracted  $\text{FeA}_3$  and  $\text{FeA}^{2+}$  in the aqueous phase can be analyzed by a double-wavelength measurement. The molar absorptivities of these complexes used in the calculation are  $3650 \text{ M}^{-1} \text{ cm}^{-1}$  at 450 nm and  $2910 \text{ M}^{-1} \text{ cm}^{-1}$  at 490 nm for the extracted  $\text{FeA}_3$  and  $750 \text{ M}^{-1} \text{ cm}^{-1}$  at 450 nm and  $900 \text{ M}^{-1} \text{ cm}^{-1}$  at 490 nm for  $\text{FeA}^{2+}$ .

It was observed that the distribution ratios of iron(III) in different concentrations of Triton X-100 varied, although the total concentration of the extractant and the hydrogen-ion concentration were similar. When the surfactant concentration became high, the distribution ratio became low. The extraction into micelles is proportional to the number of micelles, and thus the differences must be due to a variation in the distribution of the three types of extractant as expressed in Eq. 4, namely, by a change of ligand anion concentration in the bulk aqueous phase. Although the values of the partition constants for the extractants were unknown, the following data analysis was possible. As seen in Eq. 5, it is evident that the distribution ratios of the metal are similar to each other when the anion concentrations are similar, even though the volume fractions of the micelles differ. The anion concentration is expressed as a function of the partition and dissociation constants of the extractant and the volume fraction of the micelle, as in Eq. 4. Thus, the partition constant can be calculated by a successive approximation using data for the distribution ratio of iron(III) in different concentrations of Triton X-100 based on Eqs. 4 and 5. Figure 1 shows the results of the calculation for BZA and BFA extractions. The data thus obtained for different Triton X-100 concentrations are fitted well when the value of  $\log K_d$  is 2.15 for BZA and 1.85 for BFA. The values of  $\log K_d$  in a hexane-water system were obtained separately, being 1.95 for BZA and 2.05 for BFA. These values are similar to those in the micellar system.

As seen in Fig. 1, the distribution ratio of iron(III) with BFA is third order dependent on the ligand anion concentration within the range used in the present study, since the complex species formed in the system is mostly extracted into the micellar phase. In contrast, the slope for BZA extraction seems to change from +3 to +2 with increasing anion concentration, indicating that in this system, the mono complex,  $\text{FeA}^{2+}$ , is the dominant species in the aqueous phase in the high ligand

anion concentration region. These results strongly support the observation of changes in the absorption spectra described above. The values of  $\log K_{ex}$  were calculated to be  $-0.1$  for BZA and  $1.1$  for BFA.



**Figure 1.** Distribution ratio of iron(III) extraction with BZA and BFA into Triton X-100 micellar phase from aqueous sulfuric acid solutions as a function of the ligand anion concentration. The concentrations of Triton X-100 in the sample solutions were; 0.2% ( $\Delta$ ), 1% ( $\square$ ) and 5% ( $\circ$ ). The values of  $\log K_d$  for the extractants used were 2.15 for BZA and 1.85 for BFA. The lines in the figure give the best fitted values calculated using Eq. 5.

In the course of the present work, the extraction equilibria of iron(III) with these extractants into hexane from similar aqueous solutions were investigated in order to compare the extractability of the two systems. The experiments were carried out in a manner similar to previous studies -Sekine and Inaba (1982); Inaba *et al.* (1985)-. The extraction constant in the liquid-liquid system can be defined in a similar way to that in the micellar system in Eq. 6, the values of  $\log K_{ex}$  obtained being  $-0.6$  for BZA and  $1.6$  for BFA. The magnitude of the extraction constant obtained in the micellar and liquid-liquid extraction systems is similar for each  $\beta$ -diketone.

The similarities of both the partition constant of the extractant and the extraction constant of the metal between the micellar and the liquid-liquid systems suggest that both the extractant and metal complex exist mainly in the hydrophobic interior of the micelle, or at least that the molecular interaction between the solutes and the hydrophilic part of the surfactant is small.

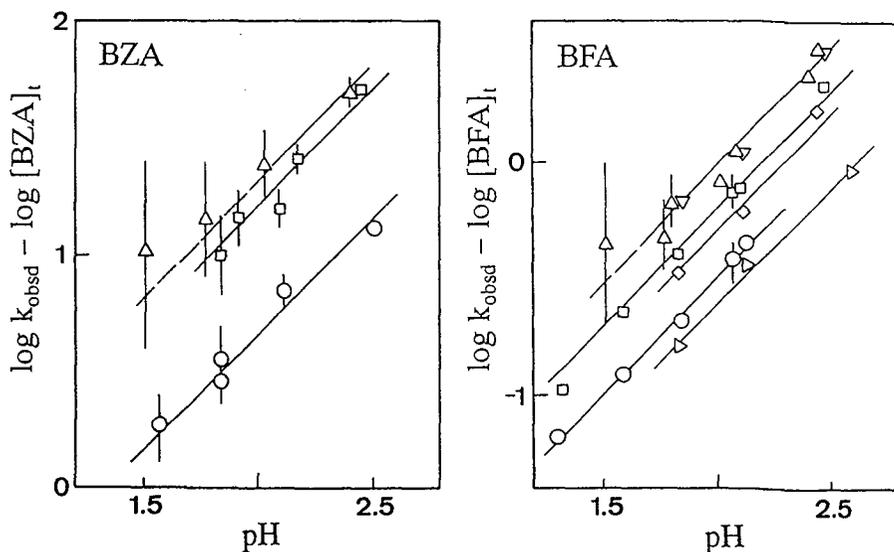
**Rate and Mechanism of Extraction of Iron(III) with  $\beta$ -Diketones into a Triton X-100 Micellar Phase.** As mentioned in the section describing the equilibrium, the existence of a mono complex,  $FeA^{2+}$ , in the bulk aqueous phase cannot be negligible upon extraction with BZA.

However, similar corrections for calculating the total amount of complex species formed during kinetic runs can also be made, and the rate of complex formation in the whole system can be estimated. In the extraction with BFA, on the other hand, the concentrations of unextracted complex species may be negligible, and thus the rate of complex formation in the whole system can be estimated directly from that of the extraction in Eq. 8 -Sekine and Inaba (1982); Inaba *et al.* (1985); Inaba and Sekine (1987)-.

The rate of extraction of iron(III) into the micellar phase was observed to be first order with respect to both the metal and the extractant concentrations, but inverse first order with respect to the hydrogen-ion concentration. Figure 2 shows the dependence of the observed rate constant (normalized to the extractant concentration in the total volume) in several concentrations of Triton X-100 on the hydrogen-ion concentration. As described above, since the samples contain only sulfate anion, the ion-pair extraction of ferric ion is negligible. The controlling step of the extraction reaction must proceed in the bulk aqueous phase and/or at the interface, as in Eq. 10.

$$R = k_{aq}[Fe^{3+}][HA][H^+]^{-1} + \alpha k_{if}[Fe^{3+}][HA]_m[H^+]^{-1} \quad (10)$$

Here  $k_{aq}$  is the rate constant for complex formation in the aqueous phase,  $k_{if}$  is the interfacial rate constant for complex formation and  $\alpha$  is an interfacial factor involving the adsorption constants of the extractant and the metal onto the interface, the specific interfacial area and the thickness of the interface -Dietz and Freiser (1991)-. When it is possible to assume that the formation reaction occurs only in the bulk aqueous phase, the constant  $k_{aq}$  in Eq. 10 can be calculated from the data in Fig. 2 using the values of the partition constants of the extractants,  $K_d$ , and the concentration of Triton X-100 on the basis of Eq. 10. The calculated values of  $\log k_{aq}$  are -0.42, -0.23 and -0.19 for BZA in 0.2, 1 and 5% Triton X-100 solutions, and -1.90, -1.80, -1.78, -1.71, -1.59 and -1.42 for BFA in 0.2, 0.5, 1, 2, 5 and 10% Triton X-100 solutions.



**Figure 2.** Dependence of the rate of extraction of iron(III) with BZA or BFA into Triton X-100 micellar phase (normalized to the total initial concentration of the extractant) as a function of the hydrogen-ion concentration. Straight lines in the figure give a slope of +1. The concentrations of Triton X-100 in the sample solutions were; 0.2% ( $\Delta$ ), 0.5% ( $\nabla$ ), 1% ( $\square$ ), 2% ( $\diamond$ ), 5% ( $\circ$ ) and 10% ( $\triangleright$ ).

Previously, the author and coworkers investigated the rate of solvent extraction of iron(III) with several  $\beta$ -diketones into carbon tetrachloride from an aqueous perchlorate solution -Sekine and Inaba (1982); Inaba *et al.* (1985)-. We concluded that the controlling step of the whole extraction is the formation of a mono complex in the aqueous phase, the rate constants,  $\log k_{aq}$ , being -0.2 for BZA and -1.4 for BFA. By comparing these constants, it is found that the constants obtained in the micellar system approached those in the literature due to the magnitude of the concentration of Triton X-100. On the other hand, the values of  $k_{ag}$  obtained from the micellar system become lower than those in the literature when the concentration of Triton X-100 became low. These findings indicate that the extraction reaction proceeds only in the bulk aqueous phase, and that the reaction at the interface is negligible. Although the reason for the deviations of these rate constants is unclear, it may be due to a change in the interfacial area. A smaller interfacial area may cause slower interfacial transport of the extractant from the micellar to the aqueous phase and/or that of the uncharged complex formed in the aqueous phase to the micellar phase.

### CONCLUSION

The values of the partition constant of two  $\beta$ -diketones, BZA and BFA, and the extraction constant of iron(III) with these extractants into a Triton X-100 micellar phase obtained in the present study are similar to those in a hexane-water extraction system. The similarity probably indicates that, on average, the extractant and the complex reside in the nonpolar region of the micelle, or that the interaction between the solute molecules and the hydrophilic part of the surfactant is small. The whole extraction reaction is controlled by formation of the mono complex only in the bulk aqueous phase, and the reaction at the interface of the micelle can be neglected. The value of the rate constant for the formation in the aqueous phase is decreased with a decrease of surfactant concentration, since the kinetic behavior of the extraction in the micellar system seems to differ somewhat from that in a conventional liquid-liquid system. The micellar extraction system is an easy-to-use method for analyzing the distribution behavior of materials, although it is noteworthy that the kinetics may sometimes be affected by interfacial factors such as the rate of transport of the extractant and/or the complex formed through the interface when the surfactant concentration is low.

### ACKNOWLEDGMENT

The author is grateful to Professor H. Freiser, Drs. S. Muralidharan and R. Sperline of the University of Arizona, who first stimulated the author's interest in the field of micellar extraction.

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## NEW METHOD FOR CALCULATION OF LIQUID-LIQUID EXTRACTION

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### ABSTRACT

A new method has been developed for calculation of multicomponent counter-current liquid-liquid extraction. The mathematical model comprises the liquid-liquid saturation point equation, similarly with the bubble point equation from vapor - liquid equilibrium. Besides, it was assumed that the distribution ratios are dependent on the composition of the extract phase only, at the given temperature, and are independent of the composition of the raffinate phase. This assumption is confirmed by many commercial extractions. The use of the liquid - liquid saturation point equation together with the above assumption gives to the elaborated programme a considerable reduction in computation time and in memory requirements compared with programmes published until now. To illustrate the method, there are comparatively shown the results obtained by numerical simulation and by physical simulation on a pilot extraction tower including extract reflux for the separation of aromatic - nonaromatic hydrocarbons from a five-hydrocarbon mixture by means of mixtures containing monoethyleneglycol - N-methyl-pyrrolidone. For all cases, the agreement of the results was reasonably good.

### INTRODUCTION

Until now, various authors proposed calculation methods for liquid-liquid extraction based on the use of the Newton-Raphson algorithm (Tierney and Bruno, 1967; Roche, 1969 and 1971; Holland, 1975; Kehat and Ghitis, 1981). Within these methods, the equilibrium liquid-liquid extraction constants are rigorously expressed as functions of the compositions of both raffinate and extract phases.

In this work there is presented a new model for calculation of liquid-liquid extraction, obtained by adaptation of Jensen's distillation model (Jensen, 1981). The adaptation consists of the following two aspects: 1) the renunciation of the enthalpy balances considering isothermic extraction only and 2) the use of suitable calculation relationships for the equilibrium liquid-liquid extraction constants.

### LIQUID-LIQUID SATURATION POINT EQUATION

The state of equilibrium for a two phase liquid-liquid system is described by the following equations in which any number of components  $C$  are distributed between the two phases:

$$y_j = K_j x_j \quad 1 \leq j \leq C \quad (1a)$$

$$\sum_{j=1}^C y_j = 1 \quad (1b)$$

$$\sum_{j=1}^C x_j = 1 \quad (1c)$$

When the first expression is summed over all components and the sum of the  $y_j$ s eliminated by use of equation (1b), the following result is obtained:

$$1 = \sum_{j=1}^c K_j x_j \quad (2)$$

Equation (2) is named the liquid-liquid saturation point equation. This equation may be written in terms of flows, as follows:

$$L = \sum_{j=1}^c K_j l_j \quad (3)$$

Equation (3) is used in the new model for calculation of the liquid-liquid extraction which is presented in this work.

The equilibrium liquid-liquid extraction constant for every component of the system may be calculated with the following relationship (Prausnitz et al., 1980):

$$K_j = \gamma_j^h / \gamma_j^u \quad (4)$$

The activity coefficient  $\gamma_j^h$  is a function of the composition of the heavy phase and of the system temperature and the activity coefficient  $\gamma_j^u$  is a function of the composition of the light phase and of the system temperature. The liquid-liquid extraction equilibrium constants may be calculated either with relationship (4) using a thermodynamic model for calculation of the activity coefficients such as NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975), or straightforward with some empirical relationships (Chimowitz et al., 1983).

### Simplifying assumption

Rigorously, in concordance with relationship (4), the equilibrium liquid-liquid extraction constant for any component of the system, at the given temperature, is dependent on the composition of both the extract and the raffinate phases. For all that, in order to obtain a robust and efficient program of calculation of extraction it is supposed that the liquid-liquid extraction equilibrium constants are dependent on the composition of the extract phase only, at the given temperature, and are independent of the composition of the raffinate phase. This assumption does not diminish too much the applicability of the calculation program associated with the new model proposed in the next section, because in the case of extractions of industrial interest the solubility of the solvent in the raffinate phase is relatively small, so that, the raffinate phase nonideality does not change and the liquid-liquid extraction equilibrium constants may be expressed as functions of the extract phase only.

## MATHEMATICAL MODEL FOR LIQUID-LIQUID EXTRACTION

The mathematical model is established for a generalized configuration of extraction column, presented in figure 1, which allows elaboration of a simulation program for all kinds of counter-current extraction. The case is considered of an N theoretical stage extractor separating C components. In concordance with the scheme in figure 1, at the level of each stage, there are considered the options: one feed flow, one light phase product and one heavy phase flow. The feed compositions and flows and sidestream flows are always known.

For each stage the following independent relationship types may be written:

### I. Component mass balances

$$DM_{i,j} = \left(1 + \frac{S_i^u}{V_i}\right) v_{i,j} + \left(1 + \frac{S_i^h}{L_i}\right) l_{i,j} - l_{i+1,j} - v_{i-1,j} - f_{i,j} = 0 \quad (7)$$

where  $1 \leq j \leq C$ .

### II. Liquid-liquid saturation point relation

$$DS_i = \sum_{j=1}^c K_{i,j} l_{i,j} - \sum_{j=1}^c l_{i,j} = 0 \quad (8)$$

### III. Rate restriction

$$L_i = \sum_{j=1}^c l_{i,j} \quad (9)$$

In equations (7) and (8) the  $DM_{i,j}$  and  $DS_i$  functions are discrepancy functions introduced by Naphtali and Sandholm (1971). These functions become zero when the correct set of the independent variables have been found. For all stages from the column, equations (7) and (8) give a total of  $N(C+1)$  equations, and the independent variables are the  $N$ - $C$  molar component heavy phase flow rates  $l_{i,j}$  and  $N$  total light phase flow rates  $V_i$ . The  $L_i$  and  $v_{i,j}$  dependent variables are calculated from equations (9) and respectively from

$$v_{i,j} = V_i \frac{K_{i,j} l_{i,j}}{\sum_{r=1}^c K_{i,r} l_{i,r}} \quad (10)$$

The substitution of these dependent variables with the quantities from equations (9) and (10) in equations (7) and (8) leads to the following equations:

-for stage 1

$$D_{1,j} \equiv DM_{1,j} = (V_1 + S_1^u) \frac{K_{1,j} l_{1,j}}{\sum_{r=1}^c K_{1,r} l_{1,r}} + \left(1 + \frac{S_1^h}{\sum_{r=1}^c l_{1,r}}\right) l_{1,j} - l_{2,j} - f_{1,j} = 0 \quad (11a)$$

-for stages 2 to (N-1)

$$D_{i,j} \equiv DM_{i,j} = (V_i + S_i^u) \frac{K_{i,j} l_{i,j}}{\sum_{r=1}^c K_{i,r} l_{i,r}} + \left(1 + \frac{S_i^h}{\sum_{r=1}^c l_{i,r}}\right) l_{i,j} - V_{i-1} \frac{K_{i-1,j} l_{i-1,j}}{\sum_{r=1}^c K_{i-1,r} l_{i-1,r}} - l_{i+1,j} - f_{i,j} = 0 \quad (11b)$$

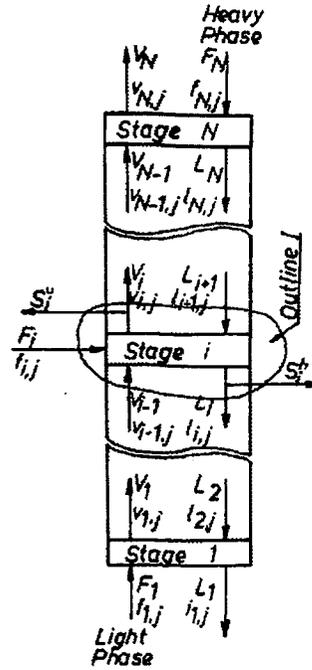


Fig. 1. Generalized configuration of extraction column

-for stage N

$$D_{N,j} \equiv DM_{N,j} = (V_N + S_N^u) \frac{K_{N,j} l_{N,j}}{\sum_{r=1}^c K_{N,r} l_{N,r}} + \left( 1 + \frac{S_N^h}{\sum_{r=1}^c l_{N,r}} \right) l_{N,j} - f_{N,j} = 0 \quad (11c)$$

-and for stages 1 to N

$$D_{i,kk} \equiv DS_i = \sum_{r=1}^c K_{i,r} l_{i,r} - \sum_{r=1}^c l_{i,r} = 0 \quad (12)$$

where  $kk=C+1$ .

The mathematical model is constituted from the equations (9), (10), (11a), (11b), (11c) and (12). The model contains  $2 \cdot N \cdot (C+1)$  equations and as many unknown quantities. These unknowns refer to  $l_{i,j}$ ,  $v_{i,j}$ ,  $V_i$  and  $L_i$  for all components and all stages.

### SOLUTION OF THE MODEL EQUATIONS

The mathematical model is solved in two stages. In the first stage, the  $N \cdot (C+1)$  equation subsystem formed from equations (11a) to (11c) and (12) is solved with respect to the  $N \cdot (C+1)$  unknowns constituted from  $l_{i,j}$  and  $V_i$  for all components and all stages. Then, in the second stage, the  $N \cdot (C+1)$  unknowns constituted from  $L_i$  and  $v_{i,j}$  are straightforwardly determined from equations (9) and (10) respectively.

The subsystem formed from equations (11a) to (11c) and (12) is solved by the Newton-Raphson method with limited step. In accordance with this iterative method, the values of the unknowns  $L_i$  and  $v_{i,j}$  are estimated in the first iteration and then in the next iterations they are corrected with the following relationship:

$$X_{m+1} = X_m + t P_m \quad (13)$$

where  $P_m = -J^{-1} g(x_m)$ .

The column vectors  $X$  and  $g$  are expressed with the following relationships:

$$X = [X_1 X_2 X_3 \dots X_i \dots X_N]^T \quad \text{respectively} \quad g = [g_1 g_2 g_3 \dots g_i \dots g_N]^T$$

where  $X_i = [l_{i,1} l_{i,2} l_{i,3} \dots l_{i,c} V_i]^T$  and  $g_i = [DM_{i,1} DM_{i,2} DM_{i,3} \dots DM_{i,c} DS_i]^T$  for  $i=1$  to  $N$ . The contents of the Jacobian matrix are described completely by Cheta (1992).

### ILLUSTRATIVE EXAMPLES

We consider a pilot plant for the separation of the aromatic hydrocarbons from a mixture of the following composition (% mole): n-hexane - 24.2, n-heptane - 19, benzene - 20.9, toluene - 26.5 and p-Xylene - 9.4. The separation is made by means of some solvent mixtures containing monoethyleneglycol (MEG) and N-methyl-pyrrolidone (NMP). The scheme of the principle of the pilot plant is presented in figure 2. For numerical simulation of this plant as well as of that from industry we worked out an IBM compatible computer program. The subroutine for calculating the extraction column uses the mathematical model from this work. The calculation of the extraction column is simultaneously made with that of the extractive distillation column (Extr. Dist. Column) because these

columns are coupled, the extract flow being the feed flow of the Extr. Dist. Column and the distillate of Extr. Dist. Column being a feed of the extraction column. The liquid-liquid extraction equilibrium constants for the 7 components of the system are calculated with empirical relationships.

These relationships have been obtained by correlation of the experimental liquid-liquid data of the 7 component system (Cheta, 1992).

Here, we present results for the extraction column only, which have been obtained by numerical simulation and by physical simulation of the pilot plant.

The extraction column has a  $27 \cdot 10^{-3}$  m diameter and contains a 2.02 m tall  $4 \times 4 \times 1.5$  mm glass Raschig ring bed. The column achieves 5 theoretical stages. The input and output data of the physical and numerical simulations are presented in tables 1 and respectively 2.

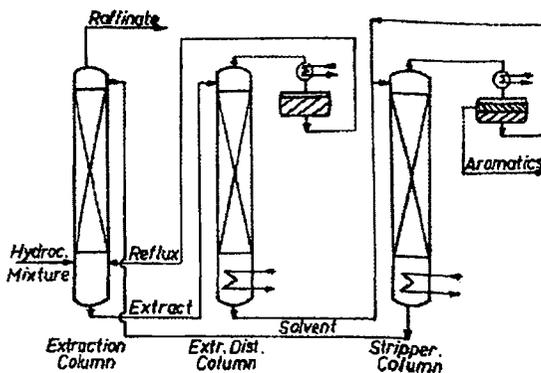


Fig.2. Principle scheme of the pilot plant

TABLE 1  
Simulation conditions

Experiment number	Extraction temperature, °C	Solvent composition, %vol MEG	Flows, mole·h <sup>-1</sup>	
			Solvent	Hydrocarbon mixture
1	40	50	14.735	2.400
2	60	50	12.880	2.408
3	80	60	12.928	1.865
4	40	70	35.050	3.029

TABLE 2  
Experimental and calculated results

Experiment number	Streams	Flows, mole·h <sup>-1</sup>		Concentrations, mole fractions					
				Nonaromatics		Aromatics		Solvent mixture	
		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
1	Raffinate	1.0630	1.0610	0.9716	0.9727	0.0074	0.0009	0.0210	0.0264
	Extract	17.611	17.711	0.0277	0.0312	0.1364	0.1380	0.8359	0.8308
	Reflux	1.5390	1.6490	0.3146	0.3323	0.6795	0.6629	0.0059	0.0048
2	Raffinate	1.077	1.066	0.9638	0.9634	0.0023	0.0028	0.0339	0.0338
	Extract	16.491	16.703	0.0435	0.0492	0.1766	0.1813	0.7799	0.7695
	Reflux	2.2800	2.5240	0.3135	0.3229	0.6785	0.6735	0.0080	0.0036
3	Raffinate	0.8274	0.8390	0.9736	0.9618	0.0095	0.0048	0.0169	0.0334
	Extract	15.891	15.752	0.0404	0.0350	0.1461	0.1453	0.8135	0.8197
	Reflux	1.9253	1.7830	0.3330	0.3085	0.6602	0.6848	0.0068	0.0067
4	Raffinate	1.3823	1.3620	0.9470	0.9604	0.0392	0.0279	0.0138	0.0117
	Extract	37.202	37.254	0.0069	0.0075	0.0514	0.0520	0.9417	0.9405
	Reflux	0.5050	0.5380	0.5111	0.5223	0.4859	0.4739	0.0030	0.0038

## CONCLUSIONS

The calculation method presented in this paper gives good results in cases in which the solvent solubility in the raffinate phase is up to 10-12 % mole, under the operating conditions of the extraction column. In cases of greater solubilities, the method is excellent for generation of guess compositions necessary to more rigorous methods.

## ACKNOWLEDGMENTS

The author is grateful to the University of Ploiesti for permission to publish this paper.

## NOMENCLATURE

C = number of components	y = mole fraction of every component in the light phase
D = discrepancy function	
F = total feed flow	
f = partial feed flow	<b>Greek Letter</b>
g = vector of discrepancy function	$\gamma$ = activity coefficient
J = Jacobian matrix	
K = equilibrium liquid-liquid extraction constant	<b>Subscripts</b>
L = total heavy phase molar flow	j, r = components j, r
l = partial heavy phase molar flow	i = stage
N = number of theoretical stages	m = iteration
S = total sidestream molar flow	
t = matrix of limiter factors	<b>Superscripts</b>
V = total light phase molar flow	h = heavy phase
v = partial light phase molar flow	u = light phase
X = vector of unknowns	
x = mole fraction of every component in the heavy phase	

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## A GROUP CONTRIBUTION METHOD FOR THE PREDICTION OF DIFFUSION COEFFICIENTS IN LIQUID PART 2: FOR NON-IDEAL BINARY SOLUTIONS

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### ABSTRACT

A model for predicting mutual diffusion coefficients for non-ideal binary solutions based on a group contribution concept is proposed in this work. More than 150 binary systems including aqueous, highly viscous, and hydro-bond associated solutions in all concentration ranges and at various temperatures have been used to verify the model. It is shown that for ideal and dilute solutions, the average deviation between experimental and predicted data is less than 5%. For non-ideal and viscous solutions, the average deviations is less than 10%. For a few of the acetone, and alcohol systems, the maximum deviation is usually less than 25%.

### DIFFUSIVITY IN INFINITE DILUTIONS

The mutual diffusion coefficient liquid is an important parameter for the design of extraction equipment, especially when the non-equilibrium stage model is used for simulation. However, theoretical approaches have not yet been successful because the strong interaction among molecules in liquid. The effects of intermolecular forces and of the molecular structure cannot be precisely described with theoretical mathematics models.

Several semi-empirical correlations have been proposed since 1930. The published correlations for diffusivity of solute A in solvent B include Stokes-Einstein, Othmer, Scheibel, Wilke-Chang, Lussis-Ratcliff, Reddy-Doraiswamy, Arnold, Sitarman, Ertl, Eyring, and Hayduk-Cheng. All of those correlations can be expressed as

$$D_{AB}^0 = f(M_A, M_B, \mu_B, V_A, V_B, T) \quad (1)$$

Where  $D_{AB}^0$  is the diffusivity of solute A in the infinite solvent B, M is molar weight, V is molar volume,  $\mu$  is viscosity, T is temperature, and the subscripts A and B represent solute and solvent respectively. It was reported that the temperature range suitable for these equations is usually 0 to 30°C, and the deviation for most systems is 5-25%, some may be over 50%.

A new method for predicting molecular diffusivity in a liquid based on the principle of group contribution has been developed. The work was partially reported in 1988 (Ye, 1988). In this paper, the effects of non-ideal characteristics in the solutions such as aqueous and alcohol will be further considered.

**TABLE 1**  
Some Group Diffusion Area

Group	$Q_k$	Group Assignment Example	$S = \sum \nu_k Q_k$
CH <sub>3</sub> -	0.848	n-Heptane, n-C <sub>7</sub> H <sub>16</sub> : 2 CH <sub>3</sub> -, 5 -CH <sub>2</sub> -	4.396
-CH <sub>2</sub> -	0.540	ibid	
-[CH <sub>2</sub> ]-	1.292	cyclo-Hexane, C <sub>6</sub> H <sub>12</sub> : 6 -[CH <sub>2</sub> ]-	7.751
=ACH=	1.179	Benzene, C <sub>6</sub> H <sub>6</sub> : 6 =ACH=	7.067
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	5.168	Toluene : 1 C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	5.168
CCl <sub>4</sub>	9.086	Carbon tetrachloride : 1 CCl <sub>4</sub>	9.086
CHCl <sub>3</sub>	5.793	Chloroform : 1 CHCl <sub>3</sub>	5.793
-(C=O)-	2.744	Acetone, CH <sub>3</sub> COCH <sub>3</sub> : 2 CH <sub>3</sub> -, 1 -(C=O)-	4.440
-OH	9.242	Methanol, CH <sub>3</sub> OH : 1 CH <sub>3</sub> -, 1 -OH	10.09
		n-Butanol, C <sub>4</sub> H <sub>9</sub> OH : 1 CH <sub>3</sub> -, 3 -CH <sub>2</sub> -, 1 -OH	11.71
-CH <sub>2</sub> O-	0.780	Diethyl ether : 2 CH <sub>3</sub> -, 1 -CH <sub>2</sub> -, 1 -CH <sub>2</sub> O-	3.016
H <sub>2</sub> O	13.75	Water : 1 H <sub>2</sub> O	13.75
(CH <sub>2</sub> ) <sub>4</sub> SO <sub>2</sub>	30.57	Sulpholane : 1 (CH <sub>2</sub> ) <sub>4</sub> SO <sub>2</sub>	30.57
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	4.457	Butylbenzene : 1 C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -, 2 -CH <sub>2</sub> -, 1 CH <sub>3</sub> -	6.385
=ACCl=	0.640	Chlorobenzene, C <sub>6</sub> H <sub>5</sub> Cl : 1 =ACCl=, 5 =ACH=	6.530
=ACB <sub>r</sub> =	2.231	Bromobenzene, C <sub>6</sub> H <sub>5</sub> Br : 1 =ACB <sub>r</sub> =, 5 =ACH=	8.120

### MUTUAL DIFFUSION COEFFICIENT IN IDEAL SOLUTIONS

For the mutual diffusion in ideal solutions, assume that the diffusion area of the pseudo-solute and solvent to be calculated as

$$S_1 = x_B S_A + x_A S_B \quad (9)$$

$$S_2 = x_A S_A + x_B S_B \quad (10)$$

The mutual diffusion coefficient in an ideal solution is expressed as

$$D_{id}^{\circ} = K \frac{(x_B S_A + x_A S_B)^{0.95}}{(x_A S_A + x_B S_B)^{0.15}} T^{1/2} \exp(-E/RT) \quad (11)$$

The diffusion activation energy is also calculated by Eq.(6). When the diffusivity in infinite dilution  $D_{AB}^{\circ}$  or  $D_{BA}^{\circ}$  is known, the following equations can be used.

$$D_{id}^{\circ} = \frac{(x_B S_A + x_A S_B)^{0.95} S_B^{0.15}}{(x_A S_A + x_B S_B)^{0.15} S_A^{0.95}} D_{AB}^{\circ} \quad (12a)$$

OR

$$D_{id}^{\circ} = \frac{(x_B S_A + x_A S_B)^{0.95} S_A^{0.15}}{(x_A S_A + x_B S_B)^{0.15} S_B^{0.95}} D_{BA}^{\circ} \quad (12b)$$



The group contribution method assumes that the diffusivity is governed by diffusion area and activation energy of molecules A and B, while both diffusion area and activation energy are the contributions of each group composing the molecules. The model for predicting diffusivity in dilute solutions is summarized below:

$$D_{AB}^0 = K \frac{S_A^{0.95}}{S_B^{0.15}} T^{1/2} \exp(-E/RT) \quad (2)$$

$K=16 \times 10^{-5}$  for aqueous solution

$K=4.0 \times 10^{-5}$  for alcohol solution except methanol

$K=2.0 \times 10^{-5}$  for other systems including methanol solution

$$S_A = \sum_{k=1}^m v_{Ak} Q_k \quad (3)$$

$$S_B = \sum_{k=1}^n v_{Bk} Q_k \quad (4)$$

$$Q_k = \phi A_k / 2.5 \times 10^9 \quad (5)$$

$$E = \sum_{i=1}^m \sum_{j=1}^n v_{Ai} v_{Bj} E_{ij} \quad (6)$$

$S_A$  and  $S_B$  are the molecular diffusion areas of solute A and solvent B.  $v_{ak}$  and  $v_{bk}$  are the numbers of the group  $k$  in molecule A and B.  $m$  and  $n$  are the numbers of group type  $k$  in A and B.  $Q_k$  is the group diffusion area.  $A_k$  is the van der Waals group area given by Bondi (1967). The constant  $2.5 \times 10^9$  is suggested by Abrams (1975).  $\phi$  is the correction factor evaluated from certain mutual diffusion coefficient data. Since  $Q_k$  is the specific value of group area  $A_k$  to a standard factor, it is dimensionless.  $E$  is the diffusion activation energy [J/mole],  $E_{ij}$  is the diffusion activation energy of group  $i$  in solute A for overcoming the obstacle caused by group  $j$  in solvent B. It is assumed in this work that  $E_{ij}=E_{ji}$ .

It is more accurate for normal alkane systems to estimate the diffusion activation energy by the following equation than by equation (6)

$$E = 4E_{CH_3-CH_3} + 4(P-2)E_{CH_3-CH_2} + (P-2)^2 E_{CH_2-CH_2} \quad (7)$$

$$P = (MN)^{1/2} \quad (8)$$

Where  $M$  and  $N$  are the carbon numbers in molecules A and B.

The updated group parameters are listed in Table 1 and 2. More than 600 experimental data sets from research or from various published literature for about 150 systems in a wide temperature range (from m.P. to b.p.) were used to verify the model (Ye, 1988). The deviation for most systems is less than 5%. The maximum deviation is generally less than 10% for a few aqueous and alcohol systems.

After verification with 11 nearly ideal binary systems in full composition and experimental

temperature ranges, it is demonstrated that the deviation using above equations to predict mutual diffusion coefficient of ideal solutions is less than 5%(Ye, 1988).

### MUTUAL DIFFUSION COEFFICIENT IN NON-IDEAL SOLUTIONS

When the thermodynamic correction factor  $\beta$  is introduced, the mutual diffusion coefficients of a non-ideal solution can be predicted by:

$$D_{id}^0 = K \frac{(x_B S_A + x_A S_B)^{0.95}}{(x_A S_A + x_B S_B)^{0.15}} T^{1/2} \beta \exp(-E/RT) \quad (13)$$

The diffusion activation energy is also calculated by Eq.(6).  $\beta$  is defined as

$$\beta = 1 + \frac{d \ln \gamma_A}{d \ln \gamma_B} \quad (14a)$$

Where  $\gamma$  is the activity coefficient of solute A in the solution. The UNIFAC group contribution model proposed by Fredenslund(1981) can be combined into this model to evaluate the activity coefficient. Since it is very difficult to develop a differential relation of  $(d \ln \gamma_A / d \ln x_A)$ , the following approximation can be used:

$$\beta = \lim_{\Delta x_A \rightarrow 0} \frac{x_A \Delta \gamma}{\gamma_A \Delta x_A} \quad (14b)$$

$$\Delta \gamma = \gamma_{(x_A + 0.5 \Delta x_A)} - \gamma_{(x_A - 0.5 \Delta x_A)} \quad (14c)$$

When UNIFAC models are used, we prefer using LLE to VLE parameters. Comparing the deviations that result from using LLE and VLE to evaluate the correction factor  $\beta$  of cyclo-Hexane-Benzene system(Rodwin, 1965 and Hammond, 1955), it is shown that using LLE will be twice as accurate as VLE (Fig. 1). When LLE parameters are not available, VLE can also generate reasonably good results. The availability and reliability of using the group contribution method to calculate the mutual diffusion coefficients of non-ideal binary solutions have been examined extensively with the following published experimental data: cyclo-Hexane+benzene (Rodwin, 1965 and Hammond, 1955), n-Octane+CCl<sub>4</sub> (Hammond, 1955), n-Decane+CCl<sub>4</sub> (Hammond, 1955), n-Nonane+CCl<sub>4</sub>

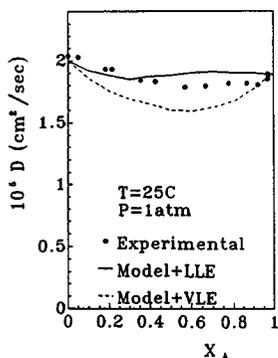


Fig.1 cyclo-Hexane (A)  
+ Benzene (B)

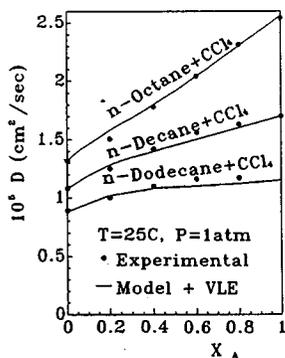


Fig.2 Paraffin (A)  
+ CCl<sub>4</sub> (B)

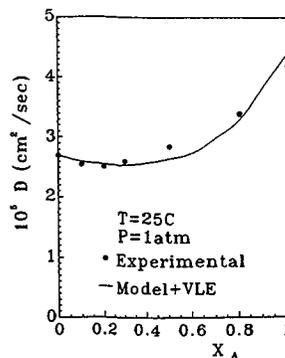


Fig.3 Acetone (A)  
+ Benzene (B)

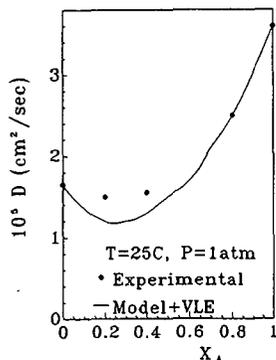


Fig.4 Acetone (A)  
+ CCl<sub>4</sub> (B)

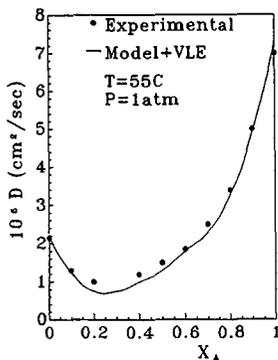


Fig.5 Acetone (A)  
+ Water (B)

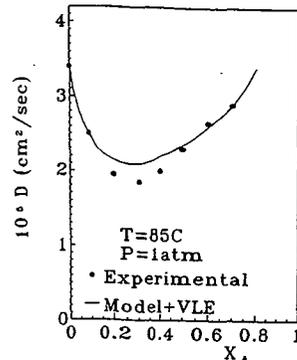


Fig.6 Ethanol (A)  
+ Water (B)

(Hammond, 1955), n-Dodecane+CCl<sub>4</sub> (Hammond, 1955), Acetone+Benzene (Anderson, 1962), Acetone+CCl<sub>4</sub> (Anderson, 1962), Acetone+Water (Comper, 1986), Methanol+Water (Derlacki, 1985), and Ethanol+Water (Tyn, 1975). Some experimental and calculated results are compared in Fig.2 through 6. It is notable that the precision of this model not only depends on the diffusional group parameters, but also strongly depends on the models of activity coefficient. The author discovered that using experimental activity coefficients to calculate  $\beta$  will generate the best results, and LLE parameters will be better than VLE parameters when UNIFAC model is combined.

### CONCLUSION

The group contribution model for predicting molecular diffusion coefficients in liquid has been established. Combining UNIFAC or other group contribution models for activity coefficients in liquid to evaluate the correction factor  $\beta$ , this model can be used widely for all kind of liquid solutions. This model is much more precise than any other models published. The average deviation is less than 5% for ideal solutions, 10% for most non-ideal solutions, and 25% for few hydrogen-bond associated solutions.

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## Diffusional MASS TRANSFER in Liquid-Liquid EXTRACTION

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### ABSTRACT

Ternary diffusion coefficients were measured with laser holography as a function of concentration in the partially miscible type 1 acetone/water/glycerol system up to the saturated (or binodal) state. These data were compared with the change of the chemical potential gradient and with experimentally determined equilibration trajectories of liquid-liquid mass transfer data. The results confirm the strong diffusional coupling and demonstrate that the Onsager reciprocal relations are not satisfied for this system. The description of mass transfer processes based on the measured diffusional matrices shows a good agreement in unsaturated states.

### INTRODUCTION

Previous investigations gave the first hint that diffusional mass transfer can be neglected at saturated states (Hampe et al., 1991; Pertler and Blass, 1993). As in these investigations, the saturated state was reached by varying the temperature, the data could not be related to liquid-liquid extraction data directly. Therefore, we started with the more important case, from the view point of liquid extraction research, to investigate diffusion coefficients with the change of concentration.

Only few data on the variation of diffusion coefficient with the concentrations close to saturated states are available in the literature. These data have been collected for binary systems that form two liquid phases and were combined with the results of diffusion measurements obtained by laser holography. These results show that the diffusivity declines near the saturated state, the diffusion coefficient depends linearly on the thermodynamic factor and the cluster theories seem to work well only in systems with water on the water-rich side (Pertler et al., 1995).

Since the situation is still unclear in ternary systems we have extended our studies of the concentration dependent diffusivity up to ternary systems. With these data, it is possible to replace the constant diffusion coefficients in the models for the calculation of the mass transfer in solvent extraction. Therefore, the generalized Fick's law is used for the description of multicomponent diffusional mass transfer assuming for an  $n$  component system a linear relationship between the  $(n-1)$  independent fluxes  $J_i$  and the  $(n-1)$  independent concentration gradients  $\nabla C_i$ . A three component system is fully described by the following equation (1) written in matrix form:

$$\begin{pmatrix} -J_1 \\ -J_2 \end{pmatrix} = \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} * \begin{pmatrix} \nabla C_1 \\ \nabla C_2 \end{pmatrix} \quad (1)$$

In general, the diffusion coefficients are not symmetric, i.e.  $D_{ij} \neq D_{ji}$ . The diagonal terms (the  $D_{ii}$ ) are called the "main-term" diffusion coefficients, since they commonly are high and their magnitude is similar to binary values. The off-diagonal terms, called the "cross-terms" can almost be neglected for ideal systems (Cussler, 1976).

For systems that are considerably non-ideal and show strong diffusional coupling, mass transfer coefficient matrices based on diffusional data with quite significant off-diagonal coefficients are required (Krishna et al., 1985). For bulk-phases that are close to saturation but not in equilibrium with each other, the rate of mass transfer can be calculated only with fluid dynamic correlations (Schermuly and Blass, 1991). The result is a mass transfer coefficient matrix with equal diagonal elements and zero off-diagonal elements.

The aim of this research is to investigate the role of the diffusional mass transfer in liquid-liquid extraction with the partially miscible type 1 acetone/water/glycerol and water/acetone/ethyl-acetate systems. Both systems show broad regions of miscibility between the main components and measured trajectories for unsaturated and saturated bulk-phases, concentration and equilibration profiles are available (Häberl and Blass, 1996; Krishna et al., 1985; Schermuly and Blass, 1991). Hence, a direct comparison between diffusivity data and liquid extraction experiments can be done.

### MEASURING TECHNIQUE

For determination of ternary diffusion coefficients an improved laser holography method is used (Pertler et al., 1995). With this technique it is possible to observe the change of the refractive index as a function of position in real time by characteristic fringe patterns. For the analysis of the data, the method proposed by Miller (1988) is used along with a non-linear-least-squares fit of the experimentally observed fringe positions after different time intervals.

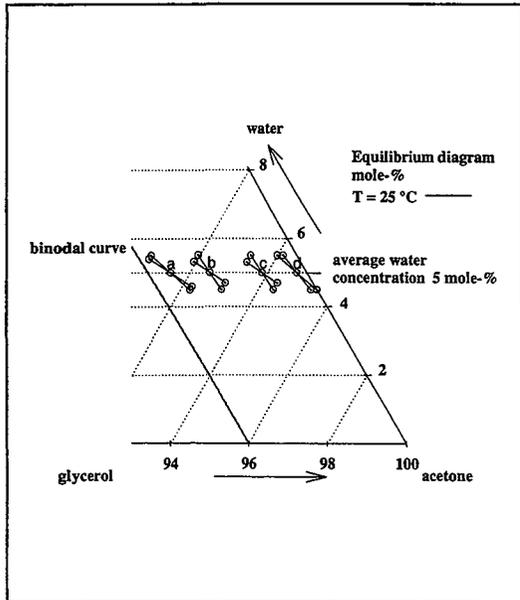


Fig.1 Experimental compositions of the cross diffusion experiments

To prove the reliability of our data we compared the positions of the fringe patterns observed experimentally with simulated data from the fitted diffusion coefficients.

### EXPERIMENTAL

Figure 1 shows the acetone corner of the equilibrium diagram of the acetone/water/glycerol system. At an average water concentration of 5 mole-% we determined ternary diffusion matrices as a function of glycerol concentration at 25 °C by cross diffusion experiments.

## RESULTS

In the non-ideal water(1)/glycerol(2)/acetone(3) system a strong diffusional coupling is observed and the diffusional flux of water  $J_1$  is strongly influenced by the concentration gradient of glycerol, that results in a remarkably high and positive cross coefficient  $D_{12}$ , as it can be seen from the measured diffusion coefficients in the volume fixed reference frame shown in Fig.2. This kind of non-ideality can only be explained by a 'salting-out' effect that the two solutes exert one on the another.

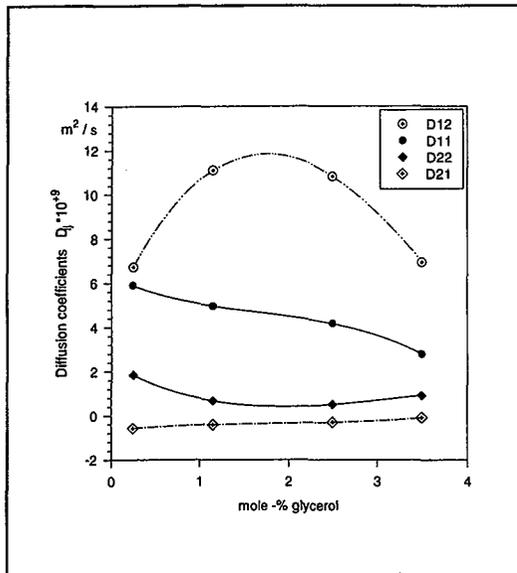


Fig. 2 Measured ternary diffusion coefficients for the water(1)/glycerol(2)/acetone(3) system at 25°C in the volume fixed reference frame.

When this salting-out effect is large enough a phase separation will start (Tyrrell and Harris, 1984). Therefore, in the miscibility region the stability criteria :

$$|D| = D_{11} * D_{22} - D_{12} * D_{21} \geq 0 \quad (2)$$

and

$$|\mu| = \mu_{11} * \mu_{22} - \mu_{12} * \mu_{21} \geq 0 \quad (3)$$

are valid, with the equal signs applying to a plait point and in the case of a phase separation. The individual diffusion coefficients  $D_{ij}$ , transferred to the molar average velocity frame given in table 1, do not show a serious drop, but the determinants are continuously reduced coming closer to the separation state as predicted by eqn. (2).

To calculate the change of the chemical potential gradient  $\mu_{ij}$  from the Gibbs' free energy, equilibrium data are necessary. For

TABLE 1

Coefficients  $D_{ij}$  in the molar average velocity frame and determinant  $|D|$  of the diffusion data.

mole-% glycerol	$D_{11} * 10^9$ / [m <sup>2</sup> /s]	$D_{12} * 10^9$ / [m <sup>2</sup> /s]	$D_{21} * 10^9$ / [m <sup>2</sup> /s]	$D_{22} * 10^9$ / [m <sup>2</sup> /s]	$ D  * 10^{18}$ / [m <sup>4</sup> /s <sup>2</sup> ]
0.25	5.90	6.47	-0.61	1.82	14.69
1.15	5.06	10.68	-0.46	0.58	7.85
2.50	4.35	10.41	-0.39	0.30	5.38
3.50	2.95	6.68	-0.17	0.72	3.27

**TABLE 2**  
Coefficients  $\mu_{ij}$  and determinant  $|\mu|$  of the Hessian matrix of the Gibbs' free energy

mole-% glycerol	$\mu_{11} * 10^{-4}$ / [J/mol]	$\mu_{12} * 10^{-4}$ / [J/mol]	$\mu_{21} * 10^{-4}$ / [J/mol]	$\mu_{22} * 10^{-4}$ / [J/mol]	$ \mu  * 10^{-8}$ / [J <sup>2</sup> /mol <sup>2</sup> ]
0.25	4.47	-1.13	-1.13	97.09	432.9
1.15	4.48	-1.11	-1.11	19.52	86.2
2.50	4.49	-1.08	-1.08	7.93	34.4
3.50	4.50	-1.06	-1.06	5.14	21.9

the system studied two sets of equilibrium data are published. Hampe et al. (1989) gave the equilibrium data at 20°C and the fitted parameters for the UNIQUAC equation of state, from Krishna are parameters available for the NRTL equation at 25°C (Rutten, 1992). Both sets nearly yield to the same thermodynamic data, so the NRTL parameters have been used at the appropriate temperature of 25°C.

The coefficients  $\mu_{ij}$  and the decrease of the determinant  $|\mu|$  of the Hessian matrix of the Gibbs' free energy, according to eqn. 3, are presented in table 2. By multiplying the Hessian matrix of the Gibbs' free energy  $[\mu]$  with the inverse of the Fickian matrix  $[D]$  (from table 1) the Onsager phenomenological coefficients can be determined (Taylor and Krishna, 1993). The matrices of

Onsager phenomenological coefficients calculated from our diffusion coefficients have positive main and negative cross coefficients and are positive definite as required from the second law of thermodynamics, but the cross coefficients differ between one and two orders of magnitude. Hence, the Onsager reciprocal relations are not satisfied at the investigated conditions and we have to question the ability of the Gibbs free energy models to describe the change in the chemical potential, the reliability of the microscopic reversibility as assumed by the thermodynamics of irreversible processes and also our diffusion measurements.

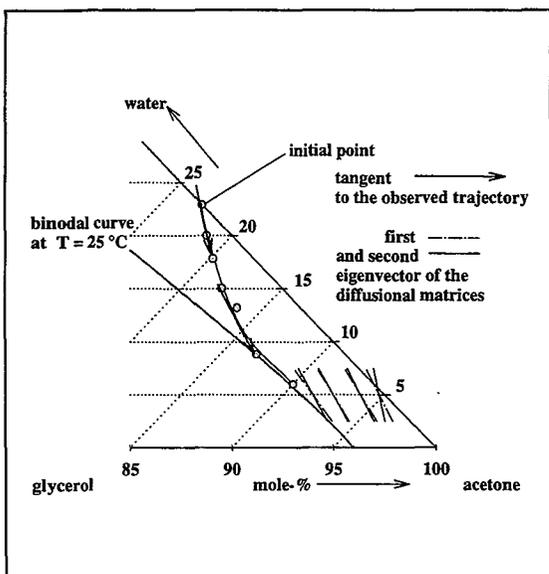


Fig. 3 Comparison of experimentally observed equilibration trajectories with the directions of the eigenvectors of the diffusion matrices

Independently of further reliability tests, that still have to be done, the results of the diffusion measurements can be compared with experimentally observed equilibration trajectories, concentration profiles, and rates of mass transfer. If the film theory model is used for the description of the rate of mass transfer,

the matrix of diffusion coefficients is directly proportional to the matrix of mass transfer coefficients. For the investigated acetone/water/glycerol system, Krishna et al. (1985) determined mass transfer matrices with extremely large off-diagonal elements by isothermal interphase mass transfer measurements in a modified Lewis batch extraction cell at saturated and unsaturated states, that agree with our data of the diffusion measurements.

The experimentally observed equilibration path from Krishna et al. (1985), for the case when both phases (glycerol and acetone) have been initially unsaturated, is shown for the acetone-rich phase in Figure 3. The water concentration varies from 23 to 6 mole-%. If for different average concentrations of water a qualitatively similar behaviour for the dependence on the glycerol concentration of the diffusion coefficient matrix is assumed, the data from our diffusion measurement and from the extraction experiment can be compared. As shown in Figure 3, the directions given by the second eigenvectors of the measured diffusional matrices are consistent with the tangents of the observed equilibration trajectories in the unsaturated state. In the case when the trajectories do not follow the directions given by the eigenvectors of the diffusional matrices, a change of the dominant transport mechanism must occur and the diffusional transport is superimposed or replaced by a fluid dynamical transport. Therefore, the existing data of the above mentioned liquid extraction experiments have still to be compared.

### CONCLUSION

The acetone/water/glycerol system shows strong diffusional coupling effects that determine the mass transfer in the unsaturated acetone-rich phases. There the equilibration trajectory of a liquid-liquid extraction experiment can be described well by the eigenvectors of the diffusional matrix even up to the saturated state. We still have to find criteria when, for the calculation of the mass transfer matrix, the concentration dependent diffusion coefficients have to be considered and when the calculations can be based only on fluid dynamical correlations. With the comparison actually done between diffusional and liquid extraction data we can get this information to reduce the uncertainties in the design of extraction columns.

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## Oxidation and Reduction of Cerium During Solvent Extraction with Benzoyltrifluoroacetone into Nonpolar Organic Solvents in the Absence and Presence of Trioctylphosphine Oxide

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### ABSTRACT

During the solvent extraction of cerium(III) with benzoyltrifluoroacetone (Hbfa) into air-saturated carbon tetrachloride, the oxidation to cerium(IV) was found from the change in the optical spectrum of the organic solution. The rate of oxidation was not very dependent on the Hbfa concentration. This oxidation was suppressed by trioctylphosphine oxide (TOPO). When a carbon tetrachloride solution contained the  $Ce^{IV}(bfa)_4$  complex, the reduction of the metal ion to cerium(III) occurred by an addition of TOPO. This was measured by the change in the absorption spectrum of the solution. The rate of reduction of the  $Ce^{IV}(bfa)_4$  complex in the organic solution was first order with respect to the TOPO but it was not dependent on the Hbfa concentration.

### INTRODUCTION

Although solvent extraction data for the trivalent lanthanides in many solvent extraction systems have been reported, the data for cerium are not often given in such papers. This could be due to the fact that cerium(III) can be oxidized to cerium(IV) and cerium(IV) can be reduced to cerium(III) during solvent extraction. Thus, the extraction data of cerium are not always reproducible when the experimental conditions are not well controlled. In the course of studying the solvent extraction of cerium(III) with  $\beta$ -diketones in our laboratory, such an oxidation of cerium(III) was found in the organic phase and a reduction of cerium(IV) in the  $\beta$ -diketonate complexes during stripping was also found both in the organic and in the aqueous phase.

The present paper describes the oxidation and reduction of cerium during solvent extraction with benzoylacetone (Hbza) or benzoyltrifluoroacetone (Hbfa). Also, the rate of oxidation of the extracted cerium(III) and that of reduction of cerium(IV) in the complexes are determined. Trioctylphosphine oxide (TOPO) which enhances the solvent extraction of trivalent lanthanides with several  $\beta$ -diketones (synergistic enhancement) also affected the rate of oxidation and reduction of cerium in the  $\beta$ -diketonates in the organic phase.

### EXPERIMENTAL

All the experiments were made at 298 K. Analytical grade  $\beta$ -diketones and cerium(III) and (IV) acetylacetonate were used. The solvent extraction experiments were carried out using

stoppered glass tubes (capacity 20 cm<sup>3</sup>). The aqueous phase was a 1 mol dm<sup>-3</sup> sodium perchlorate solution buffered by acetate and the organic phase was carbon tetrachloride initially containing a given amount one of the β-diketones. The organic solutions of the complex of cerium(III) and cerium(IV) with benzoylacetone (Hbza) or benzoyltrifluoroacetone (Hbfa) were prepared by dissolving the crystals of cerium(III) or (IV) acetylacetonate in a water-saturated solvent containing the β-diketone (by a ligand exchange method). Since the Hbza or Hbfa was in a large excess to the acetylacetonate, the ligand in the complex, exchanged with bza<sup>-</sup> or bfa<sup>-</sup>. The effect on the extraction of acetylacetonate (Hacac) released from the complex to the solvent was checked by experiments with samples to which were added the equivalent amount of Hacac released from the initial complex. It was found that even under conditions where the amount of Hacac was double, the results were the same and thus, no effect of the Hacac released from the complex was recognized. The volume of the two phases was always the same. The two phases in the tubes were agitated vigorously by a mechanical shaker. The cerium was determined as a cerium(III)-chlorophosphonazo-III complex at 680 nm. The absorption spectrum of the carbon tetrachloride solution of Ce<sup>III</sup>(bfa)<sub>3</sub> and Ce<sup>IV</sup>(bfa)<sub>3</sub> containing TOPO in the range of 370 to 500 nm was measured as a function of the standing time. A Hitachi U-3410 Spectrophotometer was used for these measurements. The sample solution was covered with aluminum foil in order to keep the sample in the dark. The optical absorption of the organic sample solution was measured as a function of the standing time.

### STATISTICAL

All the chemical species in the organic phase are denoted by the subscript "org" while those in the aqueous phase have no subscript.

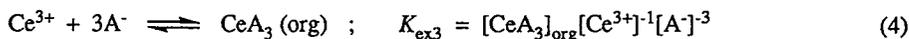
A β-diketone is denoted by "HA". The two-phase distribution constant and the acid dissociation constant of HA are defined as :

$$K_d = [\text{HA}]_{\text{org}}[\text{HA}]^{-1} \quad (1) \qquad K_a = [\text{H}^+][\text{A}^-][\text{HA}]^{-1} \quad (2)$$

From these, the concentration of A<sup>-</sup> in the aqueous phase can be calculated as:

$$[\text{A}^-] = [\text{HA}]_{\text{org,init.}} \{1 + (1 + K_d)K_a^{-1}[\text{H}^+]\}^{-1} \quad (3)$$

The extraction equilibrium of Ce<sup>3+</sup> can be written as:



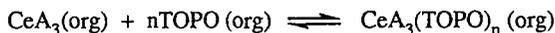
When the extracted cerium(III) species is oxidized in the organic phase containing HA, the CeA<sub>4</sub> species should be formed. However, such an oxidation in the aqueous phase is found to be negligible under the conditions of the present study.

For this reason, the distribution ratio in the solvent extraction system can be written as  $D = ([\text{Ce(III)}]_{\text{org}} + [\text{Ce(IV)}]_{\text{org}}) / [\text{Ce(III)}]$  when the complex formation in the aqueous phase is negligible.

$$D = ([\text{Ce}^{\text{III}}\text{A}_3]_{\text{org}} + [\text{Ce}^{\text{IV}}\text{A}_4]_{\text{org}}) / [\text{Ce}^{3+}] = K_{\text{ex3}}[\text{A}^-]^3 + K_4[\text{A}^-]^4 \quad (5)$$

Here  $K_4$  is a conditional constant which should become larger as the oxidation proceeds.

When the extraction of  $CeA_3$  is enhanced by TOPO, the equilibrium can be written as:



and then the distribution ratio is written as:

$$\begin{aligned} D &= ([CeA_3]_{org} + [CeA_3(TOPO)]_{org} + [CeA_3(TOPO)_2]_{org})/[Ce^{3+}] \\ &= K_{ex3}[A^-]^3(1 + \beta_{(org)1}[TOPO]_{org} + \beta_{(org)2}[TOPO]_{org}^2) \end{aligned} \quad (6)$$

where

$$\beta_{(org)n} = [CeA_3(TOPO)_n]_{org}[CeA_3]^{-1}[TOPO]_{org}^{-n} \quad (7)$$

The rate of reduction of Ce(IV) in the chelate,  $CeA_4$ , in the organic phase can be written as:

$$-d[Ce(IV)]_{org}/dt = k [Ce(IV)]_{org}[HA]_{org}^a [TOPO]_{org}^b \dots \quad (8)$$

From Eq. 8, the following equation is introduced:

$$\log([Ce(IV)]_{org} / [Ce(IV)]_{org,init}) = -(k_{obsd} / 2.303)t \quad (9)$$

$$\text{where } k_{obsd} \text{ is the observed rate constant ; } k_{obsd} = k[HA]_{org}^a [TOPO]_{org}^b \dots \quad (10)$$

Thus the value for "a" can be obtained from the slope of the  $\log k_{obsd}$  vs  $\log[HA]_{org}$  plot when  $[TOPO]_{org}$  is kept constant, while the value for "b" can be obtained from the slope of the  $\log k_{obsd}$  vs  $\log[TOPO]_{org}$  plot when  $[HA]_{org}$  is kept constant.

## RESULTS AND DISCUSSION

The solvent extraction equilibrium of cerium(III) was reached within a short time: a vigorous agitation of the two phases for 30 s was usually enough for this. The extraction of cerium(III) with Hbfa was nearly similar when the two-phase agitation was continued for 30 s and for 24 h as is seen from Fig. 1(a). Although the distribution ratio did not change for the prolonged two-phase agitation, it was observed that the color of the organic phase changed from colorless to weak brown which showed the formation of a small amount of  $Ce^{IV}(bfa)_4$  in the organic phase. However, as has been pointed out, such an oxidation of a small amount of cerium(III) did not change the shape of extraction curve markedly. [Sekine T., Nguyen Thi Kim Dung, 1993]

On the other hand, the distribution ratio in the extraction of cerium(III) with Hbza increased when the two phases were agitated for a long time as is seen from Fig. 1(b). The shape of extraction curve,  $\log D$  vs  $\log[bza^-]$ , also changed by the prolonged two-phase agitation. The slope of the plot was about +3 when the agitation was carried out for a short time but for a long times it became larger and approached +4. This could well be explained by the oxidation of cerium(III) in the complex. The cerium(IV) thus formed was more extractable than cerium(III). The change in the value of the slope from +3 to +4 may be explained by Eq. 4.

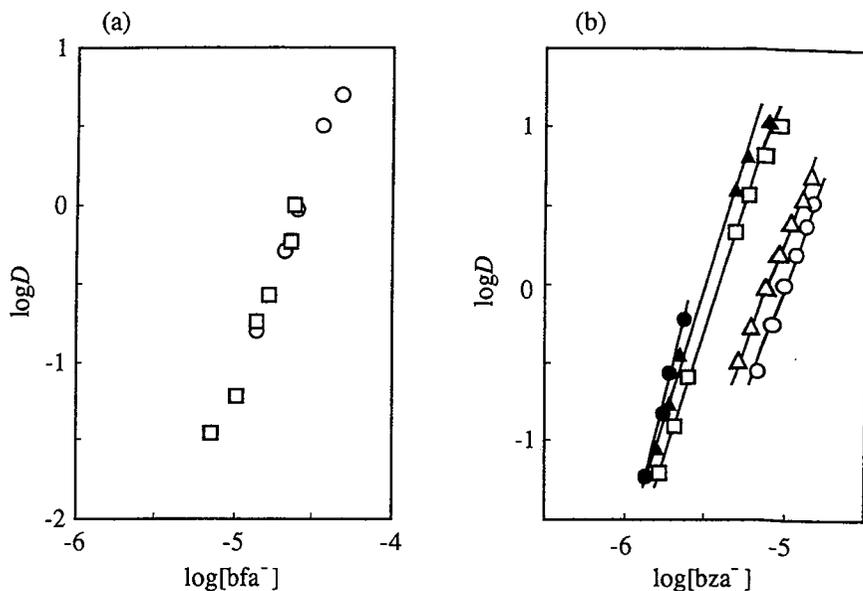


Fig. 1 Solvent extraction of cerium(III) by two-phase agitation for different time intervals.

Org.phase: carbon tetrachloride containing  $0.1 \text{ mol dm}^{-3}$  of the  $\beta$ -diketone

Aq.phase:  $1 \text{ mol dm}^{-3}$   $\text{NaClO}_4$  at various pH.

- (a) With benzoyltrifluoroacetone. The two-phase agitation was continued for 30 s (O) and 24 h ( $\square$ );  
 (b) With benzoylacetone. The two-phase agitation was continued for 30 s (O), 5 min ( $\Delta$ ), 30 min ( $\square$ ), 45 min ( $\blacktriangle$ ), and 60 min ( $\bullet$ ).

The oxidation of cerium(III) in the chelates was further studied by spectrophotometry. In a carbon tetrachloride solution containing the metal chelate, the  $\beta$ -diketone, and no TOPO and saturated with water and air, the rate of oxidation was found to be about one order higher with the cerium(III) chelate of Hbza than with that of Hbfa. It was also found that the rate of oxidation of cerium(III) in the chelates was not very affected by the concentration of coexisting  $\beta$ -diketone. This oxidation of cerium(III) during the solvent extraction with Hbza was hindered when the organic phase contained added TOPO. Figure 2 shows the results.

The same interference of the oxidation by TOPO was also observed when the metal chelate was in the organic solution which was separated from the aqueous phase. When the carbon tetrachloride solution contained the  $\text{Ce}^{\text{III}}(\text{bfa})_3$  chelate, the oxidation of cerium(III) was nearly completely suppressed by the addition of  $0.01 \text{ mol dm}^{-3}$  TOPO. On the other hand, in the absence of TOPO,  $\text{Ce}^{\text{IV}}(\text{bfa})_4$  in carbon tetrachloride saturated by water and air was stable. This was found from the fact that the absorption of the  $\text{Ce}^{\text{IV}}(\text{bfa})_4$  chelate solution essentially did not change during

the time the solution was standing, for example, for one day. However, it was found that an addition of TOPO gradually decreased the absorption due to the  $Ce^{IV}(bfa)_4$  complex. This should indicate the reduction of  $Ce^{IV}(bfa)_4$  to  $Ce^{III}(bfa)_3$  in the carbon tetrachloride solution. The observed rate constant in Eq. 8 was determined as a function of the TOPO concentration. The results are given in Fig. 3. As is seen from Fig. 3, the rate constant for the reduction is first order with respect to the TOPO concentration. When the TOPO concentration was  $0.01 \text{ mol dm}^{-3}$ , it was also found that the rate measured as a function of the coexisting Hbfa was essentially not affected by Hbfa in its concentration range from  $10^{-3}$  to  $10^{-1} \text{ mol dm}^{-3}$ . Thus the addition of TOPO caused the reduction of  $Ce^{IV}(bfa)_4$  but the coexisting Hbfa did not change the rate.

However, the effect of reduction of cerium(IV) to cerium(III) on the extraction with Hbfa is not very marked. This could be due to the fact that although the extraction of cerium(IV) with Hbfa is better than cerium(III), the cerium(IV) essentially does not show any synergistic effect with TOPO while, as is known, the extraction of the trivalent lanthanides with  $\beta$ -diketones, for example, with 2-thenoyltrifluoroacetone (Htta) is very much enhanced by a solvating type extractant, for example, TBP or TOPO. [Sekine T., Dyrssen D., 1967]

It was observed that the extraction of cerium(III) with Hbfa was enhanced very much by an addition of TOPO and the enhancement is second order with respect to TOPO in the concentration range of TOPO studied. However, since the cerium(IV) extraction with Hbfa is essentially not enhanced by TOPO, and since cerium(III) extraction with this  $\beta$ -diketone is very much enhanced by the addition of TOPO, the impairment of the extraction of the metal due to the reduction from cerium(IV) to cerium(III) is approximately cancelled out and a further enhancement is recognized by the synergistic effect of the extraction of cerium(III) with Hbfa and TOPO.

From these results, it is seen that during the solvent extraction of cerium(III) with the  $\beta$ -diketones into carbon tetrachloride which is saturated with air and water, the extracted cerium(III) is oxidized to cerium(IV). This oxidation occurred much more readily with the benzoylacetone chelate than with the benzoyltrifluoroacetone chelate. Moreover, the extraction with Hbza is enhanced by the oxidation of cerium(III) even after two-phase agitation for 5 min but that with Hbfa was nearly negligible within the

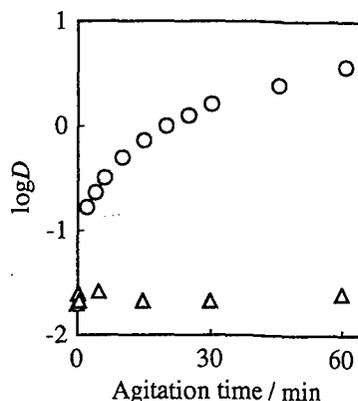


Fig.2 The enhancement of solvent extraction with benzoylacetone by the oxidation of cerium(III) during the two-phase agitation and its hindrance by TOPO.

Organic phase : carbon tetrachloride containing  $0.1 \text{ mol dm}^{-3}$  Hbza and no TOPO(O) or  $0.01 \text{ mol dm}^{-3}$  TOPO( $\Delta$ ).

Aqueous phase :  $1 \text{ mol dm}^{-3}$   $NaClO_4$  at pH 3.4 (O), and pH 1.7 ( $\Delta$ ).

limit of experimental error although the partial oxidation of cerium(III) in the complex was clearly found by the change in the color of the organic phase. Since no oxidant other than  $O_2$  dissolved in the organic phase may be found and the oxidation occurs only in the organic phase, the oxidation of cerium(III) during the solvent extraction could be caused by dissolved atmospheric oxygen in the organic phase. The reduction of cerium(IV) in the benzoyltrifluoroacetate chelate could be caused by the  $\beta$ -diketone. However, as the rate of reduction was not dependent on the coexisting Hbfa over the large concentration range, it could most probably be caused by the leaving  $bfa^-$  group from the  $Ce^{IV}(bfa)_4$  chelate in the organic phase. The same type of assumption for the reduction has already been given for the reduction of cobalt(III) in the acetylacetonate complex to cobalt(II). [Sekine T., Alim Abdurahman, *et al.* 1992]

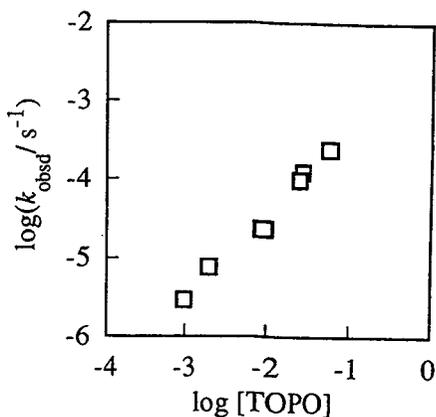


Fig.3 The dependence of  $k_{obsd}$  (cf. Eq. 10) for the reduction of  $Ce^{IV}(bfa)_4$  in carbon tetrachloride on the TOPO concentration.

The solution is carbon tetrachloride containing  $1 \times 10^{-4} \text{ mol dm}^{-3} Ce^{IV}(bfa)_4$ ,  $3.3 \times 10^{-3} \text{ mol dm}^{-3} Hbfa$ , and various initial amounts of TOPO.

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## REACTIVE SOLVENT EXTRACTION of Amino Acids

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Amino acids are hydrophilic and difficult to extract or separate by solvent extraction. This study examines the possibility of extracting amino acids into an organic solvent with the aid of cationic extractants. By performing extractions at different equilibrium pH values, it might be possible selectively to extract amino acids with different  $pK_a$  values.

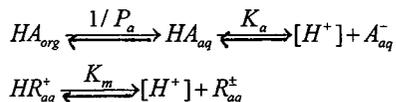
The extraction of amino acids with tri-*n*-octylmethylammonium chloride (TOMAC) has been studied at high pH by Hano et al (1990). They found that the extraction equilibrium constants correlated well with the hydrophobicity scale of each amino acid defined by Nozaki and Tanford (1971). Schügerl and Degener (1989, 1994) have reviewed amino acid extraction and fractionation and have published work on aspartic acid (1992). Most of the work involved quaternary ammonium extractants especially TOMAC. Bitar *et al.* claim the partial separation of amino acid mixtures with two extractants (Di-(2-ethylhexyl)phosphoric acid (D2EHPA) in 2-ethylhexanol and kerosene, and Aliquat 336 in Solvesso) at various pH values. Tjerneld (1994) has partitioned amino acids in two-phase aqueous systems.

### THEORY

The solvent extraction of metal cations from aqueous solution with lipophilic organic acids is conceptually straightforward. At low pH, the acid is protonated and does not give ions to form ion pairs. As the pH is raised, the acid ionises. The resulting lipophilic anions form ion pairs with the metal cations and draw them into the organic phase. Thus extraction rises with pH, and its extent is governed by the  $pK_a$  and lipophilicity of the acid and the hydrophilicity of the metal.

In the case of extraction of amino acids, the situation is more complicated. At low pH, the extractant acid is protonated and there should be no extraction from the aqueous phase even though the amino acid exists as a cation. If the  $pK_a$  of the extractant is lower than that of the amino acid, then it will ionise as the pH rises, and extraction into the organic phase should occur. As the pH rises further, however, the amino acid will change to a zwitterion and ion pair extraction will not occur even though extractant ions are abundant. Extraction by other mechanisms might occur, and Schügerl (1989) quotes various separations by Bitar *et al.* (1987) with high concentrations of D2EHPA at pH 2.7 and 3 which may or may not be due to solvation by the so-called PGS extractant.

If the extractant lipophilic acid is written HA and the amino acid HR, and they have acid dissociation constants in water of  $K_a$  and  $K_m$  respectively, then the two dissociation processes can be written:



where  $P_a$  is the partition constant of the extractant between water and the organic solvent and  $R^\pm$  is the zwitterion. If  $P_m$  is its equilibrium constant, the ion pairing may be written:



Let the total concentration of amino acid be  $a$  and fractions  $x$ ,  $y$  and  $(1-x-y)$  of it exist as  $HR^+ A_{org}^-$ ,  $R^\pm_{aq}$  and  $HR^+_{aq}$ . Let the total concentration of extractant be  $b$  and let the concentrations of  $A_{aq}^-$  and  $HA_{org}$  be  $bz$  and  $b(1-z)-ax$ . If concentrations are assumed equal to activities, then the three equilibria may be written:

$$\frac{K_a}{P_a} = \frac{bz[H^+]}{b(1-z)-ax} \quad K_m = \frac{y[H^+]}{1-x-y} \quad \text{and} \quad P_m = \frac{x}{bz(1-x-y)}$$

$$\text{whence } x = \frac{-B - \sqrt{B^2 - 4ab}}{2a} \quad \text{where } B = a + b + \frac{1}{P_m} + \frac{K_m}{P_m[H^+]} + \frac{P_a(K_m + [H^+])}{K_a P_m} \quad (2)$$

Graphs of % extraction ( $x$ ) vs. pH can be plotted for different values of the constants. The left of Fig. 1 shows the extraction curves predicted for glycine ( $pK_a = 2.34$ ) and dinonylnaphthalenesulphonic acid ( $pK_a = 0.68$ ). As the acid dissociation constant of D2EHPA is larger than that of glycine, little extraction of glycine by D2EHPA is predicted at any pH. Some amino acids, however, have two amino groups and exist at intermediate pH as singly charged cations and at low pH as doubly charged cations. Such acids may be extracted by D2EHPA and even by Versatic 10 ( $pK_a \sim 4.8$ ). The right of Fig. 1 shows the predicted extraction of histidine ( $pK_a$  ( $RH_2^+ \rightarrow RH^+ + H$ ) = 5.97) by D2EHPA ( $pK_a = 3.95$ ).  $P_m = 900 \text{ dm}^3 \text{ mol}^{-1}$  is assumed in both cases for purposes of illustration. The extraction of the doubly charged species at low pH is not shown, but presumably the  $HR^+ A_{org}^-$  curve will merge with an  $R^{2+} A_2^-$  curve and continue to rise as pH drops.

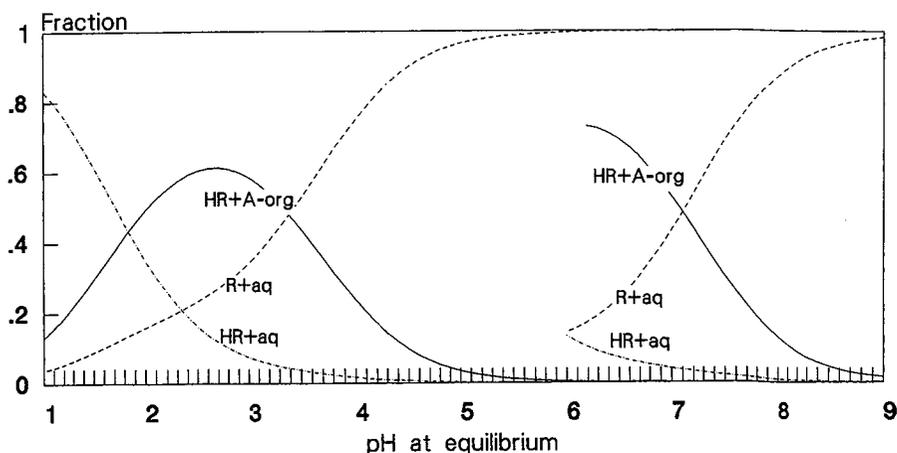


Figure 1: Predicted extractions of glycine by DNNSA (left) and histidine by D2EHPA (right).

Differentiation of equation (2) and equating to zero gives the pH ( $pH_{max}$ ) at which maximum extraction would be expected to occur.  $pH_{max}$  is independent of reaction (1) and is given by:

$$pH_{max} = \frac{1}{2}(pK_a + pK_m + \log P_a) \quad (3)$$

## EXPERIMENTAL

Experiments were carried out at room temperature in separating funnels, the fractions being centrifuged when necessary. Equal volumes of aqueous and organic phases were used throughout. The equilibrium pH was measured on a Jenway 3070 meter. Amino acid concentrations were measured by the ninhydrin method (Plummer, 1978) with a Perkin-Elmer Lambda 2 uv/vis spectrophotometer. Amino acids were obtained from Sigma; all except DL-alanine were of the L-form. Dinonylnaphthalenesulphonic acid (DNNSA) in heptane (72% solution) (NACURE 1052, King Industries) and Di(2-ethylhexyl)phosphoric acid (ICN) were kindly supplied by K & K-Greeff. All reagents were used without further purification.

The use of conventional buffers was avoided because the hydrophilicity of amino acids is such that preferential extraction of buffer could never be ruled out. Instead, mixtures were made up by careful formulation, which would give the desired range of pH values at equilibrium. Sulphuric acid and sodium hydroxide were used to adjust pH. Such a method was difficult to operate at intermediate pH values and consequently data are sparse between pH 3.5 and 10.

## RESULTS

The extraction with DNNSA in hexane of a number of amino acids with single amino and carboxyl groups is shown in Figure 2. As predicted in the theory, the extraction curves go through a maximum. Data at intermediate pH values were difficult to obtain but low extractions at high pH (not shown on the diagram) confirm unequivocally the predicted decline.

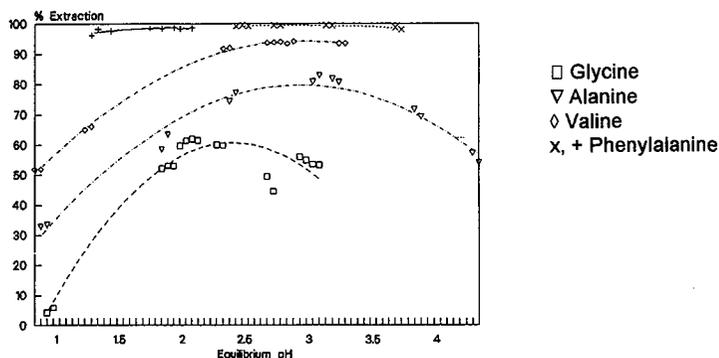


Figure 2: Extraction of monoamino monocarboxylic acids with DNNSA in hexane at low pH.

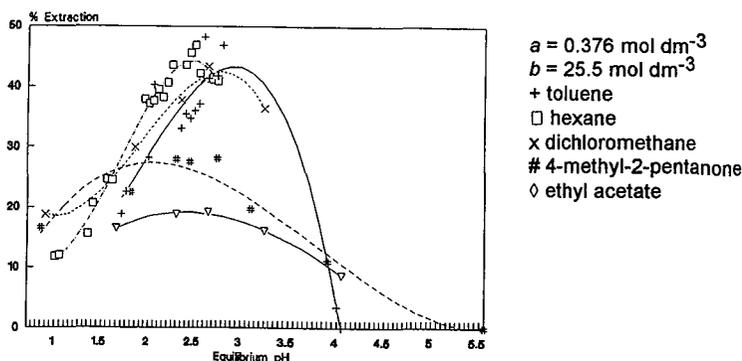
Data for tyrosine, threonine and aspartic acid were also obtained. The partition coefficients ( $P_a$ ) of DNNSA between water and *n*-hexane, dichloromethane, 4-methyl-2-pentanone and ethyl acetate were measured by extraction of the acid at low pH giving values of 213, 244, 476, 278 and 227 respectively. With these and literature values for the dissociation constants of the various components, it was possible by a least squares method to match the experimental extraction curves with those generated by theory. Values of  $P_m$  were derived and linked to free energies of phase transfer involved in process (1). The data are shown in Table 1.

**TABLE 1**  
Phase transfer of monoamino monocarboxylic acids

Acid	<i>a</i>	<i>b</i>	p <i>K</i> <sub>a</sub>	<i>P</i> <sub><i>m</i></sub> (dm <sup>3</sup> mol <sup>-1</sup> )	Δ <i>G</i> <sup>o</sup> <sub><i>t</i></sub> (kJ mol <sup>-1</sup> )	p <i>K</i> <sub>max</sub>	
	(mmol dm <sup>-3</sup> )	(mmol dm <sup>-3</sup> )				expt.	predicted eq. (3)
Glycine	0.667	18.0	2.34	900	16.8	2.4	2.67
Alanine	0.562	21.0	2.35	1850	18.5	3.2	2.68
Valine	0.427	7.37	2.29	20000	24.5	2.3	2.65
Phenylalanine	0.303	24.3	2.58	43000	26.4	2.9	2.79
	0.303	39.6		40000	26.3		
Tyrosine	0.276	9.56	2.20	12000	23.3	2.6	2.6
Threonine	0.420	21.8	2.15	1600	18.3	2.4	2.58
Aspartic acid	0.376	18.2	1.88	900	16.8	2.5	2.44

Glycine and aspartic acid with its two carboxyl groups are evidently more hydrophilic than the other amino acids in the table. Almost 100% of phenylalanine was extracted, so the experiment was repeated at lower extractant concentrations. The results are satisfactorily close. Agreement between experimental and predicted p*K*<sub>max</sub> values was moderate, but the experimental curves have broad maxima that are difficult to identify accurately.

The effect of solvents is shown in Figure 3 for the extraction of aspartic acid. All solvents contained a small amount of heptane present in the initial NACURE 1052. The lower curves are calculated as the difference between two large numbers and are subject to large errors. The effectiveness of the solvents correlates with their *P*<sub>*a*</sub> values, hexane, toluene and dichloromethane being similar and the oxygenated solvents inferior.



**Figure 3: Effect of solvent on the extraction of aspartic acid with DNNSA**

Amino acids with two amino groups (e.g. ornithine, histidine, asparagine and arginine) have first acid dissociation constants in the region of 2 and further dissociation constants, for the side

chain amino group, at intermediate pH values. The final dissociation constant comes at about  $pK_a$  10. These exist as doubly charged cations at low pH, as singly charged cations at intermediate pH and as zwitterions and negative ions only at high pH. They would thus be expected to be readily extracted at low pH. Fig. 4 shows the results for the acids above. At pH values near the first dissociation constant, extraction is close to 100% for all acids except asparagine. There is a slight drop at intermediate pH and a large drop as the transition to the zwitterion occurs. Six of the seven experimental curves in Fig. 4 are indistinguishable on the scale of the diagram and only a single line has been drawn through them, but examination of the reduced levels of unextracted amino acid indicate that asparagine is more readily extracted than histidine and ornithine, which are similar but are in turn more readily extracted than arginine. Higher concentrations of extractant in the region of doubly charged cations cause increased extraction but the data are not good enough to establish whether this is related to the concentration to the power one or two.

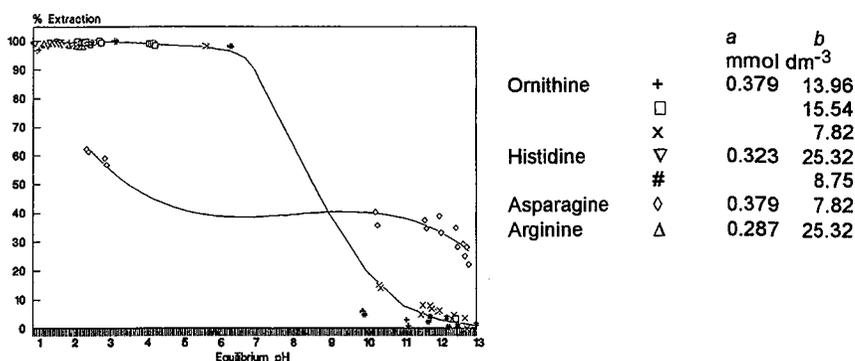


Figure 4: Extraction of amino acids with two amino groups

## DISCUSSION

The extraction curves for amino acids that do not give doubly charged ions fit into a simple theoretical model. Free energies of reaction 3 for different acids were derived and shown in Table 1. Fig. 5 compares these with the hydrophobicity scale of Nozaki and Tanford (1971).

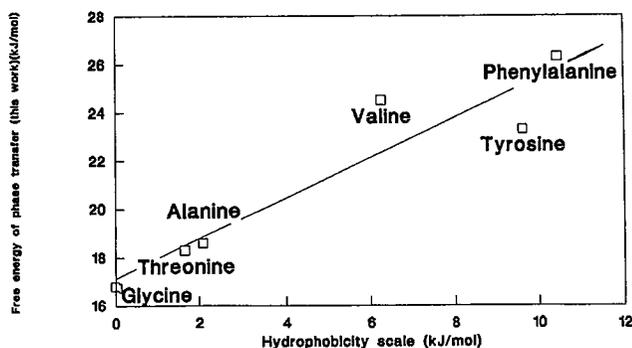


Figure 5: Free energy changes for reaction 1 vs. Nozaki and Tanford's hydrophobicity scale

Our values for the free energy change are plotted against the free energy of transfer of the amino acid side chain from 100% organic solvent to water at 298K. The correlation is good in that all the acids except tyrosine/valine come in the same order in both sets of measurements, but the slope of the line is 0.83 rather than unity, which would represent complete correlation. This is an interesting result which, for the moment, we attribute to the physical differences between phase transfer processes involving straightforward solubility compared with those involving ion pairing.

### CONCLUSIONS

Amino acids can be extracted by cationic extractants so long as the extractant has a lower first acid dissociation constant than the amino acid. All amino acids can be extracted into hexane with dinonylnaphthalene sulphonic acid at pH values in the region of 2. Amino acids with two amino groups (ornithine, histidine, arginine, asparagine) may be extracted with di(2-ethylhexyl)phosphoric acid at intermediate pH values and it is predicted that Versatic acid would be successful with a number of these. In the pH~2 region, where they exist as doubly charged cations, very high levels of extraction are achieved.

The extraction equilibria agree broadly with a simple quantitative theory of the extraction and enable the calculation of the equilibrium constant of reaction (1). Derived free energies of phase transfer for a series of amino acids gives a hydrophobicity scale for amino acid side chains broadly in agreement the values of Nozaki and Tanford (1971).

Fractionation of amino acids with widely differing  $pK_a$  values appears possible by choice of extractant and pH. Further work focuses on the possibility of separating mixtures with closer  $pK$  values.

### ACKNOWLEDGEMENTS

One of us (ML) thanks SmithKline Beecham and EPSRC for a CASE award

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## A NEW ROLE OF SOLVENT - SOLVENT EXTRACTION OF SOME TRANSITION METALS WITH A MIXED SOLVENT

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### ABSTRACT

A novel method is proposed for the chelate extraction of transition metal ions. A ternary mixed solvent containing carbon disulfide, primary amine, and alcohol can quantitatively extract  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Fe}^{3+}$  from aqueous nitrate medium without using any chelate extractants. The mixed solvent seemed to generate a dithiocarbamic acid by mixing solvents and to extract metal ions as an dithiocarbamate complex. The optimum extraction conditions, such as pH, mixing ratio of solvents, and shaking time for equilibrium were established.

### INTRODUCTION

In the solvent extraction of metals, solvent and extracting reagents are essential irrespective of extraction system, whether it be a chelate extraction system or ion pair extraction one. If it were possible to extract metal ions from an aqueous phase into an organic phase without using any extractants, it would be expected

= that (1) the operation would be more convenient, (2) problems of stocking the unstable extracting reagent solution, for example as shown in dithizone extraction, would be free, and (3) the cost would be less expensive compared to the usual extraction method. However, such kind of extraction system, in which solvent plays not only the role of solvent dissolving the extracted metal species but also the role of chelate extracting reagent, has not been reported to the best of our knowledge, although some studies have been reported on the inverse system, e.g., acetylacetonone extraction system without using any solvents (Steinbach and Freiser (1953), (1954), Fujinaga and Lee (1978)).

From this standing point of view, the present study was undertaken to prove that ternary mixed solvent containing alkyl- or allyl-amine, alcohol, and  $\text{CS}_2$  has the ability to produce the chelate extractants and to extract metals.

### EXPERIMENTAL

A 10-ml portion of buffered metal ion solution, containing potassium nitrate ( $\text{KNO}_3$ ) to maintain ionic strength at 1.0 M, and an equal volume of the mixed solvent were equilibrated in a 30-ml extraction vial by vigorously shaking for 1 h. After phase separation by centrifugation, the metal ion concentration in the aqueous phase was determined by atomic adsorption spectrophotometry. The extraction ratio was obtained by subtracting the determined metal ion concentration from the known total concentration in the aqueous phase.

### RESULTS AND DISCUSSION

#### *Effect of mixing ratio.*

The effect of mixing ratio of solvents on the extraction of cobalt(II) was examined (Fig. 1). The values inside the triangle are the extraction ratios, and letter *h* indicates that the mixed solvents of these compositions were miscible and mixed freely with water. The

parenthesized value represents that this kind of solvent was partly miscible, and therefore the extraction ratio was corrected for the volume change. The underlined value indicates that the mixed solvents of these compositions came upper layer, and others came lower layer on shaking with water. Hence, organic phase can be controlled to be either the upper or the lower layer by changing the mixing ratio of solvents as the occasion demands. Units of three axes are all volume to volume percentage, and for example, the composition of solvent A is 5:2:3 for  $\text{CS}_2$ : $\text{C}_5\text{H}_5\text{N}$ : $\text{C}_5\text{H}_{11}\text{OH}$ . Figure 1 demonstrates that each component of mixed solvent is essential for the metal extraction. The area surrounded by a dotted line is the optimum solvent composition for quantitative extraction. This area is fairly wide, so that it is not necessary to measure their volumes precisely for the preparation of mixed solvent and the

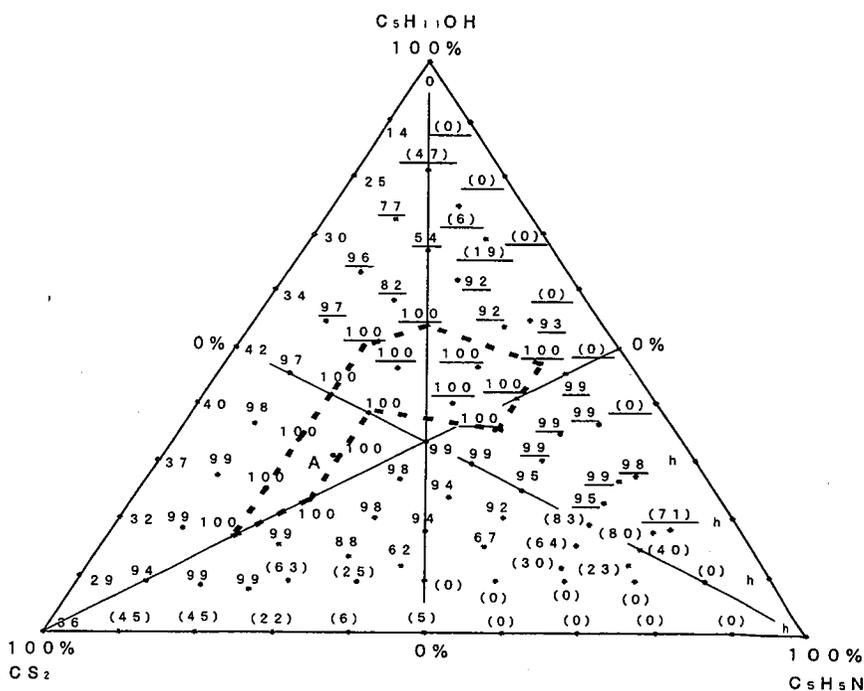


Fig. 1. diagram of mixing ratio of three components for the extraction of  $\text{Co}^{2+}$ .  $[\text{Co}^{2+}] = 10^{-4} \text{ M}$ ; values in parentheses, corrected values of extraction ratio for volume change; underlined values, organic phases is upper layer; h, phase did not separate and a homogeneous solution was obtained.

procedure becomes very simple and convenient. However, this mixed solvent did not necessarily form sufficient isoamylxanthic acid and consequently its extractability was poor. The concentrations of isoamylxanthic acid in the aqueous phase were determined spectrophotometrically by equilibrating the mixed solvent with 0.1N KNO<sub>3</sub> and were  $3.7 \times 10^{-5}$  M at pH 3.0 and  $8.5 \times 10^{-4}$  M, respectively, which were lower than that of added metal ions,  $10^{-4}$  M. The maximum extractable amount of Co<sup>2+</sup> with this mixed solvent was  $4.3 \times 10^{-4}$  M at pH 3.0. This mixed solvent could extract Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup>, but not Fe<sup>3+</sup> and Mn<sup>2+</sup>.

**Effect of amine and alcohol.**

In order to improve the extractability of this mixed solvent, the effect of alcohol and amine on the extractability of the mixed solvent was examined by using Ni<sup>2+</sup>, because Ni<sup>2+</sup> gave the narrowest pH range for 100% extraction among the examined metal ions in the CS<sub>2</sub>-C<sub>5</sub>H<sub>5</sub>N-C<sub>5</sub>H<sub>11</sub>OH ternary mixed solvent system(Fujinaga (1991)). It was reported previously that the extractability of the mixed solvent for Co<sup>2+</sup> improves as the chain length within alcohol congeners grow longer and *n*-C<sub>6</sub>H<sub>13</sub>OH which has the longest carbon chain among the examined alcohols gave the best extractability(Fujinaga (1992)). The extractability of *n*-C<sub>6</sub>H<sub>13</sub>OH and C<sub>6</sub>H<sub>11</sub>OH were further compared and were found to be almost same(Fig. 2).

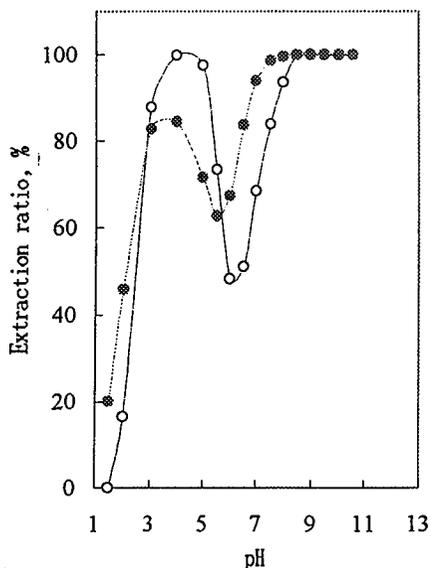


Fig. 2. Effect of alcohol on the extraction of Ni<sup>2+</sup>.

○ :n-Hexylalcohol, ● :cyclohexylalcohol, [Ni<sup>2+</sup>]=1 mM. *n*-C<sub>8</sub>H<sub>17</sub>NH<sub>2</sub>:CS<sub>2</sub>:hexanol composition(v/v%) is 0.5:0.5:99.

Cyclohexanol was used as a component of the mixed solvent in the present study since C<sub>6</sub>H<sub>11</sub>OH is less expensive. As for the amine, it has been found that strongly basic amines with pK<sub>b</sub> value smaller than around 7.0 caused an exothermic reaction and a solidification on mixing with CS<sub>2</sub>. This is the reason why pyridine(pK<sub>b</sub> = 8.62) was previously chosen as a component

of the mixed solvent as strongly basic amine was considered to be unsuitable for it. The violent reaction between  $\text{CS}_2$  and strongly basic amine indicates that the formation of alkylxanthic acid proceeds quantitatively, and solidification can be avoided by decreasing the mixing ratios of  $\text{CS}_2$  and amine. When the ratio of  $\text{CS}_2$  and amine is greater than 10v/v%, the mixture obtained was hot and precipitation occurred. For ratios greater than 5v/v%, less heat and less precipitation were obtained and no change was observed for ratios less than 5v/v%. The effect of the composition of solvents was then examined by changing the mixing ratios of *n*-octylamine and  $\text{CS}_2$  from 0.5% to 2%. Since *n*-octylamine gave the widest pH range for 100% extraction among the examined amines in the  $\text{CS}_2$ - $\text{C}_5\text{H}_5\text{N}$ - $\text{C}_6\text{H}_{11}\text{OH}$  ternary mixed

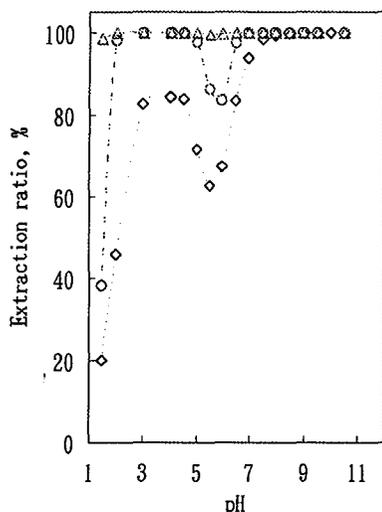


Fig. 3. Effect of the composition of the mixed solvent on the extraction of  $\text{Ni}^{2+}$ . *n*- $\text{C}_8\text{H}_{17}\text{NH}_2$ : $\text{CS}_2$ :cyclohexanol compositions(v/v%) are 0.5:0.5:99 for ◇ , 1:1:98 for ○ , and 2:2:96 for △ , respectively.

solvent system(Fujinaga (1992)), it was therefore used as an amine component for this study. As can be seen from Fig. 3,  $\text{Ni}^{2+}$  was extracted quantitatively from the acidic aqueous medium using the mixed solvent system with the *n*-octylamine and  $\text{CS}_2$  compositions of more than 1%. The effect of amine on the extraction of  $\text{Ni}^{2+}$  was also examined by using the mixed solvent system with the composition of 1:1:98 for  $\text{CS}_2$ :amine: $\text{C}_6\text{H}_{11}\text{OH}$ . Figure 4 shows that the stronger basic and more water miscible amine gave better extractability and *iso*- $\text{C}_3\text{H}_7\text{NH}_2$  gave the best result among the amines examined. Finally, the extraction of  $\text{Fe}^{3+}$  was examined with the *iso*- $\text{C}_3\text{H}_7\text{NH}_2$ - $\text{CS}_2$ - $\text{C}_6\text{H}_{11}\text{OH}$  ternary mixed solvent by changing the mixing ratios of *iso*- $\text{C}_3\text{H}_7\text{NH}_2$  and  $\text{CS}_2$  from 1 to 5v/v%(Fig. 5). A mixed solvent containing  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{CS}_2$ ,  $\text{C}_6\text{H}_{11}\text{OH}$  could not extract  $\text{Fe}^{3+}$  at all, but >98% extraction was obtained by the *iso*- $\text{C}_3\text{H}_7\text{NH}_2$ - $\text{CS}_2$ - $\text{C}_6\text{H}_{11}\text{OH}$  mixed solvent when the mixing ratios of *iso*- $\text{C}_3\text{H}_7\text{NH}_2$  and  $\text{CS}_2$  were 5 v/v%. This indicates that the same extraction effect can be achieved simply by changing the mixing ratio of solvents.

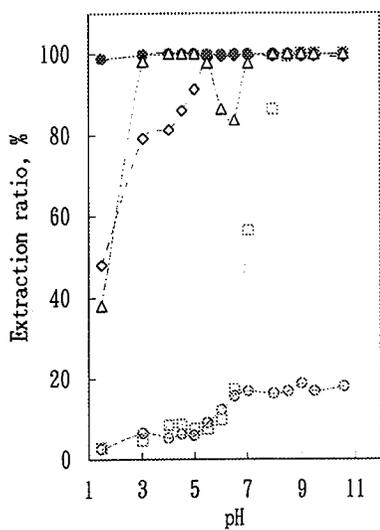


Fig. 4. Effect of amine on the extraction of Ni<sup>2+</sup>.

○ :Tri-*n*-propylamine, ● :*iso*-propylamine, □ :aniline, ◇ :triethanolamine, △ :*n*-octylamine, and [Ni<sup>2+</sup>]=1 mM. Amine:CS<sub>2</sub>:cyclohexanol composition(v/v%) is 1:1:98.

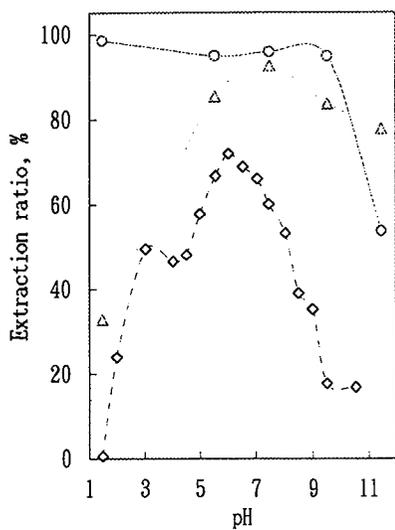


Fig. 5. Extraction of Fe<sup>3+</sup> by mixed solvent of different compositions.

*iso*-C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>:CS<sub>2</sub>:C<sub>6</sub>H<sub>11</sub>OH compositions(v/v%) are 1:1:98 for ◇ ; 3:3:94 for △ ; 5:5:90 for ○ , respectively.

#### ***Extraction mechanism.***

UV spectrum of the aqueous solution that was obtained by shaking the mixed solvent with the blank solution was measured and compared with those of potassium cyclohexylxanthate and sodium diethyldithiocarbamate(Na-DDTC) aqueous solutions. The absorption spectrum of the aqueous solution equilibrated with the mixed solvent is characterized by the double absorption maximums at 253 and 283 nm and agrees very closely with that of aqueous Na-DDTC, 257 and 282 nm. While the potassium cyclohexylxanthate aqueous solution gave a single maximum at 301 nm. The visible spectrum of the mixed solvent containing extracted  $\text{Fe}^{3+}$  species were further measured. Iron( III ) was extracted with potassium cyclohexylxanthate and Na-DDTC into cyclohexanol, separately, and the cyclohexanol layers were subjected to the measurement of visible spectrum which were compared with that of the above mixed solvent. The shape and  $\lambda_{\text{max}}$ (506 and 597 nm) of the spectrum obtained with the mixed solvent is similar to those of  $\text{Fe}^{3+}$ -DDTC complex cyclohexanol solution (511 nm and shoulder at around 600 nm). Therefore, it can be concluded that dithiocabamic acid was formed by mixing  $\text{CS}_2$ , *iso*- $\text{C}_3\text{H}_7\text{NH}_2$ , and cyclohexanol, and metals were extracted in the form of dithiocarbamate complex.

In conclusion, transition metals could be extracted without using any further added extractants in this extraction system. The method can be carried out very simply and conveniently compared with the usual methods.

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# ASPECTS OF MULTICOMPONENT MASS TRANSFER KINETICS IN LIQUID-LIQUID SYSTEMS

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## INTRODUCTION

The development of new applications of extractive processes is often obstructed through a general lack of the understanding in the design of the liquid-liquid extractors. This results in the incomplete understanding of the relationship between the mass transfer and the hydrodynamics in binary and, most importantly, in multicomponent mixtures with more than one species being transferred. The kinetics of multicomponent systems with several simultaneously transferred species are of industrial interest since they are predominant in industrial processes. This work deals with the choice of a quaternary liquid mixture which can be recommended for future experimental and theoretical studies. Preliminary results were obtained in the investigation of the liquid-liquid interface during mass transfer with a Schlieren system.

Multicomponent mass transfer is in most cases a very complex process, which is strongly influenced by the interaction between all transferred species. Possible concentration profiles in both the continuous and dispersed phase and the resulting mass fluxes across the phase interface for a multicomponent mixture are shown in Fig. 1. In the multicomponent case it is also possible that the mass

transfer direction of a component is opposite to its concentration profile (Component n in Fig. 1).

The mass transfer rates of all the components are also influenced by the drop size distribution in each section of a column which are hard to determine. Therefore the currently available column design methods fail in most

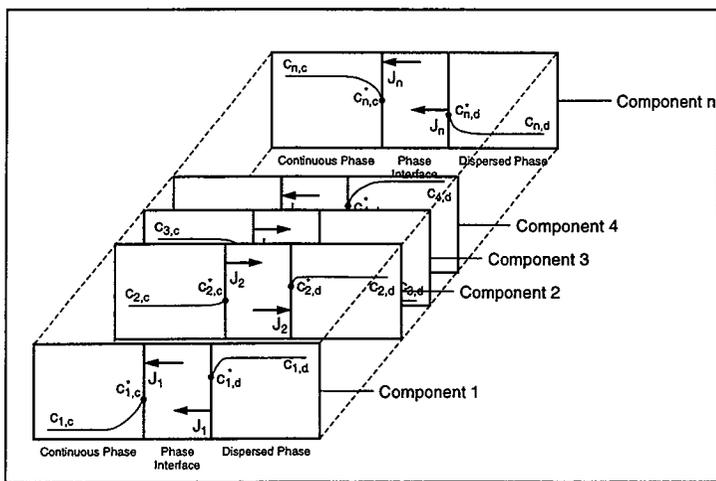


Fig. 1: Multicomponent mass transfer

cases and the extraction column overdesign of 50 % or more is usual.

### SELECTION OF THE MULTICOMPONENT MIXTURE

We would like to introduce a new liquid mixture that allows a study of multicomponent mass transfer of more than one transferred species in the mass transfer section of an extraction column. This mixture should have the following properties:

- two essentially immiscible liquid phases,
- two solutes which are soluble in both phases,
- no formation of pseudo-components through dimerization or dissociation,
- significantly different molecular diffusion coefficients of solutes in both phases,
- absence of interfacial turbulence at measurable low concentrations of solutes (Marangoni Phenomena),
- presence of interfacial turbulence at high concentrations of solutes,
- components of environmental and industrial interest,
- easy to handle (flammability and toxicity) and
- availability in high purities at reasonable costs.

The consideration of the commonly investigated acetic acid is ruled out since it dissociates in the aqueous phase and dimerizes in the organic phase (Bart et al., 1994). The addition of a fourth component to the EFCE system n-butanol/succinic acid/water is unattractive because of its very low interfacial tension (EFCE = European Federation of Chemical Engineering).

The EFCE system toluene/water/acetone was taken as a starting point because toluene and water are essentially immiscible whereas the other systems exhibit partial miscibility. By comparing the cumene process for acetone and phenol synthesis (Kirk-Othmer, 1991) it was decided to consider phenol as a fourth component. The component numbering arose from the historical background with toluene(1)-acetone(2)-water(3) as an EFCE test system and phenol(4) as an added component.

The physical properties of the ternary mixture toluene/acetone/water are well known (Misek, 1978 and Misek et al., 1985). The simple addition of phenol as a fourth component increases the complexity of mixture behaviour because we now have to consider a quaternary mixture. There is very little information on quaternary mixtures. A few data are published by Rasmussen et al., 1987.

A first estimate of the liquid-liquid phase behaviour of the quaternary mixture was made, based on the data of the ternary and binary mixtures. Two of the binary mixtures are known to exhibit miscibility gaps at a temperature of 20 °C. The first mixture, toluene/water, can be considered as completely immiscible while the second binary mixture shows a small miscibility gap starting at a low phenol concentration of 1.55 mol% up to 33.3 mol% (Sørensen et al., 1979).

A quaternary mixture consists of four ternary mixtures and the presentation of the equilibrium can only be done in a three dimensional diagram (Walas, 1985). For that purpose the edges of the diagram shown in Fig. 2 were folded to obtain a tetrahedron. The miscibility gap stretches now over a three dimensional range with boundaries given by the two ternary equilibria.

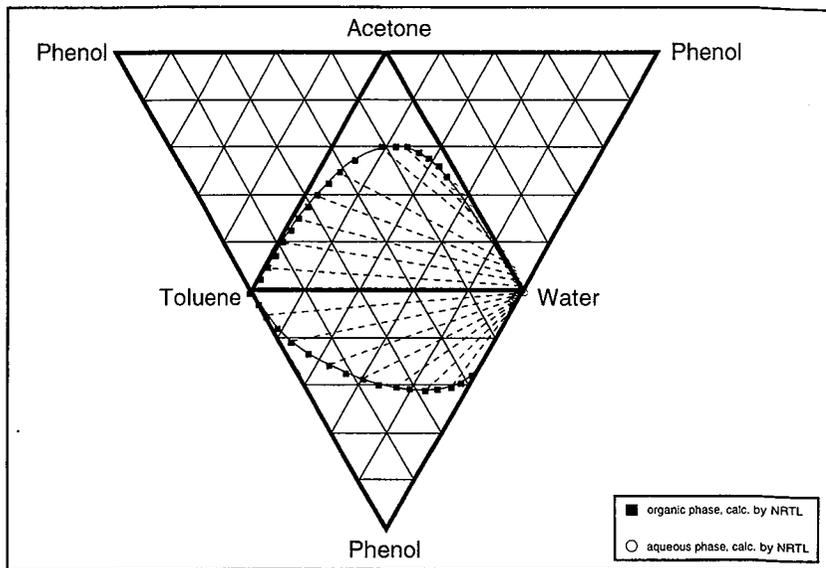


Fig. 2: Calculated binodal curves and tie lines of the quaternary mixture; only every second tie line is shown.

### INTERFACIAL EFFECTS

The liquid-liquid interface between two solvent phases is very sensitive to the mass transfer processes. Two different kinds of effects caused by the mass transfer to or across an interface can be observed in general. Some solutes can act as surface active constituents, the so-called surfactants, which block the interfacial area by adsorption and therefore lead to a decrease in mass transfer rates through either increasing the interfacial resistance or through changing the hydrodynamic regimes inside and outside a rising drop. Another completely opposite effect is the spontaneous interfacial flow, the so-called Marangoni Phenomena. These interfacial flows can

increase mass transfer rates by several magnitudes in comparison to an undisturbed interface. They are driven by interfacial tension gradients caused by local changes of solute concentration, temperature and interfacial electrical potential (Ortiz, 1991). Since liquid extraction is almost always carried out as an isothermal process and the chosen mixture does not show significant electrolyte activity, only local changes of solute concentrations may cause Marangoni Phenomena. In the following the results of observing the liquid-liquid interface of the mixture toluene/acetone/water/phenol during mass transfer are presented.



Fig. 3: Mass transfer at start of transition concentration

A direct observation of gas-liquid and liquid-liquid interfaces is not yet available, but it is possible to observe the effects occurring during mass transfer in the vicinity of a fluid interface. Any mass

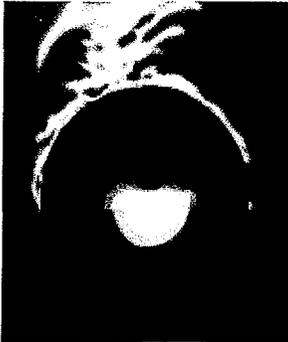


Fig. 4: Mass transfer of acetone (1 mol/L)

transfer process is connected with local changes of physical properties in the continuum where it takes place. Mostly affected are mixture properties such as component concentration and therefore viscosity, interfacial tension and density. Even local density differences are interesting since they have a direct influence on the refractive index of the mixture. Local changes of refractive index can be observed with a Schlieren system (von Reden et al., 1995). In all experiments a clear distinction of the solute concentrations for which the mass transfer regime was completely diffusional or completely turbulent could be made. There was no way to specify at which concentration the transition from diffusional to turbulent mass transfer took place. In some cases at low solute concentrations a rippling or periodic formation of schlieren near the liquid-liquid interface could be seen (Fig. 3).

This is the first sign that mass transfer is not longer completely diffusional and therefore these concentrations were defined as the starting concentrations of a transition range where the mass transfer changes from completely diffusional to completely turbulent. The higher end of the transition range is marked by a concentration at which the observed Marangoni Phenomena could not be increased by an increase of solute concentration (Fig. 4).

Since it was possible to determine a transition range of the starting concentrations which mark the beginning of different mass transfer regimes, the reverse situation should also be possible. A drop is



Fig. 5: mass transfer at  $t \approx 10$  s



Fig. 6: mass transfer at  $t \approx 15$  s



Fig. 7: mass transfer at  $t \approx 30$  s



Fig. 8: mass transfer at  $t \approx 1$  min

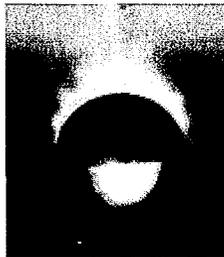


Fig. 9: mass transfer at  $t \approx 3$  min

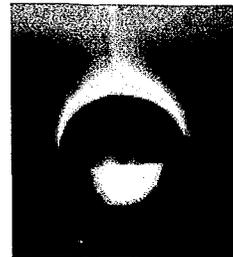


Fig. 10: mass transfer at  $t \approx 4$  min

introduced into a solvent with a starting concentration of solute close to a completely turbulent mass transfer. Mass transfer then starts which is accompanied by intensive Marangoni Phenomena. If the drop is observed over a longer period of time the mass transfer regime becomes completely diffusional. An example is shown in a sequence of pictures of simultaneous mass transfer of acetone and phenol (Fig. 5-10). This sequence shows clearly the time and concentration dependence of the occurrence of Marangoni Phenomena. All experimental results are included in Fig. 11 which shows the dependence of mass transfer regimes on initial concentration of all solutes in the aqueous phase. The initial solute concentration in the toluene drops is zero. The transition range for acetone as solute starts at a concentration of 0.75 mol/L and ends at 1 mol/L. A completely different transition range was found for phenol, which starts at 0.125 mol/L and ends at 0.25 mol/L and is quite different to the acetone concentrations. A second remarkable result shown by Fig. 11 is a further increase of the starting concentrations of the transition regime for acetone and phenol simultaneously transferred in an equimolar ratio. The transition range became more narrow in comparison to that of phenol transfer and starts now at a phenol concentration of 0.05 mol/L and ends at 0.1 mol/L. This behaviour shows that some interactions between phenol and acetone must occur during simultaneous mass transfer, but it is still unexplained. The experiments did not show a significant effect of the total acetone concentration on the transition range concentrations since they remain constant even at large excess of acetone (molar ratio 1 : 10). The level is the same as that during mass transfer with an equimolar ratio of solutes. It follows that phenol has a stronger influence than acetone on interfacial stability but also is influenced by the presence of acetone since the starting concentrations of the transition range during simultaneous mass transfer of both species is significantly lower than that of single transferred phenol. One possible explanation is that phenol dissociates in the aqueous phase and the dissociation products influence the interfacial stability. This can be excluded since the degree of dissociation at the present phenol concentrations is in a range of 0.002 up to 0.0046 %.

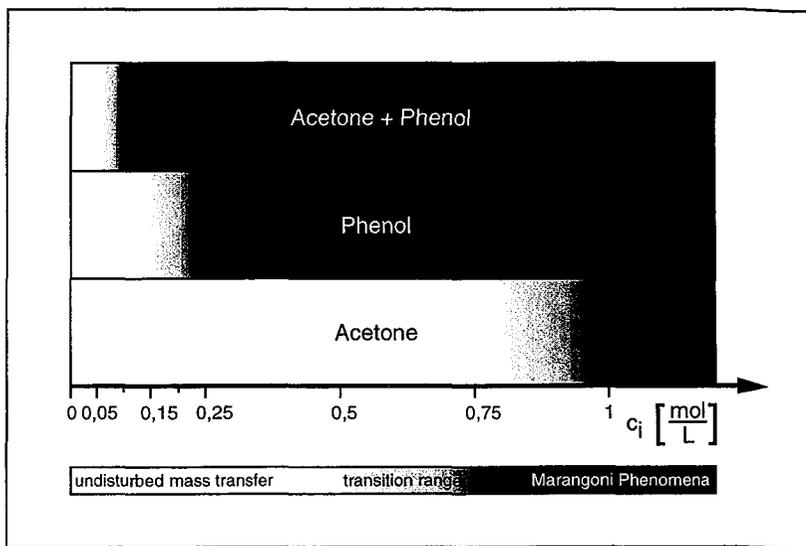


Fig. 11: Mass transfer regimes dependent on solute concentrations

## CONCLUSIONS

Further work is necessary in this field since the map of concentrations shown in Fig. 11 is not of a high density and more experiments should be carried out with the purpose of a more accurate description of transition range concentrations. We would like to determine the influence of the observed Marangoni Phenomena on mass transfer enhancement on single drops. The future theoretical work should try to quantify these enhancements which are exclusively valid for the examined mixture. The influence of diffusion on mass transfer processes should not be neglected. Even the multi-component case is noticeable for some surprising effects. The consideration of diffusional processes needs the investigation of reliable prediction methods of binary and multicomponent diffusion as the function of concentration and temperature. This task may take a long time since there is no mathematical model available that describes the behaviour of liquids.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge the Engineering and Physical Sciences Research Council for supporting the research described in this paper through Grant GR/K38526.

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# THE EXTRACTION KINETICS OF IRON(III) WITH 2-ETHYLHEXYL PHOSPHONIC ACID MONO-2-ETHYLHEXYL ESTER

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## ABSTRACT

The extraction kinetics of Fe(III) by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP, HA) in different diluents from  $1.00 \text{ mol} \cdot \text{dm}^{-3}$  (Na,H)NO<sub>3</sub> media were examined at 298K. It was found that the diluent polarity can affect not only the extraction rate, but also the kinetic mechanism. At low diluent polarity, the rate controlling steps are two parallel reactions with different pathways, one in bulk aqueous phase and one at the interface. With the increase of diluent polarity, the kinetic mechanism will transmit to an interfacial reaction controlling pattern. And at low diluent polarity, the extraction tends to be controlled only by the aqueous phase reaction.

## INTRODUCTION

Extraction of Fe(III) is always of special interest because of the industrial importance of iron removal in hydrometallurgical processes. Large amount of work has been done on the extraction equilibrium and kinetics of Fe(III) by various extractants from different kind of inorganic acid media by Danesi (1976), Fleming and Nicol (1980), Lee and Tavlaneles (1986), Kholkin (1988).

There are some different opinions about the extraction kinetics of Fe(III). As to the Fe(III) extraction kinetics of oxine reagents, Fleming et al. thought the reaction was controlled by diffusion in both phases, but Lee et al. considered that an interfacial reaction is the rate-determining step.

In order to know more about the extraction mechanism of Fe(III) and to find the best condition for Fe(III) extraction and separation, a series of work has been done in our group on the extraction kinetics of Fe(III). Our purpose in this paper is to observe the diluent effect on the extraction kinetics, investigate how the variation of the diluent property causes the change of the extractant's behaviour and further leads to the transformation of the extraction kinetic mechanism.

## EXPERIMENTAL

### Apparatus

High-Speed Stirring Equipment for Extraction Kinetics Experiment, Department of Chemistry, Shandong University, Shandong, China. SCGB-11 Photoelectric Revolution Sensor, Shanghai Revolution Meter Factory, Shanghai, China. 800 Centrifugal Machine, Shanghai Medical Appliance Factory, Shanghai, China. 721 Photoelectric Spectrometer, The Third Analytical Instrument Plant, Shanghai, China.

### Reagents

HEHEHP(HA), purified by the published method of patrige and Johnson (1969), the content of HA is higher than 99%. n-Octane, carbon tetrachloride, chloroform, benzene, toluene, methyl iso-butyl ketone, and iso-pentyl acetate are all analytical reagent grade and were washed with deionized water three times. All other reagents used in this paper are of analytical grade.

### Procedure

All the experiments were carried out at 298K.

Equal volumes of the Fe(III) aqueous solution and the HA organic solution were agitated together vigorously.  $1.00 \text{ cm}^3$  of the mixture was taken as a sample from the system at certain time intervals. The samples were centrifuged immediately to separate the two phases. Fe(III) concentrations in the aqueous phase were measured with the method reported by Zhuzhou Smelter (1979).

## RESULTS AND DISCUSSION

### Determination of apparent extraction rate equation

The mass transfer of Fe(III) from the aqueous phase to the organic phase was treated as pseudo-first-order reaction, i.e.,

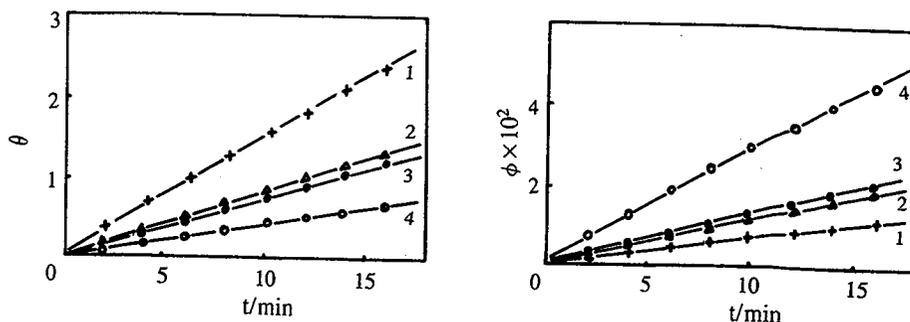


Fig.1 Time dependence of  $\theta$  and  $\phi$ .

$[\text{H}^+] = 0.250 \text{ mol} \cdot \text{dm}^{-3}$   $[\text{NO}_3^-] = 1.00 \text{ mol} \cdot \text{dm}^{-3}$

$[\text{H}_2\text{A}_2]$ : 1,  $0.0500 \text{ mol} \cdot \text{dm}^{-3}$ ; 2,  $0.0450 \text{ mol} \cdot \text{dm}^{-3}$ ; 3,  $0.0400 \text{ mol} \cdot \text{dm}^{-3}$ ; 4,  $0.0350 \text{ mol} \cdot \text{dm}^{-3}$

Its net mass transfer rate equation is,

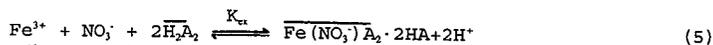
$$d[\text{Fe}]/dt = k_f' [\text{Fe}] - k_b' \overline{[\text{Fe}]} \quad (2)$$

Integrating eq.2 (Flett, 1975), we get

$$\theta = \frac{[\text{Fe}]_i - [\text{Fe}]_e}{[\text{Fe}]_i} \ln \frac{[\text{Fe}]_i - [\text{Fe}]_e}{[\text{Fe}]_i - [\text{Fe}]_e} = k_f' t \quad (3)$$

$$\phi = \frac{[\text{Fe}]_e}{[\text{Fe}]_i} \ln \frac{[\text{Fe}]_i - [\text{Fe}]_e}{[\text{Fe}]_i - [\text{Fe}]_e} = k_b' t \quad (4)$$

From the extraction equilibrium of Fe(III) from  $\text{HNO}_3$  medium by HEHEHP (Li, 1990)



According to eq.3 and eq.4, we can get the  $\theta \sim t$  and  $\phi \sim t$  curves under different conditions. Fig1 shows those curves in the n-octane diluent system when  $[\text{H}_2\text{A}_2]$  is fixed. Lines in Fig.1 all pass through the coordinate zero point. This indicates that the assumption of pseudo-first-order reaction is proper. The slopes of these lines represent the  $k_f'$  and  $k_b'$  values. From the relation between  $k_f'$  or  $k_b'$  and  $[\text{H}^+]$  (Fig2 and Fig3), we can get the power of  $[\text{H}^+]$  in the extraction rate equation. The power of  $[\text{H}_2\text{A}_2]$  can be calculated in the similar way. From the results, the extraction rate equation should be

$$d[\text{Fe}]/dt = k_f [\text{H}_2\text{A}_2] [\text{H}^+]^{-1} [\text{Fe}] - k_b [\text{H}_2\text{A}_2]^{-1} [\text{H}^+] \overline{[\text{Fe}]} \quad (6)$$

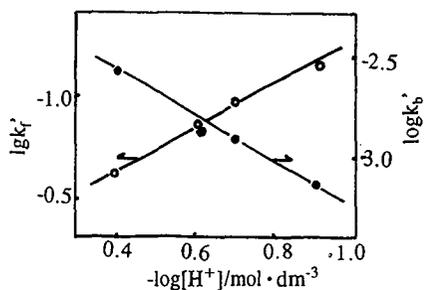


Fig. 2 The effect of  $H^+$  concentration on  $k'_f$  (1) and  $k'_s$  (2).  $[H_2A_2]=0.0500\text{mol}\cdot\text{dm}^{-3}$

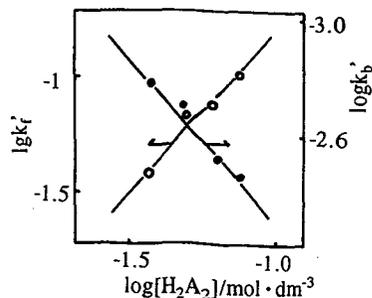


Fig. 3 The effect of HEHEHP concentration on  $k'_f$  (1) and  $k'_s$  (2).  $[H^+]=0.250\text{mol}\cdot\text{dm}^{-3}$

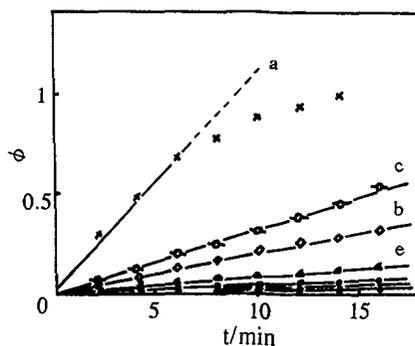
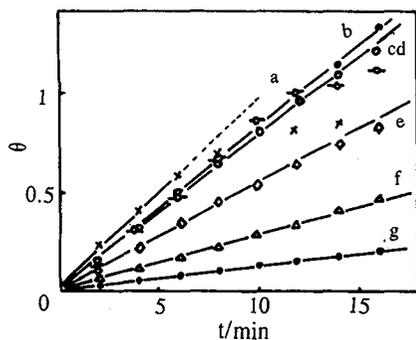


Fig. 4 Time dependence of  $\theta$  and  $\phi$  in different diluent systems.  $[H^+]=0.250\text{mol}\cdot\text{dm}^{-3}$   $[NO_3]=1.00\text{mol}\cdot\text{dm}^{-3}$   $[H_2A_2]=0.0500\text{mol}\cdot\text{dm}^{-3}$   
 (a) chloroform (b) benzene (c) toluene (d) n-octane (e) carbon tetrachloride  
 (f) iso-pentyl acetate (g) methyl iso-butyl ketone

Similarly, we studied the benzene and chloroform systems. It proves that the extraction rate equation is the same in different diluent systems.

#### The effect of diluent on $k'_f$ and $k'_s$ values

Fig 4 shows the  $\theta \sim t$  and  $\phi \sim t$  curves in different diluent systems under the same conditions. The resulting  $k'_f$  and  $k'_s$  values from Fig 4 together with the DP parameter (Marcus, 1989) of the diluent, the distribution ratio(D) and the  $C_{\text{min}}$  value of HEHEHP (Li,1990) were listed in Table 1. It can be seen that the property of the diluent obviously affects the  $k'_f$  and  $k'_s$  values.

TABLE 1

$k_r'$  and  $k_s'$  values in different diluent systems (under the same conditions as Fig.4)

diluent	$\lg k_r'$	$\lg k_s'$	DP	LgD	$C_{\min}$
chloroform	-1.030	-1.006	2.93	5.10	0.36
benzene	-1.051	-1.613	1.80	4.57	0.25
toluene	-1.072	-1.456	1.55	4.53	0.25
n-octane	-1.123	-2.884	-0.9	3.33	0.0064
carbon tetrachloride	-1.259	-1.965	1.06	4.48	0.01
iso-pentyl acetate	-1.535	-2.281		4.62	
methyl iso-butyl Ketone	-1.938	-2.770	2.74	4.82	

### Analysis of extraction mechanism

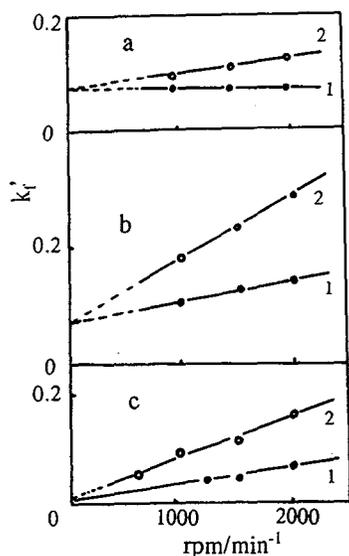


Fig.5  $k_r'$  as a function of stirring speed at different  $H^+$  concentrations  
 $[NO_3^-]=1.00\text{mol}\cdot\text{dm}^{-3}$   
 $[H_2A_2]=0.0500\text{mol}\cdot\text{dm}^{-3}$   
 $[H^+]$ : 1.  $0.250\text{mol}\cdot\text{dm}^{-3}$   
 2.  $0.120\text{mol}\cdot\text{dm}^{-3}$   
 (a) n-octane (b) benzene  
 (c) chloroform

It was generally accepted that the effects of diffusion can be removed by vigorous agitation of systems, and the mass transition is mainly controlled by chemical reactions.

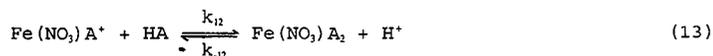
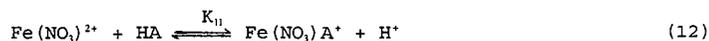
The reaction site of the rate-controlling step is very important for the extraction mechanism. If the controlling reaction took place in the aqueous phase, the  $k_r'$  value should be in reverse proportion to the distribution ratio of the extractant (Ma and Gu, 1986). If the controlling reaction occurred at the interface,  $k_r'$  should be increased with the increase of the interfacial activity of the extractant. Figures in Table 1 show that the  $k_r'$  value neither increases with the interfacial activity nor decreases with the D value of the extractant. This indicates that the rate-controlling reaction was neither only in the aqueous phase nor only at the interface.

The effect of the stirring speed on  $k_r'$  at different acid concentration was studied in the three diluent systems (n-octane, benzene and chloroform) with different polarities (Fig.5). The specific interfacial area will increase with the increase of rpm. The slopes and intercepts of  $k_r'$ -rpm curves will represent interfacial and aqueous phase reactions, respectively (Freiser, 1988). The slopes and intercepts of the lines in Fig.5 are all not zero. Hence the reaction must have two pathways, an interfacial reaction (pathway I) and a bulk aqueous phase reaction (pathway II).

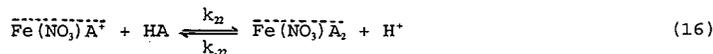
With the decrease of  $H^+$  concentration, the slopes of all lines increase, but the intercepts do not change. This indicates that low acidity is favourable to the interfacial reaction, and the decrease of  $[H^+]$  from 0.250M to 0.120M makes almost no difference to the bulk aqueous phase reaction. Then it can be proved that it is the negative ion of the extractant that takes part in the interfacial reaction, and the neutral molecule of the extractant that takes part in bulk aqueous phase reaction. Therefore the extraction mechanism can be described as follows,



reactions in the aqueous phase adjacent to the interface,



interfacial reactions,



and reactions in organic phase adjacent the interface



Eq.13 and Eq.16 are the rate-determining reactions.

The extraction rate should be the sum of the rate of aqueous and interfacial reactions, i. e.

$$R = R_1 + R_2$$

According to eq.13 to eq.16, the rate equation is,

$$\begin{aligned} R &= -d[Fe]/dt \\ &= (k_{12}K_{11}K_2K_d^{-1}K_{d1}\beta + a_1k_{22}K_{21}K_2K_{d1}K_{d1}^2\beta) [H^+]^{-1} [\overline{H_2A_2}] [Fe^{3+}] [NO_3^-] \\ &\quad - (k_{12}K_{13}^{-1}K_{33}^{-1} + a_1k_{22}K_{33}^{-1}) [H^+] [\overline{H_2A_2}]^{-1} [Fe] \end{aligned} \quad (18)$$

Comparing eq.18 with eq.6, then,

$$k_1' \propto [H^+]^{-1} [\overline{H_2A_2}]$$

$$k_2' \propto [H^+] [\overline{H_2A_2}]^{-1}$$

This was in accordance with the experimental results.

#### The effect of diluent polarity on the extraction mechanism

From eq.18 and eq.6 and considering  $[NO_3^-]=1.00 \text{ mol} \cdot \text{dm}^{-3}$ , then,

$$k_f = (k_{12}K_{11}K_d^{-1} + a_1k_{22}K_{21}K_d^2) K_2K_d\beta \quad (18)$$

$$k_b = k_{12}K_{13}^{-1}K_{33}^{-1} + a_1k_{22}K_{33}^{-1} \quad (19)$$

Normally, the extraction of Fe(III) by HEHEHP is controlled by both aqueous and interfacial reactions. But when the  $K_d$  value is very large (generally,  $K_{d1}$  is also very large), for example, when chloroform act as diluent, the first term in eq. 18 and 19 will be almost zero, therefore the reaction will be controlled only by interfacial reactions. Because of the low distribution ratio and low interfacial activity of HEHEHP in the octane system, the aqueous phase reaction plays a more important role. As shown in Fig5a, there is almost only aqueous phase reaction at high  $H^+$  concentration.

As shown in Table 1, the distribution ratio of HEHEHP increases with increase of the diluent polarity; the interfacial activity of HEHEHP follows a similar rule. Hence, it is the alteration of the distribution and interfacial absorption of HEHEHP made by the change of the polarity of the diluent that leads to the transformation of the extraction mechanism.

### NOMENCLATURE

X	species in the aqueous phase
X	species in the organic phase
X	species at the interface
[X]	the mole concentration of species X
[Fe] <sub>i</sub>	the instantaneous concentration of Fe(III) in the aqueous phase
[Fe] <sub>e</sub>	the equilibrium concentration of Fe(III) in the aqueous phase
[Fe] <sub>0</sub>	initial concentration of Fe(III) in aqueous phase
$k_f'$	the apparent forward extraction rate constant
$k_b'$	the apparent backward extraction rate constant
$k_f$	the forward extraction rate constant
$k_b$	the backward extraction rate constant
$a_i$	the specific interfacial area

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**COMMEMORATION** The late Professor Zili Gao contributed much to this work. We finish it for the memory of professor Gao.



## SINGLE DROPS: A FUNDAMENTAL APPROACH TO THE CALCULATION OF THE VELOCITY PROFILES AND MASS TRANSFER RATES

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### ABSTRACT

The present work aims at the prediction of mass transfer rates from single drops to a continuous phase at intermediate Reynolds numbers up to 220. In this range, no accurate analytical solutions to the unsteady-state convective diffusion equation have been previously reported. The drops were assumed to be free from surface-active contaminants and spherical in shape, which is true for Weber numbers less than one and  $Re$  up to few hundred. Solutions of the equations of motion with assumed polynomials for the simplified stream functions were obtained at the region near the interface.

Obtained velocity profiles were then substituted into the diffusion equation to solve, by means of a similarity transformation, for mass transfer rates which were then compared with experimental data. The agreement between the experimental and the predicted mass transfer coefficients was found to be satisfactory. The results from single-drop analysis will be applied to the study of multidrop systems and extended from binary to multicomponent mass transfer processes.

### INTRODUCTION

Many attempts have been tried in the past to simulate the fluid flow and mass transfer processes for drops and bubbles rising or falling through still, unbounded, liquids. However, to the present day no general analytical approach has been completely successful in representing these phenomena due to the many complex factors influencing them. At very low Reynolds numbers ( $Re$ ) the inertia forces can be neglected, rendering the Navier-Stokes equations simple enough to make possible an analytical solution, whereas at very high  $Re$  the viscous forces become very small and can be likewise neglected, resulting in more simple equations making an easy analytical solution also possible. However, in real practice the  $Re$  in single drop systems generally lie between these two extremes (often between 10 and 200). Because of the mathematical complexity of the governing equations, the analytical treatment generally has been done under certain restricted conditions.

Two of the first attempts to obtain a solution for the flow around a sphere were made by Hadamard(1911) and Rybczynski(1911) separately, but their solution was made by dropping out the inertial effects and therefore their solution is only valid at the creeping flow regime ( $Re$  less than about 0.1). Hill(1894) used a different approach considering the case where viscous forces are insignificant. Because of this omission of viscous forces, Hill's results have very little practical application.

Several authors, specially in the sixties, attempted to extend the work to cases where  $Re$  lies in the intermediate range, among them are the works of Chao(1962), Levich(1964), Winnikow and Chao(1966), Nakano and Tien(1967), Gürkan and Wellek(1976), Gürkan(1989) and many others. Levich(1964) was the first person to apply the concept of the boundary layer theory to the fluid-fluid interface in drops assuming that the exterior flow differs only slightly from that of the potential flow. Chao(1962) used a perturbation model to extend the results from the potential theory in the exterior flow, and Hill's model for the interior flow, to yield expressions for both phases. Nakano and Tien(1967),

Wellek and Gürkan(1976), and Gürkan(1989) proposed a different approach to the flow at intermediate  $Re$  by using two polynomial-form stream functions. They calculated the coefficients by satisfying the boundary conditions and reducing the error by the Galerkin method. Using this method, they obtained approximated velocity profiles and drag coefficients at intermediate  $Re$  up to a few hundred. In the later two works, the authors applied the results to the study of non-Newtonian power-law fluids.

All the derived velocity profiles from these works were applied to the study of the mass transfer process in binary systems. In other works, Ruckenstein(1967) and Ruckenstein and Davis(1970) developed an analytical method for calculating the unsteady state mass transfer process between a single drop and a continuous phase using a similarity transformation. This is viewed as a modification of the penetration theory.

In this work, we are addressing the binary mass transfer problem between single drops and a continuous phase assuming the drops to be spherical with no surface active components at low Weber numbers. We attempt to present an alternative for the analytical calculation of the mass transfer rates, combining the method of Ruckenstein(1967) with the velocity profiles of Nakano and Tien(1967), simplified at the region near the interface, for  $Re$  ranging from 10-220.

## THEORY

The derivation of the equations and the appropriate boundary conditions in spherical coordinates are found elsewhere (Ruckenstein(1967)) and are not repeated here. The main assumptions made for this derivation are that the drops are perfect spheres, the fluids are incompressible and Newtonian with negligible temperature gradients, the flow is axisymmetric and in steady state, whereas the mass transfer process is in unsteady state, and the systems are pseudobinary, where only the solute is transferring between the two immiscible liquid phases. It is also considered that the depth of penetration of mass is very small compared with the drop radius and the elements of liquid brought into contact with the interface at the front stagnation point have the initial concentration  $c_a^0$ . Adjacent to the interface, it is conceived that there is a thin layer on either side of the drop surface where the viscous effects are important. Such layers behave in a similar manner to Prandtl's boundary layer near solid walls, with the obvious differences originated by the transport of mechanical energy from the outer flow to the inner fluid.

According to this unsteady state mass transfer model, the fluid elements brought into contact with the outside fluid at the front stagnation point, remain at the interface travelling to the rear stagnation point as the drop rises or falls. When they reach this point, they travel along the vertical axis of the drop to the front stagnation point again. While moving through the interface, they interchange mass with the elements in the outer flow by diffusion, whereas while moving inside the drop they interchange mass with the bulk of fluid. This allows the elements to be relatively fresh at the front stagnation point. This process is depicted in Fig. 1. The circulation patterns shown in Fig. 1 are known as "Hadamard's Rings". According to these assumptions, the time the

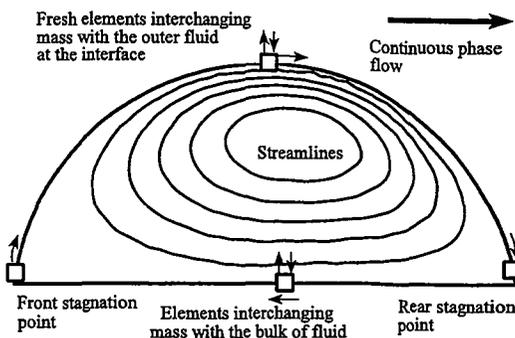


Fig. 1 Representation of the mass transfer process between the drop and the continuous phase.

elements remain at the interface is equivalent to that taken by the drop to rise its own diameter. Since the diffusion coefficient for a liquid is generally very small, if the time of contact of the fluid elements with the interface is not too large, the depth of penetration by diffusion is also very small. In the continuous phase, a similar phenomena occurs. The fluid elements at the front stagnation point remain in contact with the inner fluid at the interface, until they reach the rear stagnation point. From here, they mix with the fluid in the bulk of the continuous phase.

Since the depth of penetration is small, the concentration gradients are appreciable only in the immediate vicinity of the interface, and, practically, are zero at larger distances. We will define a variable  $y$  as the distance taken from the interface into, and away from, the drop surface as

$$y = 1 - r \quad \text{hence} \quad dy = -dr \quad (1)$$

To obtain the dimensionless form of the diffusion equation we use the following relations

$$r = \frac{r'}{a'}; \quad \Psi_p = \frac{\Psi_p'}{U_\infty' a'^2}; \quad v_p = \frac{v_p'}{U_\infty'}; \quad \tau_p = \frac{t' D_p'}{a'^2}; \quad Pe_p = \frac{a' U_\infty'}{D_p'}; \quad Re_p = \frac{a' U_\infty' \rho_p'}{\mu_p'} \quad (2)$$

where the subscript  $p = o$  for the continuous phase and  $p = i$  for the dispersed phase. The superscript (') denotes dimensional variables,  $a$  is the radius of the drop, and  $U_\infty$  is its rising velocity.  $\tau_p$  is the Fourier number,  $Pe_p$  is the Peclet number, and  $Re_p$  is the Reynolds number of the phase  $p$ .  $\Psi_p$  is the dimensionless stream function and  $D_p$  is the diffusivity of the solute within the  $p$  phase.  $\rho$  is the density and  $\mu$  is the viscosity. The dimensionless concentration is given by the expression

$$c_p = \frac{c_{a_p}' - c_{a_o}'}{c_{a_i}' - c_{a_o}'} \quad (3)$$

where the superscript  $o$  denotes initial concentrations of chemical species  $a$ . Using these relations, the dimensionless diffusion equation becomes

$$\frac{\partial c_p}{\partial \tau} + Pe_p v_r' \frac{\partial c_p}{\partial r} + Pe_p \frac{v_\theta'}{r} \frac{\partial c_p}{\partial \theta} = \frac{\partial^2 c_p}{\partial r^2} \quad (4)$$

The following initial and boundary conditions are used to solve these equations. At  $t = 0$ , or  $\tau = 0$ , the initial concentrations are everywhere

$$c_i = c_i^o \quad \text{and} \quad c_o = c_o^o \quad (5)$$

At the interface  $r = 1$ , or  $y = 0$ , there exists continuity of mass flux and chemical equilibrium between the phases, therefore

$$(c_i)_{y=0} = m (c_o)_{y=0} \quad \text{and} \quad \frac{1}{Pe_i} \left( \frac{\partial c_i}{\partial y} \right)_{y=0} = \frac{1}{Pe_o} \left( \frac{\partial c_o}{\partial y} \right)_{y=0} \quad (6)$$

where  $m$  is the distribution coefficient of the chemical species  $a$  between the phases. At the centre of the drop  $r = 0$ , or  $y = 1$ , there is no mass flux, therefore

$$c_i \rightarrow c_i^o \quad (7)$$

At large distances from the drop  $r \rightarrow \infty$ , or  $y \rightarrow \infty$ , the concentration remains constant, hence

$$c_o \rightarrow c_o^o \quad (8)$$

The empirical expressions for the stream functions used by Nakano and Tien(1967) at intermediate  $Re$ , reported as equations (12) and (13) in their paper, are used here as approximations. Introducing equation (1) into these expressions to simplify them for the region near the interface, we obtain the following equation for the stream function

$$\psi_p = -y (\alpha \sin^2\theta + \beta \sin^2\theta \cos\theta) \quad (9)$$

$$\text{where } \alpha = \left( \frac{AI - X CI + 5}{4 + 2X} \right) \quad \text{and} \quad \beta = \left( \frac{BI - X DI}{4 + 2X} \right) \quad (10)$$

In these expressions,  $X = \mu_i / \mu_o$ ,  $Re_o = a U_\infty \rho_o / \mu_o$ , and  $Re_i = a U_\infty \rho_i / \mu_i$ , and the coefficients  $AI$ ,  $BI$ ,  $CI$ , and  $DI$ , are functions of  $X$ ,  $Re_o$ , and  $Re_i$ , to be determined by the Galerkin method. A good treatment to find these coefficients is found in the works of Nakano and Tien(1967) and Gürkan(1989).

The velocity profiles are calculated from the stream function in equation (9) and inserted into the diffusion equation (4), substituting  $r$  by  $y$  and expanding it into series using equation (1). We neglect the terms of higher order since  $y^2 \ll y$ . The authors would provide details of the procedure to anyone interested. After some manipulation, we obtain the diffusion equation for the phase  $p$  as

$$\frac{\partial c_p}{\partial \tau} + 2Pe_p y \left[ \alpha \cos\theta + \beta \left( \cos^2\theta - \frac{1}{2} \sin^2\theta \right) \right] \frac{\partial c_p}{\partial y} - Pe_p [\alpha \sin\theta + \beta \sin\theta \cos\theta] \frac{\partial c_p}{\partial \theta} = \frac{\partial^2 c_p}{\partial y^2} \quad (11)$$

This equation has the same form for both the interior and the exterior regions of the drop, therefore we will follow the same procedure for their treatment. Equation (11) and the boundary and initial conditions (5)-(8) are compatible with solutions of the form

$$c_p = c_p(\eta_p) \quad \text{where} \quad \eta_p = \frac{y}{\Delta_p} \quad \text{and} \quad \Delta_p = \Delta_p(\tau, \theta) \quad (12)$$

Introducing these new variables into equation (11), we can separate the second order partial differential equation into a first order partial differential equation and a second order ordinary differential equation. This is done by using a separation parameter  $\gamma$ , being an arbitrary positive constant. For convenience we will choose a value of 2, so that the ODE has an easy solution. Applying this, we will obtain two separate differential equations as follows

$$\frac{d^2 c_p}{d\eta_p^2} + \gamma \eta_p \frac{dc_p}{d\eta_p} = 0 \quad (13)$$

$$\frac{\partial \lambda_p}{\partial \tau} - 4Pe_p \lambda_p \left( \alpha \cos\theta + \beta \left( \cos^2\theta - \frac{1}{2} \sin^2\theta \right) \right) - Pe_p (\alpha \sin\theta + \beta \sin\theta \cos\theta) \frac{\partial \lambda_p}{\partial \theta} = 2\gamma \quad (14)$$

in these equations  $\lambda_p = \Delta_p^{-2}$  and  $\gamma = 2$ . The solution to equation (13) is

$$c_p = A_p \frac{\sqrt{\pi}}{2} \operatorname{erf}(\eta_p) + B_p \quad (15)$$

The boundary conditions (5), (6), (7), and (8) allow the calculation of the constants as follows

$$A_i = \frac{2}{\sqrt{\pi}} \left[ \frac{c_i^o - mc_o^o}{1 + mD^{1/2}} \right] \quad B_i = m \left[ \frac{c_i^o D^{1/2} + c_o^o}{1 + mD^{1/2}} \right] \quad (16)$$

$$A_o = \frac{2D^{1/2}}{\sqrt{\pi}} \left[ \frac{c_i^o - mc_o^o}{1 + mD^{1/2}} \right] \quad B_o = \left[ \frac{c_i^o D^{1/2} + c_o^o}{1 + mD^{1/2}} \right]$$

where  $D = D_i' / D_o'$ . To find the variable  $\Delta_p$ , we solve equation (14) for  $\lambda_p$  by the method of characteristics proposed by Ruckenstein(1967). After extensive calculations, we find the solution as

$$\Delta_p = \frac{4}{\sqrt{Pe_p}} \Psi(T, \theta) \quad (17)$$

where

$$\Psi(T, \theta) = \frac{\left[ \frac{\beta}{\Phi^4} + \frac{2(\alpha-3\beta)}{3\Phi^3} - \frac{(\alpha-\beta)}{\Phi^2} \right] - \left[ \frac{\beta}{\left(1+\tan^2\frac{\theta}{2}\right)^4} + \frac{2(\alpha-3\beta)}{3\left(1+\tan^2\frac{\theta}{2}\right)^3} - \frac{(\alpha-\beta)}{\left(1+\tan^2\frac{\theta}{2}\right)^2} \right]}{(\alpha \sin^2\theta + \beta \sin^2\theta \cos\theta)} \quad (18)$$

$$\Phi = \Phi(T, \theta) = \frac{1}{(\alpha-\beta)} \left\{ \left[ (\alpha-\beta) \tan^2\frac{\theta}{2} + (\alpha+\beta) \right] \exp\left[ \frac{(\alpha^2-\beta^2)T}{\beta} \right] - 2\beta \right\} \quad (19)$$

$$T = Pe_p \tau_p = \frac{t' U'_{\infty}}{a'} \quad (20)$$

here T is the dimensionless time resulting from the product of the Peclet and the Fourier numbers and is independent of the phase, therefore  $\Psi(T, \theta)$  is also independent of the phase. Equations (15) and (17) allows the calculation of the concentration profiles. The overall dispersed-phase-based mass transfer coefficient,  $K_{OD}$ , is obtained from the mass flux at the interface,  $N_I$ , integrated over the drop surface area to estimate the average mass flux,  $N_A$ , as follows

$$N_I = - \frac{D'_i}{a'} \left( \frac{\partial c_i}{\partial y} \right)_{y=0} = - \frac{D'_i A_i}{a' \Delta_i} \quad (21)$$

$$N_A = \frac{\int_0^{2\pi} \int_0^{\pi} N_I a^2 \sin\theta d\theta d\phi}{\int_0^{2\pi} \int_0^{\pi} a^2 \sin\theta d\theta d\phi} = - \frac{D'_i A_i}{2a'} \int_0^{\pi} \frac{\sin\theta}{\Delta_i} d\theta \quad (22)$$

$$K_{OD} = \frac{N_A}{mc_o^o - c_i^o} = \frac{D'_i}{4a' (1 + mD^{1/2})} \sqrt{\frac{Pe_i}{\pi}} \int_0^{\pi} \frac{\sin\theta}{\Psi} d\theta \quad (23)$$

## RESULTS

The calculations required to use this method can be summarized in the following steps: **I.**- Obtain all the required data for the system, including the physical properties, the drop sizes and velocities, and the dimensionless numbers from equation (2). **II.**- Calculate the parameters  $Al$ ,  $Bl$ ,  $Cl$ , and  $Dl$  using  $Re_o$ ,  $Re_i$ , and  $X$  from the work of Nakano and Tien(1967). **III.**- Calculate  $\alpha$  and  $\beta$  from equation (10). **IV.**- Obtain the parameters  $A_p$ ,  $B_p$ ,  $\Delta_p$ ,  $\Psi_p$ ,  $\Phi_p$ , and the concentration profiles from equations (15)-(20). **V.**- Estimate the mass transfer coefficients from equations (21)-(23).

The analytical results from equation (23) were compared with some experimental results obtained in a single drop column using the systems n-butanol-succinic acid-water and MIBK-phenol-water (Uribe-Ramirez(1991)). In Table 1 we summarize two of these results, comparing the overall dispersed-phase

based mass transfer coefficients. As it can be seen, the values obtained from both methods are very similar for these two systems, which suggests that for the systems studied these equations predict reasonably close values.

**TABLE 1**

Comparison of the theoretical and the experimental  $K_{OD}$

System	X	Re <sub>o</sub>	Pe <sub>o</sub>	K <sub>OD</sub> , cm/s experimental	K <sub>OD</sub> , cm/s theoretical
butanol-succinic acid-water	2.17	72	161000	0.0033	0.0035
MIBK-phenol-water	3.15	220	274000	0.0002	0.00021

### CONCLUSIONS

In this work we have obtained analytical solutions to the diffusion equation in single drop systems at intermediate Reynolds numbers (10-220). From the results presented here, this method seems to generate mass transfer coefficients close to those observed in some experimental studies. To the best of the authors knowledge, no analytical solutions for this Re range had been previously published. A more exhaustive generation of analytical and experimental results, for comparison purposes, is being carried out as part of the present research. A different analytical approach to this problem, using different velocity profiles, is also being studied. This research is still going on and a more accurate numerical method for the solution of the diffusion equation, for binary and multicomponent systems, is being developed. We expect to compare the final results, along with the concentration profiles obtained from the three methods, which will be published in a later stage.

### ACKNOWLEDGEMENTS

We wish to acknowledge the *Consejo Nacional de Ciencia y Tecnologia* (CONACYT) and the *Universidad de Guanajuato, Mexico* for the financial support to this work.

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## THE INFLUENCE OF THE DILATION OF A LIQUID/LIQUID-INTERFACE ON MASS TRANSFER IN EXTRACTION PROCESSES

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### ABSTRACT

A theory proposed by Hampe (1981) concerning the thermodynamics of irreversible processes at interfaces is applied to the case of mass transfer across a plane dilated liquid/liquid-interface. It is deduced that for the case being studied, the mass transfer across the interface linearly depends on the rate of extension of the interface. In order to investigate this result experimentally, a new flow cell is designed where the horizontal interface between water and toluene is dilated in an extensional flow. The rate of extension of the interface is measured using Laser-Doppler-Velocimetry. With acetone as the transfer component, the concentration profiles in the immediate vicinity of the dilated interface are measured by means of holographic interferometry. From these the mass flux is calculated. The present results from the LDV measurements indicate that even in the pure system the interface rapidly becomes rigid due to the adsorption of surface-active contaminants. To allow a mobile interface for a long period of time, the interfacial contaminants are therefore continuously removed. In this way a constant extension rate of the interface is achieved for the entire contact length.

### INTRODUCTION

The models which have been used to predict the mass transfer across interfaces are based for the most part on the film model by Lewis and Whitman (1924) and the surface renewal model by Higbie (1935). In both models the interface is treated as a two-dimensional dividing surface between the two homogeneous phases as it was proposed by Gibbs (1928). At this two-dimensional dividing surface the homogeneous phases are in thermodynamic equilibrium. The application of this model to systems where a mass transfer across the interface occurs and which are inherently in a state of non-equilibrium is therefore limited. To account for the fact that interfaces differ significantly from homogeneous phases in terms of their rheological behaviour, a number of more detailed models have been proposed. Boussinesq (1913) attributes material properties to the two-dimensional interface such as the interfacial shear viscosity or the interfacial dilatational viscosity. These properties are strongly affected by, for instance, the presence of surface active agents. The important role of surface active agents is also incorporated in the structure models of Slattery et al. (1990). Here it is assumed that the surface active agents build well-ordered structures at the interfaces which are responsible for the interfacial properties and which influence the transport processes. Due to the interaction between the three-dimensional homogeneous phases and the two-dimensional interface, transport processes such as the momentum and the mass transfer are coupled. This coupling can be observed for example in the Marangoni effect which was named after Marangoni (1871) and mathematically described by Sterling and Scriven (1959).

The thermodynamics of irreversible processes (TIP) is applied to interfacial systems by Bedeaux et al. (1976, 1986), Kovac (1977) and Hampe (1980, 1981). In the TIP it is postulated that near the thermodynamic equilibrium a linear relation exists between all fluxes and all forces of the same tensorial character (de Groot and Mazur, 1962). Therefore in homogeneous phases a thermodynamic coupling between the momentum transfer - which is described by a second order tensor - and the heat and mass transfer - which is described by a first order tensor - is not possible. The TIP is applied

by Hampe (1981) to a three-dimensional model of the interface as it was first proposed by van der Waals (1894). The mass transfer in the interfacial region is described using a second order tensor. Hence a coupling between the momentum and the mass transfer is possible. This is seen as a reason for the rheological behaviour of interfaces and a thermodynamic explanation of the Marangoni effect. This theory is applied by Millies et al. (1994) to the case of the mass transfer across a dilated interface. For the examined case some simplifications are introduced which allow an experimental verification of the model.

### THEORY

In Fig. 1 it is shown how the mass transfer of a component  $A$  across a plane interface takes place, according to Hampe (1981). A mass flow of the component  $A$  is transported from the bulk phase to the interface. Within the bulk phase, the properties of the phase are determined by the concentration of the components. Thus, the mass flux is a function of the gradients of the chemical potential. It can be described with the known equations for multicomponent diffusion (Krishna and Taylor, 1986). The properties of the interfacial region are determined by the *structure vector*  $\underline{a}_i$  which is a function of the concentration of the components as well as its gradients. The mass transport therefore takes place as a structure transport. It is a function of the gradient of the *interfacial potential*  $\underline{\sigma}_i = f(p, T, \underline{a}_i)$ . The latter is also a vector. The equations which describe this transport are introduced further below. The transition from the bulk phase to the interfacial region occurs gradually.

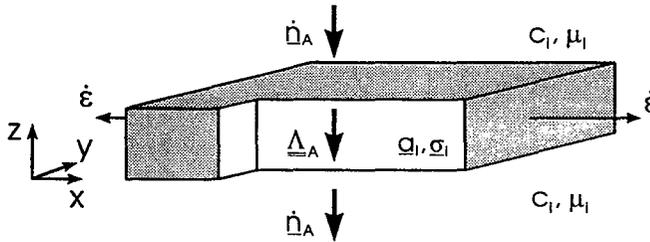


Fig. 1: Schematic of the mass transfer across an interface

To describe the transport of the structure vector, the structure transport tensor  $\underline{\Lambda}_A$  is defined:

$$\underline{\Lambda}_A \equiv \underline{a}_A (\underline{w}_A - \underline{w}), \quad (1)$$

where  $\underline{a}_A$  is the structure vector of the component  $A$ ,  $\underline{w}_A$  is the average velocity of centre of mass of the component  $A$  and  $\underline{w}$  is the average velocity of centre of mass of the mixture. From the principles of the TIP, it follows that the structure transport is not only a function of the interfacial potential gradient but depends on all driving forces. Assuming a linear relation between the fluxes and the forces, the structure transport is given as

$$\underline{\Lambda}_A^d = \sum_i L_{1i} A_{ii} - L_2 (\nabla \cdot \underline{w}) + L_3 \underline{\tau}^d - \sum_i L_{4i} (\nabla \cdot \underline{\sigma}_i). \quad (2)$$

In Eq (2)  $A$  is the chemical affinity,  $\underline{w}$  the velocity vector and  $\underline{\tau}^d$  the stress tensor of the interface.  $L_i$  denote phenomenological coefficients. Eq (2) is a scalar equation since only the mean value of the diagonal elements is used. A tensorial equation is also given by Hampe (1981), however, for the case studied here, the scalar equation is sufficient. In order to experimentally investigate the consequences arising from Eq. (2), it is applied to the case of the mass transfer across a plane dilated interface. The term of the stress tensor of an interface due to dilatational forces is given by Millies et al. (1994):

$$\underline{\tau} = \kappa(z) \underline{\dot{\epsilon}} P, \quad (3)$$

where  $\kappa(z)$  is the local interfacial dilatational viscosity,  $\dot{\epsilon}$  is the extension rate of the interface and  $\underline{P}$  is the projection tensor. According to Fig. 1, the dilatation only occurs in the  $x$ - $y$ -plane. From Eq. (3) it follows

$$\underline{\tau}^d = \frac{2}{3} \kappa(z) \dot{\epsilon}. \quad (4)$$

It is assumed that the variation of the thermodynamic properties in the  $x$ - and  $y$ -direction is negligible. Thus the  $zz$ -component is the only non-vanishing component of the structure transport tensor. Hence

$$\underline{\Lambda}^d = \frac{1}{3} \Lambda_A^z. \quad (5)$$

Neglecting chemical reactions at the interface and assuming an incompressible fluid, the first and the second term in Eq (2) vanish. Inserting Eqn. (4) and (5) into Eq. (2), it follows that

$$\Lambda_A^z = 2L_3\kappa(z)\dot{\epsilon} - \sum_i T_A^i \frac{\partial a_i^z}{\partial z}, \quad (6)$$

where  $a_i^z$  is the  $z$ -component of the structure vector and  $T_A^i$  is a transport coefficient which is defined analogously to Ficks law of diffusion

$$T_A^i = 3L_4 \left( \frac{\partial \sigma_i}{\partial a_i} \right). \quad (7)$$

With Eq (6) the structure transport across a dilated interface is described as a linear function of the gradient of the structure vector and of the stress due to the dilatation of the interface. To apply this to technical systems, the knowledge of the phenomenological coefficients is essential. However, they can not be derived from thermodynamics. To allow an experimental verification of the effect predicted by Eq. (6), the influence on the mass flux across the dilated interface resulting from Eq. (6) must be determined.

Since the transition from the bulk region - where the classical equations for diffusion are valid - to the interfacial region - where Eq. (6) holds - is gradual, in a region far away from the interface mass flux and structure flux are identical. It is

$$\dot{n}_A^z = \Lambda_A^z. \quad (8)$$

From Eqn. (6) and (8) it follows that

$$\dot{n}_A^z = \dot{n}_A^{z,stat} + 2L_3\kappa(z)\dot{\epsilon}, \quad (9)$$

where  $\dot{n}_A^{z,stat}$  is the mass flux across a stationary undilated interface. In taking the average of Eq. (9), one obtains

$$\bar{\dot{n}}_A^z = \bar{\dot{n}}_A^{z,stat} + 2L_3\kappa \frac{\dot{\epsilon}}{\Delta z}, \quad (10)$$

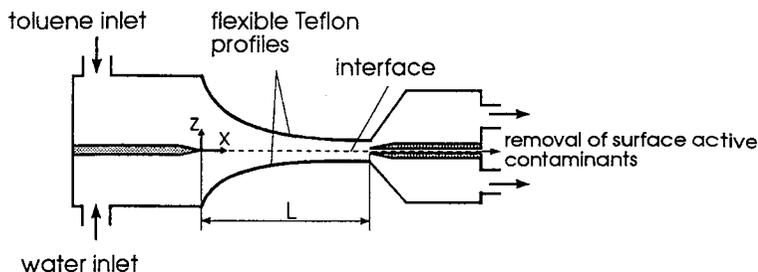
where  $\Delta z$  is the averaging interval which must at least extend over the entire interfacial region.

Eq. (10) allows the experimental investigation of the effect of the interfacial dilatation on the mass transfer. By measuring the mass flux  $\bar{\dot{n}}_A^z$  as a function of the extension rate  $\dot{\epsilon}$  the phenomenological coefficient  $L_3$  can be determined.

## EXPERIMENTAL

In Fig. 2 a schematic outline of the flow cell is illustrated which is used to measure the mass transfer across a dilated interface. The two continuous phases water and toluene enter the flow cell via Teflon tubings. Along the actual interfacial contact, the width of the flow cell is constant while its height decreases. This results in an acceleration of the flow field and thus in a dilatation of the entire flow. The wall profile is calculated to achieve a constant rate of extension. The liquid/liquid-system being used has been found to be extremely sensitive to surface active contaminants (Nitsch and Matschke, 1968). These adsorb at the interface as a monolayer which greatly reduces the mobility of

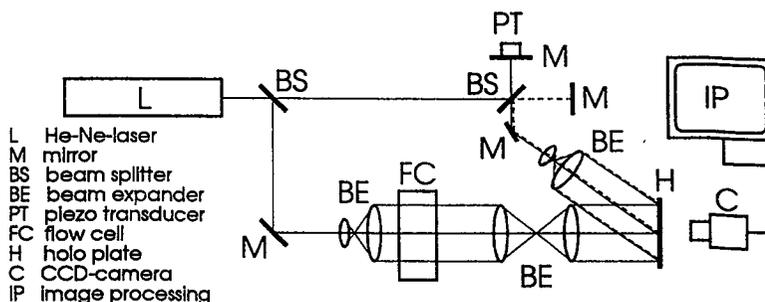
the interface and hence the interfacial dilation. To overcome this, the flow cell has been specifically designed to allow the continuous removal of these contaminants.



**Fig. 2:** Schematic of the flow cell being used to generate the dilated interface

A small amount of the two continuous phases including the interface is constantly withdrawn through a slit at the end of the interface. In this way a mobile interface is assured for the entire period of time of the experiment.

The mass transfer across the interface is determined by measuring the concentration of the transferring component as a function of time. To obtain further insight into the transport phenomena in the region close to the interface, the concentration profiles of the transfer component acetone are measured using holographic interferometry. To achieve the desired accuracy, phase shift holography is employed. The optical setup being used is shown in Fig. 3. The beam of a He-Ne-laser is split into an object and a reference beam.



**Fig. 3:** Optical setup for the phase shift holography

The object beam passes through the flow cell while the reference beam enters a Michelson interferometer. With the Michelson interferometer, the reference beam is split into two beams including a small angle. Behind the flow cell the object and the reference beams interfere on the holographic plate. Shifting one of the reference beams during reconstruction using a piezo-electronic transducer, the phase distribution of the interference pattern can be evaluated with an order of up to 1/50 of a fringe order.

### RESULTS

In the flow cell the velocity of the interface is measured using Laser-Doppler-Velocimetry (LDV). It is found that in the toluene/water-system, the interface becomes rigid due to surface active components within only a few minutes after starting the flow. This is seen in Fig. 4 as a plot of the

interfacial velocity as a function of the time. At  $t = 20$  s the interface is withdrawn to remove the adsorbed layer of surfactants and the interface becomes mobile. From the end of the interface, a new layer of adsorbed surface active components starts growing towards the beginning. After about 200 s the layer has a length of 50 mm and has reached the measurement position. Only by constantly removing a small amount of both phases including the interface, is a mobile interface achieved for an unlimited period of time. This was possible by coating the slit for the interfacial removal with a hydrophobic and a hydrophilic layer on the upper and the lower side, respectively.

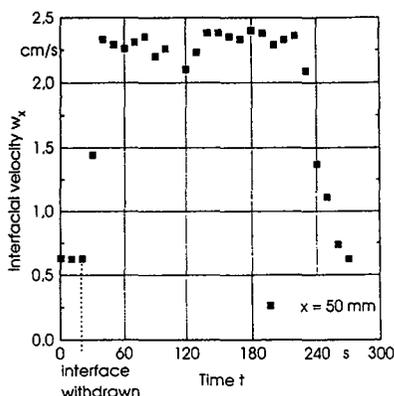


Fig. 4: The velocity of the interface as a function of the time

In Fig. 5 a plot of the interfacial velocity as a function of the contact length is shown. For the rigid interface, the interfacial velocity reaches an almost constant value at about 10 mm after the beginning of the phase contact. For the mobile interface, the interfacial velocity increases linearly with the contact length. The extension rate is nearly constant over the entire contact length. In Fig. 5 the extension rate is  $\dot{\epsilon} = 0,4 \text{ s}^{-1}$ . The extension rate of the interface is varied altering the volumetric flow rates of the phases in the flow cell. For the interface being dilated at a constant extension rate, the mass transfer is measured and compared to the theory described above. The results of these measurements will be presented in a future paper.

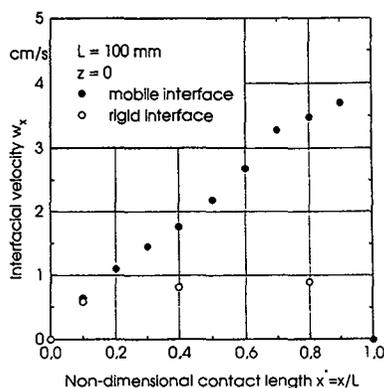


Fig. 5: The velocity of the interface as a function of the contact length

## CONCLUSION

From a theory of Hampe (1981) who employed the thermodynamics of irreversible processes to account for the mutual dependence of the transport phenomena near interfaces, it is derived that the mass transfer across a dilated interface linearly depends on the rate of extension of the interface. To verify this experimentally, a new flow cell is used in which the interface is dilated in an extensional flow. Employing LDV it is shown that a constant extension rate of the interface in the flow cell is achieved. However, this is only possible if the interface is constantly kept free from adsorbing surface active contaminants.

## ACKNOWLEDGEMENTS

Financial support for this project is provided by the Deutsche Forschungsgemeinschaft (DFG) for which the authors are very grateful. We would also like to thank Du Pont, Belgium, for the assistance in providing KALREZ® high tech sealing materials.

## NOMENCLATURE

Non-Standard nomenclature:

$A$	$J/m^3$	affinity
$\underline{a}$	$mol/m^3$	structure vector
$\underline{L}_1$	$mol\ m/J\ s$	} phenomenological coefficients   in Eq. (4)
$\underline{L}_2$	$mol/m^2$	
$\underline{L}_3$	$mol\ m/J\ s$	
$\underline{L}_4$	$mol^2/m\ s\ J$	
$\kappa(z)$	$Pa\ s$	local interfacial dilatational viscosity
$\underline{\underline{\Lambda}}$	$mol/m^2\ s$	structure transport tensor
$\underline{\sigma}$	$J/mol$	interfacial potential

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## AN EQUILIBRIUM STUDY OF THE EXTRACTION OF Gold FROM HALIDE SOLUTIONS USING ALIQUAT 336

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### ABSTRACT

A study of the extraction of gold(III) from hydrochloric and hydrobromic acids by Aliquat 336<sup>®</sup> dissolved in ShellSol 2046 is reported. The extraction data has been fitted to a model for the system which involves the extraction of a single complex of composition  $R_3MeN^+AuX_4^-$ , where X is  $Cl^-$  or  $Br^-$ . The extraction equilibrium constant has been obtained for each halide and is  $\log K_{ex} = 5.58$  and 6.79 for chloride and bromide, respectively. An interfacial mechanism is proposed for the extraction based on the high interfacial activity of Aliquat 336 in ShellSol.

### INTRODUCTION

There is interest in the extraction of gold(III) from halide solutions particularly in the recovery of gold from electronic scrap and in the processing of gold bearing deposits which are not amenable to cyanide leaching.

A study of the extraction of gold(III) from hydrochloric acid solutions has recently been reported [Villaescusa et al. (1993)]. These authors used tri-n-dodecylammonium chloride (TLAHCl) dissolved in toluene as the extractant and found evidence for the formation of two complexes in the organic phase,  $AuCl_3(TLAHCl)$  and  $AuCl_3(TLAHCl)_2$ . These stoichiometries and their extraction constants were determined graphically using normalized curves [Muhammed, Szabon and Högfeltdt (1974)] and the values for the extraction constants were refined by computer [Liem (1971)]. We have used this mathematical approach previously to study the extraction of mercury(II) and cobalt(II) from hydrochloric acid solutions by the commercial extractant, Aliquat 336<sup>®</sup>, dissolved in chloroform, however, it is mainly applicable to systems in which there is more than one extracted complex [Cattrall and Daud (1979), Paimin and Cattrall (1983)].

In this paper we report a study of the extraction of gold(III) from hydrochloric and hydrobromic acid solutions by Aliquat 336 dissolved in a commercial diluent, ShellSol 2046. This work was aimed at determining the stoichiometry of the extracted complex (or complexes) and the evaluation of the equilibrium extraction constants.

### EXPERIMENTAL

#### Reagents

Aliquat 336 (Aldrich),  $R_3MeN^+Cl^-$ , was obtained as a mixture of quaternary ammonium chlorides [Lee et al. (1981)] and was used as received. The chloride form was converted to the bromide form by shaking with 1.0 M KBr. ShellSol 2046 (Shell Chemical, Australia) contains approximately 16% aromatics, 44% paraffins and 40% naphthenes.

Gold(III) solutions were prepared in 2.5 M hydrochloric or hydrobromic acids (AnalaR) using the chloride or bromide salts (Aldrich).

### Equilibrium Studies

These were carried out by two phase titration [Cattrall and Daud (1979)]. Three concentrations of Aliquat 336 in ShellSol were used, 1.23, 2.46 and 4.92 mM. Initially, equal volumes of the appropriate organic phase and gold(III) halide solution were added to the extraction flask. After equilibration, a small aliquot of the aqueous phase was removed for analysis and an equal volume of a more concentrated aqueous phase was added to the extraction flask and equilibrated again. This procedure was repeated until the desired number of data points was obtained.

### Interfacial Energy Measurements

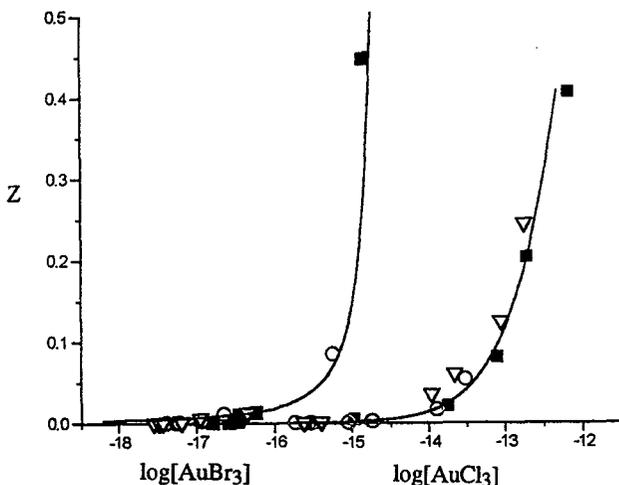
These were carried out using the single-drop technique described previously [Daud and Cattrall (1982)].

### Determination of Gold

Gold in the aqueous phases was determined by graphite furnace atomic absorption spectrometry using a Varian Model 275 instrument fitted with a GTA-95 graphite furnace system. Concentrations in the organic phases were obtained by difference. Gold standards were made by dilution of a 1000 ppm gold standard (BDH, Spectrosol®) with 2.5 M acid.

## RESULTS AND DISCUSSION

The results of the equilibrium study are shown in Figure 1 for three concentrations of Aliquat 336 for both hydrochloric and hydrobromic acid solutions of gold(III). The results are plotted in the form of  $Z$  versus the concentration of the species  $\text{AuCl}_3$  or  $\text{AuBr}_3$  at equilibrium in the aqueous phase.  $Z$  is the total concentration of gold in the organic phase divided by the total concentration of Aliquat 336 in the organic phase. The concentration of  $\text{AuCl}_3$  or  $\text{AuBr}_3$  in the aqueous phase was calculated using the appropriate formation constants.



**Figure 1** Equilibrium data for the chloride and bromide systems.  
■, 1.23 mM; O, 2.46 mM; ▽, 4.92 mM Aliquat 336  
Solid lines calculated using the values for the extraction constants.

As can be seen in Figure 1, a single curve is obtained in each case for the three Aliquat 336 concentrations and this is indicative of the extraction of only one complex. Consequently, an attempt to determine the stoichiometry of the extracted complex graphically using the method of normalized curves [Muhammed, Szabon and Högfeldt (1974)] failed due to difficulties in obtaining the areas under the curves which requires separate curves for each Aliquat 336 concentration. Thus, the

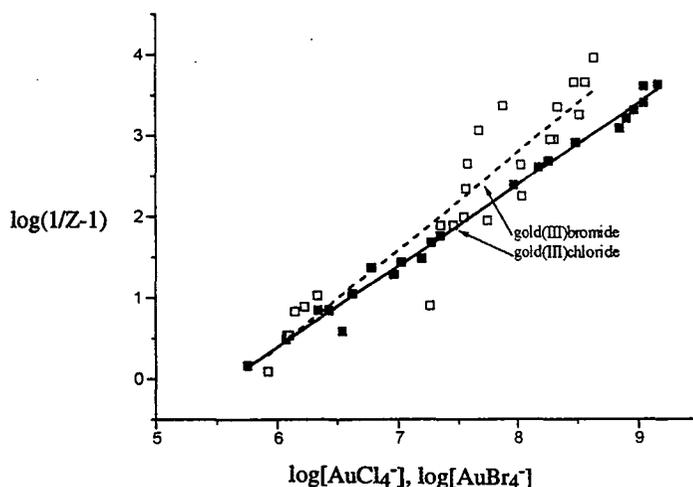
assumption was made that the extracted complex had the stoichiometry  $(R_3MeN^+AuX_4^-)$ , where X is  $Cl^-$  or  $Br^-$  and the data was tested against this model. The extraction equilibrium constant is given by equation 1 and the assumption is made that ideality is obeyed in the organic phase and the activity coefficients of all species in the aqueous phase are constant.

$$K_{ex} = \frac{[R_3MeN^+AuX_4^-]_{org}[X^-]_{aq}}{[R_3MeN^+X^-]_{org}[AuX_4^-]_{aq}} \quad \text{----- (1)}$$

Equation 1 can be written in the following form.

$$\log(1/Z - 1) = -\log[AuX_4^-]_{aq} - \log K_{ex} + \log[X^-] \quad \text{----- (2)}$$

This equation describes a linear relationship between  $\log(1/Z - 1)$  and  $\log[AuX_4^-]_{aq}$  with a slope of -1. This relationship is plotted in Figure 2 for the chloride and bromide cases, respectively. Equilibrium concentrations of the species  $[AuX_4^-]_{aq}$  were again calculated from the appropriate formation constants. Good linearity is seen in the chloride case with a slope of -1.0 and a regression coefficient of 0.995. For bromide, more scatter of the data points is seen because of the much lower concentrations of gold remaining in the aqueous phase after extraction and the lower precision of the analytical data as a consequence of this. The slope in the bromide case is 1.2 and the regression coefficient is 0.956.



**Figure 2** Relationship between  $\log(1/Z - 1)$  and  $\log[AuX_4^-]_{aq}$

These results support the proposed formation of a single complex in the organic phase with a 1:1 stoichiometry. The extraction equilibrium constants obtained from Figure 2 are  $\log K_{ex} = 5.58$  for chloride and  $\log K_{ex} = 6.79$  for bromide. The excellent fit to the experimental data is seen in Figure 1 where the solid lines have been calculated using these values for the extraction constants. The high values for the extraction constants demonstrate the very strong affinity of the Aliquat cation for the

anionic gold species and suggest that this system is very suitable for the recovery of gold from acidic halide solutions.

There is no evidence in this system for the extraction of a 1:2 complex as found for the extraction of gold by tri-n-dodecylammonium chloride (TLAHC1) dissolved in toluene [Villaescusa et al. (1993)]. The reasons for the formation of a 1:2 complex with TLAHC1 may be associated with the possibility of hydrogen bonding interactions between the anionic gold complex and a second molecule of the extractant. Such interactions are not possible with Aliquat 336.

The higher extraction of the tetrabromoaurate(III) species compared to the chloro-species is most likely due to the lower hydration energy of the bromo-species. No doubt, entropy effects also play a role in this due to the much bulkier tetrabromoaurate(III) anion.

Attempts to study the extraction of gold from acidic iodide solutions failed due to the ease of oxidation of the iodide ion with the consequent reduction of gold(III) to the metal.

In previous studies involving extraction with Aliquat 336, we have proposed an interfacial mechanism for the extraction [Paimin and Cattrall (1982)]. In these studies, considerable evidence was provided for a reaction mechanism which consisted of fast ion-exchange at the interface followed by a rate determining step which involved the replacement of the metal containing complex at the interface by reagent in the bulk organic phase. A similar mechanism is proposed in the present system and some evidence for this is seen in measurements of the interfacial energy between the aqueous and organic phases as shown in Table 1.

**Table 1**      Measurement of the Interfacial Energy

<u>organic phase</u> <sup>a</sup>	<u>aqueous phase</u>	<u>interfacial energy</u> <u>x10<sup>3</sup> (J m<sup>-2</sup>)</u>
ShellSol 2046	water	37.5
Aliquat 336 chloride	water	7.7
Aliquat 336 chloride	2.5 M HCl	9.7
Aliquat 336 bromide	2.5 M HBr	15.4
Aliquat 336 iodide	2.5 M HI	24.4
Aliquat 336 AuCl <sub>4</sub> <sup>-</sup>	2.5 M HCl	29.6
Aliquat 336 AuBr <sub>4</sub> <sup>-</sup>	2.5 M HBr	26.1

<sup>a</sup> solutions of Aliquat 336 were all 4.92 mM in ShellSol.

The results in Table 1 show a large decrease in the interfacial energy for Aliquat chloride and bromide in ShellSol compared with the pure diluent. This is consistent with the Aliquat salt concentrating at the organic/aqueous interface which supports an interfacial extraction mechanism.

It is interesting to note that the decrease in the interfacial energy follows the trend in hydration energies of the ions and is smaller for the bromide and iodide salts compared to chloride. The decrease is even smaller for the Aliquat/gold complexes reflecting the low hydration energies of the haloaurate(III) ions. This observation also supports the interfacial mechanism since the Aliquat/gold complexes will be readily replaced at the interface by Aliquat chloride from the bulk organic phase.

## CONCLUSION

Aliquat 336 dissolved in ShellSol extracts gold(III) strongly from acidic chloride and bromide solutions with the formation of a 1:1 complex in the organic phase. The mechanism for the extraction is most likely an interfacial one and this is supported by the high interfacial activity of the reagent.

This system shows promise for commercial use for treating hydrometallurgical solutions derived from halide leaching of gold bearing ores. It is of particular interest in the processing of electronic scrap to recover gold. In this application, the scrap is firstly treated with nitric acid to remove the more easily leachable metals such as silver copper and tin and then with aqua regia to dissolve gold. The gold is then extracted with Aliquat 336 in ShellSol and recovered using a strip phase such as a thiourea solution.

## ACKNOWLEDGEMENTS

One of us (G.A.) is grateful to the Australian Government Department of Education, Training and Research for the provision of a Postgraduate Research Award (Industry). We thank BHP Research for sponsorship of this award.

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## INTERFACIAL TENSION DATA OF ORGANOPHOSPHOROUS LIGANDS IN THE SOLVENT EXTRACTION OF SILVER

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### ABSTRACT

The present work is focused on the extraction of silver (I) from aqueous chloride solutions by triisobutylphosphine sulphide (TIBPS), triphenylphosphine (TPP) and triphenylphosphine sulphide (TPPS) and on the interfacial behaviours of these three reagents at the 2M HCl + 3M NaCl / toluene interface. Szyszkowski model of adsorption isotherm has been matched to the experimental interfacial data by using MINEX Computer Programme and thermodynamic parameters such as the interfacial concentration of the extractants at saturation ( $\Gamma_{\max}$ ) and their free energy of adsorption from the organic phase ( $\Delta G_{\text{ads}}$ ) have been determined. Finally, the role of the interface in the extraction of silver (I) by TIBPS is discussed.

### INTRODUCTION

Solvent extraction (SX) processes have been extensively investigated in the past few years as a promising alternative for the recovery, separation and concentration of precious metals, specially from chloride media - Rydberg et al (1992), Dalton et al (1991). From a mechanistic point of view, the limiting step of the extraction reaction of metal values is often interfacial in nature - Danesi and Chiarizia (1981), Gaonkar and Neuman (1984), Paiva (1993). This is the reason why many authors have studied the role of the interface on the kinetics of solvent extraction processes - Flett (1977), Gaonkar and Neuman (1984), Freiser (1988), Szymanowski (1987, 1992a,b, 1994). The characteristics of liquid-liquid interfaces are frequently derived from interfacial tension data which can be obtained by various techniques such as the pendant drop, drop volume, Wilhelmy plate and Du Nouy ring methods - Watarai (1993). This work is focused on the extraction of silver (I) from aqueous chloride solutions by triisobutylphosphine sulphide (TIBPS), triphenylphosphine (TPP) and triphenylphosphine sulphide (TPPS) and on the interfacial properties of these three reagents at the 2M HCl + 3M NaCl / toluene interface.

### EXPERIMENTAL

A base-electrolyte solution containing a total chloride concentration of 5M (2M HCl + 3M NaCl) was used in all the experiments. The silver feed solution ( $150 \text{ mg L}^{-1}$ ) was prepared by dissolving an appropriate amount of silver nitrate (Merck, purity > 99.0%) in the preceding base-electrolyte solution. All inorganic chemicals were pro-analysis. Organic solutions were obtained by dissolving TIBPS (American Cyanamid, >99% purity after purification), TPP (Merck, 98% purity) and TPPS (Fluka, 99% purity) in 1,2-dichloroethane (Riedel-de-Haen, >99.7%) or toluene (Riedel-de Haen, >99.7% purity). Purified TIBPS was obtained by double recrystallisation from a water - isopropanol mixture.

The procedures followed for the extraction experiments have already been described elsewhere - Paiva and Abrantes (1994).

Interfacial tensions were measured by the Du Nouy ring method using a Kruss Interfacial Tensiometer model K8. The temperature was kept constant and equal to  $20.0 \pm 0.1^\circ \text{C}$ , and at least three determinations were performed for each system under investigation.

Theoretical interfacial tension isotherms and surface excess isotherms were calculated by using the MINEX Computer Programme - Prochaska et al (1989, 1991).

## RESULTS AND DISCUSSION

### Silver extraction

Typical extraction data are reported in Table 1. The 2M HCl + 3M NaCl solution used in the present work simulates a hydrometallurgical bath the acidity of which is roughly equivalent to that of a 3M HCl solution - Sella (1989). Examination of this Table shows that TIBPS and TPPS, which are chemically similar, surprisingly behave differently as far as the extraction of silver (I) from aqueous chloride solution is concerned. Indeed TPPS exhibits almost no tendency to extract silver (I) whereas TIBPS appears to be a good extractant of this metal. The extraction of silver (I) by TIBPS occurs via a solvating reaction. The extracted species was found to be  $\text{AgCl}(\text{TIBPS})_2$  in chloride media - Paiva and Abrantes (1994) - and  $\text{AgNO}_3(\text{TIBPS})_2$  in nitrate media - Baba et al (1986a). TPP extracts silver (I) more efficiently than TIBPS. TPP is a solvating reagent, but in strongly acidic media it forms a cation  $\text{TPPH}^+$  which can participate in extraction by an anion-exchange mechanism - Mojski (1980). It can also be seen that 1,2-dichloroethane leads to higher extraction yields than toluene. However, because of serious difficulties encountered for separating the aqueous and organic phases with 1,2-dichloroethane in the presence of TIBPS, toluene was finally preferred.

**TABLE 1**  
Comparison of Ag extraction efficiencies ( $150 \text{ mgL}^{-1}$  Ag in 2M HCl + 3M NaCl)\*

Extractant	% of Ag extraction	
	Toluene	1,2-dichloroethane
TIBPS	47	77
TPPS	0	5
TPP	100	100

\* Extractant 0.1M;  $25^\circ \text{C}$ , 15 minutes of shaking, 1000 rpm, A/O = 1.

### Interfacial tension data

A comparison of the interfacial properties of TIBPS, TPP and TPPS is made in Figure 1 and Table 2. Among the reagents considered, TIBPS exhibits the weakest affinity for the interface. We point out that the TIBPS interfacial tension isotherm represented in Figure 1 is very similar to that previously obtained at the 1M HCl / toluene interface - Baba et al (1986b).

From these data, it can be seen that under the present experimental conditions, the interfacial activity decreases in the following order:  $\text{TPP} > \text{TPPS} > \text{TIBPS}$ . TPP appears at the top of the scale, probably as a result of its tendency to protonate, i.e.,  $\text{TPPH}^+\text{Cl}^-$  likely forms under the present acidity conditions and adsorbs at the interface more efficiently than TPP itself. Such an observation also suggests that the extraction of silver (I) from the 2M HCl + 3M NaCl solution occurs at least partly via an anion exchange reaction. The lack of reactivity of TPPS with silver (I)

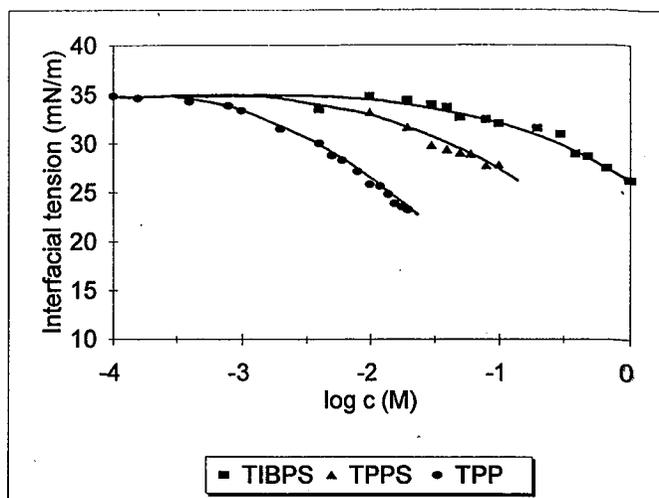


Figure 1. Interfacial tension data for TIBPS, TPP and TPPS at the 2M HCl + 3M NaCl / toluene interface, at 20°C

**TABLE 2**  
Extractant concentrations giving a significant decrease in interfacial tension  
( $c_1$ - beginning of decrease;  $c_2$ -decrease of 5mN/m)

Extractant	$-\log c_1$	$-\log c_2$
TIBPS	1.5	0.5
TPPS	2.0	1.5
TPP	3.0	2.5

cannot be explained by the interfacial properties of this extractant. Finally, although TIBPS is weakly surface active, its presence at the interface should be taken into account and an interfacial mechanism in the extraction of metals should be considered. In such a purpose, a modelling of the preceding interfacial data has been performed as reported below.

#### Modelling of the interfacial tension data

For interpreting the kinetic data in solvent extraction, it is important to know the concentration of extractant molecules at the interface. Theoretically, such a concentration (or more precisely the surface excess) is given by the Gibbs equation, Eq. (1)

$$\Gamma = - (1/RT) d\gamma / d \ln c \quad (1)$$

where  $\gamma$  denotes the interfacial tension,  $c$  stands for the concentration of the extractant,  $R$  is the gas constant and  $T$  stands for absolute temperature. However, as a result of high differentiation errors, only the surface excess at saturation can be derived in practice from the Gibbs equation. To overcome this problem, a convenient method consists of matching various theoretical adsorption isotherms to the interfacial tension data (i.e. curve  $\gamma$  vs  $c$ ) and then to calculate analytically the term  $dy/d\ln c$  and introduce it into the Gibbs Eq. (1). In this way, mathematical formulae are derived for the surface excess isotherms - Prochaska et al (1989), Szymanowski (1987, 1992a,b). Many different expressions are obtained as various adsorption equations are used to correlate the interfacial tension with the concentrations. In some cases, such mathematical relationships must be cautiously interpreted and even disregarded.

In the case of the curves plotted in Figure 1, the Szyszkowski isotherm equation (2) has been considered - Bogacki (1988), Prochaska (1991)-,

$$\gamma = \gamma_0 [1 - b \ln \{(c/a) + 1\}] \quad (2)$$

where  $a$  and  $b$  are appropriate constants and  $\gamma_0$  denotes the interfacial tension in a liquid-liquid system which does not contain any extractant (i.e.,  $c=0$ ). Szyszkowski adsorption constants  $a$  and  $b$ , surface excess at saturation ( $\Gamma_{\max}$ ), molecular area ( $A$ ) and free energy of adsorption from organic phase ( $\Delta G_{\text{ads}}$ ) are given in Table 3 for TIBPS, TPPS and TPP. The parameter  $A$  gives information on the degree of packing of the extractant molecules at the saturated interface.

**TABLE 3**

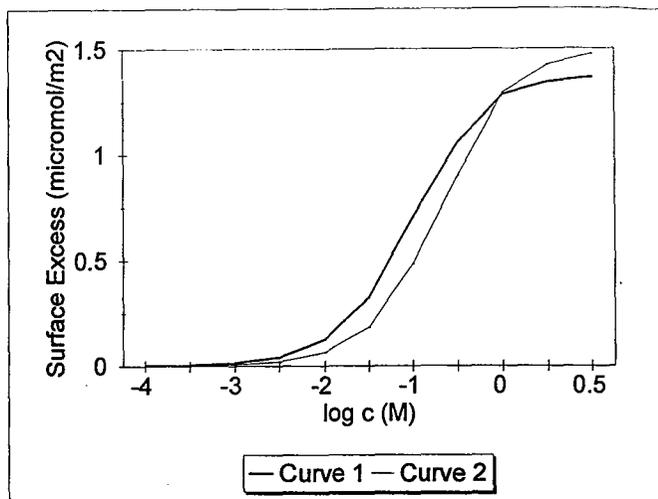
Szyszkowski adsorption constants  $a$  and  $b$ , surface excess at saturation ( $\Gamma_{\max}$ ) molecular area ( $A$ ) and free energy of adsorption from organic phase ( $\Delta G_{\text{ads}}$ ) for TIBPS, TPPS and TPP

Extractant	$\Gamma_{\max} \times 10^6$ (mol/m <sup>2</sup> )	Szyszkowski adsorption constants	$A \times 10^{18}$ (m <sup>2</sup> /mol)	$\Delta G_{\text{ads}}$ (KJ/mol)
TIBPS	1.41	$a = 9.996 \times 10^{-2}$ $b = 1.003 \times 10^{-1}$	1.18	-5.7
TPPS	1.24	$a = 8.958 \times 10^{-3}$ $b = 8.876 \times 10^{-2}$	1.34	-11.5
TPP	2.30	$a = 2.754 \times 10^{-3}$ $b = 1.607 \times 10^{-1}$	0.72	-14.4

Examination of this Table shows that TPPS and TPP (or its protonated form) exhibit very different values of  $\Gamma_{\max}$ . Such a difference can be attributed to their polar head. It can also be noticed that the absolute value of  $\Delta G_{\text{ads}}$  found for TIBPS is significantly lower than those obtained for TPPS and TPP or for extractants such as DEHPA (typically  $-22 \text{ KJmol}^{-1}$ ) - Cote and Szymanowski (1992). This reflects the weak tendency of TIBPS to adsorb at the interface.

In Figure 2, the values of the surface excess derived from Equation (3) have been plotted vs TIBPS concentration.

$$\Gamma^{\text{Sz}} = (b\gamma_0 / RT) (c / [c + a]) \quad (3)$$



**Figure 2.** Surface excess versus logarithm of TIBPS organic concentration for adsorption of TIBPS at the (1) 2M HCl + 3M NaCl / toluene interface, at 20°C; (2) 1M HCl / toluene interface, at 25°C.

The data corresponding to the adsorption of TIBPS at the 2M HCl + 3M NaCl / toluene interface at 20°C are given in curve 1 ( $\gamma_0 = 34.2 \text{ mN m}^{-1}$ ), whereas curve 2 was obtained by application of the same treatment to interfacial tension data already published - Baba et al (1986b), - representing the variation of  $\Gamma$  found for adsorption of TIBPS at the 1M HCl / toluene interface at 25°C. Examination of this Figure reveals a good agreement between the two independent series of determinations and shows that the change in ionic strength and temperature does not cause a great variation in the interfacial behaviours of TIBPS. Further examination of Figure 2 also shows that below about  $5 \cdot 10^{-3} \text{ M}$ , TIBPS is not present at the interface. As a consequence, below  $5 \cdot 10^{-3} \text{ M}$ , the rate determining step of the mechanism of metal extraction with TIBPS is necessarily located in the aqueous phase, either in the whole bulk or in a layer near the interface, but not at the interface itself. On the other hand, above  $10^{-2} \text{ M}$ , TIBPS starts to adsorb at the interface and a mechanism based on a rate determining step taking place at the interface becomes possible. An intermediate situation with more or less similar contributions of bulk (aqueous) and interfacial reactions can also be expected, at least at the beginning of TIBPS interfacial adsorption. Such a two-route mechanism was reported for the extraction of copper (II) by hydroxyoximes having alkyl chain lengths ranging between 4 and 8 carbon atoms - Szymanowski (1985). It is also of interest that the curves 1 and 2 plotted in Figure 2 do not exhibit any plateau region at high TIBPS concentration (i.e., the saturation of the interface by TIBPS molecules is not reached), thus the rate expression for the extraction of metals with TIBPS should present in all cases a dependency versus bulk (organic) TIBPS concentration. This was actually observed for the extraction of palladium (II) from 1M HCl by TIBPS - Baba et al (1986b). In the latter case, the rate-determining step was assumed to be purely interfacial in nature. Preliminary experiments carried out to elucidate the effects of interfacial area and aqueous bulk volume on the extraction rate of silver (I) from 2M HCl + 3M NaCl by TIBPS suggest the occurrence of a two-route mechanism, but further investigations are still needed to ascertain this conclusion.

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## ACKNOWLEDGEMENTS

One of the authors (GC) is thankful to Prof. J. Szymanowski of Technical University, Póznan, Poland, for the facilities given for the use of the MINEX programme. APP is thankful to JNICT, Portugal, for financial support for her Ph. D. work, as well as to ICAT for the facilities given for the use of the interfacial tensiometer. The authors are also thankful to "JNICT / Embaixada de França (Programa de Cooperação Científica e Técnica Luso-Francesa)" for financial support.



## ROLE OF REVERSED MICELLES OF ACIDIC ORGANOPHOSPHORUS EXTRACTANTS IN COBALT/NICKEL SEPARATION - A POSITION PAPER

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### ABSTRACT

The association microstructures which form in acidic organophosphorus extraction systems of nickel (II), cobalt (II) and sodium have been systematically investigated. Significantly, a number of novel findings which are contrary to conventional views of both the formation and growth of reversed micelles as well as hydrometallurgical liquid-liquid extraction have been discovered. For example, sodium di(2-ethylhexyl)phosphate (NaDEHP) in n-heptane forms *giant* quasi-one-dimensional or rodlike reversed micelles, and a model which accounts for the effect of water (as both an antimicellization and antimicellar growth agent) on the size of the NaDEHP reversed micelles has been developed. The solution behaviors of nickel- and cobalt-di(2-ethylhexyl) phosphate ( $M(\text{DEHP})_2$ ) complexes in n-heptane have also been investigated, and it is argued that the macromolecular species in the two  $M(\text{DEHP})_2$  systems are rodlike reversed micelles rather than polymers as believed by many authors. In addition, an "open water-channel" model for the structure of reversed micelles of  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes is proposed. This novel model is contrary to the traditional model of reversed micelles wherein water is solubilized in the inner micellar core. Furthermore, it appears that a correlation exists between the preferred selectivity of cobalt from nickel and the size differences of the rodlike  $M(\text{DEHP})_2$  reversed micelles.

### INTRODUCTION

In previous studies of the liquid-liquid extraction of metal ions by di(2-ethylhexyl) phosphoric acid (HDEHP) we reported that there appears to be three regimes of aggregation behavior (Neuman et al., 1990a) and that the extent and rate of metal extraction are of practical importance when the metal-extractant complexes form association microstructures, namely, reversed micelles (Neuman and co-workers, 1990a, 1990b, 1992, 1993; Gaonkar and Neuman, 1986, 1989; Park and Neuman, 1992). Furthermore, we proposed a simplified model, analogous to that for surfactants in nonpolar organic solvents (Eicke et al., 1975; Verbeek et al., 1986), for the aggregation of metal-extractant complexes in acidic organophosphorus extraction systems (Neuman et al., 1990a, 1990b).

Recently we have investigated further the physicochemical nature of the metal-extractant aggregates present in the nonpolar organic diluent of acidic organophosphorus extraction systems from the perspective of colloid and surface science. Since industrial hydrometallurgical extraction systems are very complex, the study of the aggregation behavior in simplified or model extraction systems of pure metal salts of HDEHP (e.g., NaDEHP,  $\text{Ni}(\text{DEHP})_2$  and  $\text{Co}(\text{DEHP})_2$ ) and of well-controlled mixtures which simulate practical hydrometallurgical systems has been emphasized. Although reversed micelles play an important role in liquid-liquid extraction, it is also necessary to invoke other concepts to explain the differences observed in the extractability and selectivity behavior of extraction reagents. For example, our original model of metal-extractant aggregation (Neuman et al., 1990a, 1990b) must be modified, and a new structural model of  $\text{Ni}(\text{DEHP})_2$  reversed micelles is proposed. A number of novel findings contrary to the conventional views of reversed micelles and hydrometallurgical liquid-liquid extraction are summarized and reviewed in the present paper.

## EXPERIMENTAL MATERIALS AND METHODS

HDEHP, NaDEHP, n-heptane and water were the same as described previously (Yu et al., 1992). The preparation of Ni(DEHP)<sub>2</sub> and Co(DEHP)<sub>2</sub> is described elsewhere (Yu and Neuman, 1995c). The physicochemical nature of the metal-extractant aggregates in the nonpolar organic diluent n-heptane was investigated by dynamic and static light scattering, FT-IR, NMR and VIS spectroscopy, VPO, viscometry, conductivity and various analytical techniques.

## RESULTS AND DISCUSSION

### Aggregation Behaviors of Sodium Di(2-Ethylhexyl) Phosphate

In order to understand the liquid-liquid extraction of metal ions by HDEHP, knowledge of the aggregation behavior of NaDEHP in nonpolar organic diluents is important since NaDEHP forms when the aqueous phase pH is adjusted with sodium hydroxide. Pure NaDEHP in n-heptane is also the *simplest* model acidic organophosphorus extraction system which one can study. Three very significant findings on NaDEHP-n-heptane solutions have been made.

First, reversed micellization of NaDEHP in n-heptane has been studied under controlled environmental conditions. The experimental results clearly show that a trace amount of water has a very dramatic effect on the formation of reversed micelles. However, in contrast with the current view in the literature that water is a prerequisite for the formation of reversed micelles, we find that water can function as an antimicellization agent (Yu et al., 1992). Furthermore, we have discovered that for the NaDEHP-n-heptane system there is a sharp transition in physical properties, e.g., scattered intensity, with an *operational* critical micelle concentration (cmc) range as narrow as that in aqueous surfactant solutions. This significant finding was made possible by the development of improved laser light-scattering techniques (Yu and Neuman, 1992). Therefore, the current literature views that the formation of reversed micelles in nonpolar or apolar media takes place over a wide range of surfactant concentration and that reversed micellization is a step-wise aggregation process appear to be, at least, not generally valid in nonaqueous surfactant solutions.

Secondly, NaDEHP was found to form *giant* rodlike reversed micelles in n-heptane, with a radius of gyration as large as 53 nm, which markedly contrasts with the literature view that the average aggregation numbers in nonaqueous systems are much smaller (seldom exceeding 10-20) than those in aqueous systems (Yu and Neuman, 1994a). Furthermore, we have shown that water can play the role of an antimicellar growth agent, i.e., the reversed micellar size decreases remarkably when the "dry" nonaqueous solution is exposed to humid air from which water vapor is absorbed or when bulk water is directly added -- a behavior which is distinctly opposite to that for sodium di(2-ethylhexyl) sulfosuccinate (AOT)-nonpolar solvent systems. Therefore, the literature views that large micelles can only be found in aqueous solutions and that the surfactant head groups in reversed micelles are linked together by hydrogen bonding are misleading. It is proposed that the primary driving force for the growth of NaDEHP reversed micelles is the electrostatic lattice energy advantage for incorporation of NaDEHP monomers into the rodlike region of reversed micelles (Yu and Neuman, 1994b).

CPK space-filling molecular models show that the cross section of rodlike NaDEHP reversed micelles can accommodate three NaDEHP molecules oriented with the headgroups toward the center and the hydrocarbon tails outward. We propose that a periodic structure with this molecular packing of sodium cations and negatively charged oxygen atoms in the core of the reversed micelles can be formed along the axial length of the rodlike reversed micelles (Yu and Neuman, 1994a, 1994b).

Thirdly, the solution behaviors in the three-component NaDEHP-n-heptane-water system have been investigated. A transition in the physicochemical properties was observed over a rather narrow range of  $W_0$  (molar ratio of water to NaDEHP) values. Rodlike reversed micelles and swollen rodlike reversed micelles form when  $W_0 < 4$ . Beyond this  $W_0$  range, phase separation occurs at low NaDEHP concentrations, and homogeneous one-phase microemulsions occur at high

NaDEHP concentrations. It is suggested that the n-heptane-continuous solution of water-swollen reversed micelles transforms to a bicontinuous microemulsion, without passing through a water-in-oil (W/O) microemulsion stage, when  $W_0$  increases beyond  $W_0 \approx 4$ . The bicontinuous microemulsion region ranges between two local viscosity maxima at  $W_0 \approx 4$  and  $W_0 \approx 100$ , and an oil-in-water (O/W) microemulsion exists when  $W_0 > 100$ . In order to understand the solution behaviors of the NaDEHP-n-heptane-water system, we proposed that there are local W/O and O/W microdroplet domains which are constantly in rapid disintegration, reassembly or exchange via an intermediate state through thermal fluctuations and surfactant molecular diffusion in the bicontinuous microemulsion (Yu and Neuman, 1995a). The proposed local dynamic domain structures (LDDS) model, in contrast to the usual model for bicontinuous microemulsions of a macroscopically extended structure of continuous water and oil separated by surfactant monolayers, accounts for the observed microemulsion behaviors of the NaDEHP-n-heptane-water system.

### Aggregation Behaviors of Nickel (II) and Cobalt (II) Di(2-Ethylhexyl) Phosphate

Various investigators reported that polymeric macromolecular species are formed by divalent transition metal-HPEHP complexes in nonpolar organic diluents (Brisk and McManamey, 1969; Sato and Nakamura, 1972; Kolarik and Grimm, 1976; Thiyagarajan et al., 1987). In such polymers, every DEHP anion is supposed to form two coordination bonds with two metal ions. The evidence cited for the formation of polymers has been the very high solution viscosity (Kolarik and Grimm, 1976) and the existence of long rodlike structures (Thiyagarajan et al., 1987). However, it is equally plausible to interpret this same evidence as support for the formation of rodlike reversed micelles.

The solution behaviors of divalent transition metal-di(2-ethylhexyl) phosphate complexes in n-heptane have been investigated in our laboratory.  $\text{Co}(\text{DEHP})_2$  complexes tend to form large macromolecular species with a mean aggregation number ( $N_{\text{agg}}$ ) as large as 225, and the size of the macromolecular species decreases with increasing  $\text{Co}(\text{DEHP})_2$  concentration.  $\text{Ni}(\text{DEHP})_2$  complexes (and  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes when the molar ratio of water to  $\text{Ni}(\text{DEHP})_2$  is 2) form small macromolecular species ( $N_{\text{agg}} = 5.2$ ), but large polydisperse macromolecular species are able to form with a mean apparent hydrodynamic radius as large as 15 nm at both high complex concentrations and high water contents. As evident in the ternary phase diagram for the  $\text{Ni}(\text{DEHP})_2$ -n-heptane-water system, the macromolecular species formed by  $\text{Ni}(\text{DEHP})_2$  complexes can solubilize large amounts of water ( $W_{0,\text{max}} = 10.7$  at  $20^\circ\text{C}$  where  $W_0$  is the molar ratio of water to  $\text{M}(\text{DEHP})_2$ ). These solution behaviors are completely different than those of the NaDEHP-n-heptane-water system where the maximum  $W_0$  values vary from zero to 230, but are quite consistent with those of the practical solvent extraction system with high loading of nickel.

These experimental findings are not consistent with the view that divalent transition metal-HDEHP complexes form polymers in nonpolar organic diluents. On the other hand, the concentration and temperature dependence of the size of the macromolecular species is typical of the solution behaviors of surfactant association microstructures. We therefore proposed that the process for the formation of macromolecular species is an aggregation (or reversed micellization) of the  $\text{M}(\text{DEHP})_2$  complex monomers (two DEHP anions form a chelate with one divalent transition metal ion) through nonchemical or physical interaction forces rather than a polymerization via chemical or coordination bonds (Yu and Neuman, 1995b, 1995c).

The remarkable differences in aggregation behaviors, namely, that  $\text{Co}(\text{DEHP})_2$  complexes form much larger reversed micelles than those of  $\text{Ni}(\text{DEHP})_2$  complexes or  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes, can be interpreted on the basis of the molecular packing of the  $\text{M}(\text{DEHP})_2$  complexes in rodlike reversed micelles. The ligand fields of  $\text{Co}(\text{DEHP})_2$  and  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes have tetrahedral and octahedral symmetries, respectively. On the basis that  $\text{Ni}(\text{DEHP})_2$  complexes form very small reversed micelles, we infer that the  $\text{Ni}(\text{DEHP})_2$  complexes form a square-planar structure in a similar manner as  $\text{Cu}(\text{DEHP})_2$  complexes ( $N_{\text{agg}} = 4-8$ ). CPK space-filling molecular models show that the complex monomers can be easily arranged into planar structures. Any packing of

additional monomers in the same plane would not maximize the interactions between the complex monomers, and thus the planar complex monomers will very likely be packed (or stacked) one on top of another. From CPK space-filling molecular models for reversed micelles of  $\text{Co}(\text{DEHP})_2$  and  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes, it can be seen that  $\text{Co}(\text{DEHP})_2$  complex monomers are more tightly packed than  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complex monomers in two ways: one is in the cross-sectional plane, which effectively reduces the interfacial area between nonpolar solvent and micellar core, and the other is in the axial direction, which reduces both the interfacial area and the distance between adjacent complexes in the reversed micelle, thereby increasing the strength of the dipole-dipole interactions as well as the interfacial energy advantage. Therefore, it is energetically favorable for  $\text{Co}(\text{DEHP})_2$  complexes to form much larger reversed micelles than those of  $\text{Ni}(\text{DEHP})_2$  and  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes. It should be mentioned that  $\text{Zn}(\text{DEHP})_2$  complexes, which also have a tetrahedral symmetry, form very large rodlike reversed micelles in n-heptane.

Due to the coordination of two water molecules, the  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complex behaves very differently than the other  $\text{M}(\text{DEHP})_2$  complexes: large reversed micelles can be formed at high complex concentrations upon solubilizing a large amount of water. The packing of  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes in quasi-one-dimensional reversed micelles allows the solubilized water molecules to interact with the coordinated water molecules through hydrogen bonding in an extended (either linear or staggered) structure. In other words, the solubilized water molecules in the channels of the reversed micelles can act as a bridge to link together the complex monomers and consequently provide an additional attractive force among the  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complex monomers. The proposed "open water-channel" model provides a novel interpretation for the formation of large reversed micelles of  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes. This model is distinctly different than that of the conventional view of reversed micellar structures, wherein water is solubilized in the inner core of the reversed micelles (Zulauf and Eicke, 1979). Nevertheless, the proposed "open water-channel" model for reversed micelles of  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes is consistent with the known octahedral structure, the maximum  $W_0$  value and its temperature dependence (Yu and Neuman, 1995c).

### Open Water-Structure Model of Reversed Micelles

CPK space-filling molecular models for the reversed micelles of (a)  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes and (b)  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes with solubilized water molecules are shown in Figure 1. Remarkable features are that the growth of reversed micelles of octahedral-coordinated metal-DEHP complexes is one dimensional and that two "open" water channels are formed in each

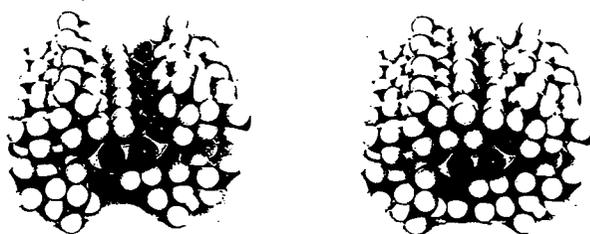


Figure 1. CPK space-filling molecular models for the reversed micelles of (a)  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes and (b)  $\text{Ni}(\text{DEHP})_2 \cdot 2\text{H}_2\text{O}$  complexes with eight added water molecules per complex monomer.

reversed micelle. The solubilized water molecules, unlike those in typical reversed micelles, are in direct contact with the nonpolar solvent molecules. It should be noted that a CPK space-filling molecular model shows that tetrahedral-coordinated metal-DEHP complexes such as  $\text{Co}(\text{DEHP})_2$  are packed in reversed micelles in such a way, in order to maximize the polar interactions, that the configuration of the P-O-M atoms in one complex monomer is arranged in mirror symmetry with that of the adjacent ones, and as a result, "open" water channels are not present in the reversed micelles of  $\text{Co}(\text{DEHP})_2$  complexes.

$^1\text{H-NMR}$  spectroscopy was employed to provide supporting evidence for the proposed "open water-channel" model by studying the location of solubilized water molecules in  $\text{Ni}(\text{DEHP})_2$  reversed micelles.  $^1\text{H-NMR}$  spectra were obtained for solutions of  $\text{Ni}(\text{DEHP})_2$ , sodium di(2-ethylhexyl) sulfosuccinate (AOT) or nickel (II) di(2-ethylhexyl) sulfosuccinate ( $\text{Ni}(\text{AOT})_2$ ) in n-heptane as a function of the molar ratio of water to surfactant. The chemical shifts of  $-\text{CH}_3$ ,  $-\text{CH}_2$ - and  $\text{H}_2\text{O}$  for  $\text{Ni}(\text{DEHP})_2$  reversed micelles display a different behavior, i.e., the chemical shifts were much greater, than those for AOT and  $\text{Ni}(\text{AOT})_2$  reversed micelles which have similar chemical shifts when the paramagnetic effect of nickel is taken into account. The  $^1\text{H-NMR}$  results indicate that the water molecules associated with the  $\text{Ni}(\text{DEHP})_2$  reversed micelles are clearly in a different environment than those associated with the AOT and  $\text{Ni}(\text{AOT})_2$  reversed micelles.

HyperChem<sup>TM</sup> molecular modelling of two  $\text{Ni}(\text{DEHP})_2$  complex monomers and added ( $W_0 = 1, 2, \dots, 9$ ) water molecules (representing a simplified reversed micelle) shows four different types of bonding of water molecules. Furthermore, HyperChem<sup>TM</sup> molecular modelling shows that water molecules exist in the channel between the hydrocarbon tails of the  $\text{Ni}(\text{DEHP})_2$  complexes. In an earlier study by Neuman and Park (1992) it was concluded on the basis of FT-IR spectroscopic measurements that the water in reversed micelles formed by nickel-HDEHP complexes exists mainly in three states, namely, the aqueous core contains free and bound water and the interfacial layer contains water trapped among the hydrocarbon chains of the extractant molecules. However, our more recent studies of the association microstructures which form in model extraction systems suggest an alternative interpretation. The  $^1\text{H-NMR}$ , HyperChem<sup>TM</sup> modelling and FT-IR results are consistent with the hypothesis that the water molecules associated with  $\text{Ni}(\text{DEHP})_2$  reversed micelles exist in "open" water channels, rather than "closed" water channels, consistent with those illustrated in the CPK space-filling molecular models shown in Figure 1.

### Reversed Micellar Structure and Selectivity

Conventional descriptions of solvent extraction mechanisms usually assume that the metal-extractant complexes in the organic phase are monomers. A full description of solvent extraction must include the equilibrium constant  $K_m$  for the equilibrium between metal-extractant complex monomers and association microstructures which, however, has generally been ignored in the past. A simple model which relates the extractability and selectivity to the size of reversed micelles has been developed. In the case of cobalt-nickel separation by acidic organophosphorus extractants, the model shows that the preferred selectivity of cobalt and nickel can be quantitatively determined from micellar size and cmc measurements, if the metal-extractant complex formation constant  $\beta$  in the aqueous phase and the distribution constant  $K_{DC}$  of the metal-extractant complex between the two phases are known. As a first approximation,  $K_m$  can be expressed as the product of the reciprocal activity of metal-extractant complex monomers  $1/a_{\text{cmc}}$  and the equilibrium constant  $K_g$  for reversed micellar growth, both of which can be experimentally determined. It is important to note that this simple model shows that the extractability and selectivity can be controlled by proper manipulation of the micellar structure.

The modification of the structure and functionality of extractant molecules is known to affect the selectivity of cobalt in cobalt-nickel separation. For example, the removal of the oxygen atom between the alkyl chain and the phosphate group allows the extractant molecules to pack more tightly about the metal ion in the metal-extractant complexes. Therefore, the micellar size (and hence,  $K_{g,\text{Co}}$ ) of  $\text{CoR}_2$  complexes is expected to increase in the order of  $\text{HDEHP} < \text{PC88A} < \text{Cyanex 272}$ .

On the other hand, since there are two water molecules coordinated with  $\text{NiR}_2$  complexes, "open" water channels form in all three types of nickel-extractant reversed micelles. The increase in size (or  $K_{g,\text{Ni}}$ ) of reversed micelles of  $\text{Ni(R)}_2 \cdot 2\text{H}_2\text{O}$  complexes is expected to be suppressed by the presence of the large interfacial area between the "open" water channels and nonpolar solvent. Thus, the selectivity  $S$  which is expressed as the ratio of the overall extraction equilibrium constants  $K_{\text{ex,Co}}/K_{\text{ex,Ni}}$  can not only be evaluated from experimentally available data, but it also can be expected to significantly increase, as is well known, when the extractant changes from HDEHP, PC88A to Cyanex 272.

The effect of organic phase additives or phase modifiers on the structure of reversed micelles is also of importance. For example, the addition of 2-octanol to n-heptane solutions of  $\text{Ni(DEHP)}_2 \cdot 2\text{H}_2\text{O}$  complexes will result in a partial replacement of coordinated water by the 2-octanol. Also, 2-octanol and water can coordinate with  $\text{Co(DEHP)}_2$  which results in reversed micelles of octahedral-coordinated cobalt-DEHP complexes. The initial large interface between "open" water channels in reversed micelles of  $\text{Ni(DEHP)}_2 \cdot 2\text{H}_2\text{O}$  complexes and nonpolar solvent is expected to decrease considerably, which favors reversed micellar growth or an increase in  $K_m$ . Furthermore, an increase in the overall extraction equilibrium constant  $K_{\text{ex,Ni}}$  and, hence, a decrease in the selectivity of cobalt in cobalt-nickel separation are expected from the increased reversed micellar size as discussed in the previous section.

#### ACKNOWLEDGMENTS

This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Department of Energy under Grant No. DE-FG05-85ER13357.

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## THE KINETICS OF METAL EXTRACTION RELATED TO EXTRACTANT SOLUBILITY AND INTERFACIAL ACTIVITY

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### INTRODUCTION

Many models have been put forward to describe the kinetics of metal extraction by acidic extractants. These models reflect the differences among researchers regarding the mechanism of metal transfer, the site of reaction and the nature of the chemical reaction step which controls the overall extraction kinetics. A number of researchers cite the very low solubility of commercial extractants in water and point to an interfacial reaction occurring at an interface of molecular dimensions. Other workers point to a reaction occurring in a thin reaction zone which is adjacent to the "molecular" interface but on the side of the aqueous phase. The thickness of this zone will depend on the rate of diffusion of the reacting species within the layer, the solubility of the extractant and the chemical rate of reaction. It is generally accepted that those reactions involving ions are more likely to take place in the 'aqueous' region of the interface rather than the hydrocarbon region of a two phase system.

Distinguishing between the two extremes of zone is important in determining the relationship between interfacial zone concentrations and bulk phase concentrations and assessing the relative importance of the distribution of reagents between the phases and other considerations such as interfacial molecular packing. Work was continued in our laboratory in order to show the influence of extractant aqueous phase solubility on liquid-liquid kinetics. Extractants in a homologous series, i.e. hydroxyoximes and dialkylphosphoric acids, where the alkyl chain length is varied, were explored.

### EXPERIMENTAL

The kinetics of metal extraction were studied by the use of the Rotating Diffusion Cell (RDC). The equipment associated with this technique was described in detail elsewhere (Albery (1976) and Patel (1988)). In this technique the cell consists of a thin membrane filter separating the organic and the aqueous phases. The liquid-liquid interface is established by interfacial tension on the surface of a Millipore filter of disk type, which is rotated. The membrane used had a pore size of  $0.22\mu\text{m}$ . The filter is mounted on a cylinder into which the organic solution is poured. This cylinder is rotated at various speeds during an experiment generating rotating disc hydrodynamics on both sides of the filter. A stationary baffle inside the cylinder provides known rotating disc hydrodynamics on the inner filter surface. This allows for the prediction of the concentration gradients on either side of the interface using the rotating disc hydrodynamics equations derived by Levich (1962) and later used by Albery et al. (1975).

In all the kinetic experiments, 50ml of organic phase was contacted with 190ml of the aqueous phase. A Radiometer automatic pH-stat system was used to follow the kinetics, i.e. the rate of proton release into the aqueous phase. The rotation speed of the RDC was varied up to 6Hz. The Levich plot, i.e. a plot of the reciprocal of the flux against the reciprocal of the square root of the rotation speed (Hz), was used to estimate the extraction flux at a particular speed.

The solubility of dialkylphosphoric acids in water was established by contacting 0.05M solutions of the extractants in either heptane or toluene with water at the appropriate pH, followed by the total oxidation of the aqueous phase samples by potassium persulphate. The liberated phosphate ion was then determined spectrophotometrically as the molybdivanado phosphoric acid complex at 460nm with a 4cm pathlength cell (Menzel and Corwin, 1965). The standard graph was plotted on results obtained by converting suitable amounts of potassium dihydrogen orthophosphate (KH<sub>2</sub>PO<sub>4</sub>) into the molybdivanadophosphoric acid complex. In the case of hydroxyoximes, aqueous washing of the organic phase, i.e. the oxime solutions, was first carried out in order to minimise the presence of any low molecular weight oximes. The Pye-Unicam ultraviolet spectrophotometer (SP8-100) was used to scan the wavelengths of the aqueous solutions of extraction using 0.05M solutions of oxime in either heptane or toluene at the appropriate pH. The wavelengths were scanned from 400nm to 190nm thus generating an area under the spectrum. The area generated from 400nm to 258nm was accurately cut and weighed. The resultant weight minus that corresponding to the blank was then read off from a calibration curve to give concentrations in ppm (wt/wt) oxime in water.

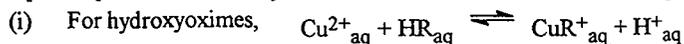
The interfacial tension between the organic and aqueous phases was determined by the drop volume method at 25±1°C and at pH 4.5 after pre-equilibrium of the two phases.

### THE MODEL

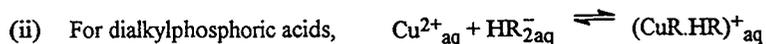
A modified version of the model of Hughes and Rod (1984) was used to describe the reaction. The model equation is deduced using the Whitman and Lewis (1924) two film theory and Astarita's equation (1967) for mass transfer coupled with chemical reaction. The model describes the extraction of metal ion, M<sup>2+</sup>, by an extractant, HR, and accommodates a mechanism where the extractant distribution coefficient is taken into account and a reaction zone thickness can be estimated. It is said that the solubility of an extractant in the aqueous phase determines, in part, the site of the reaction. In the case of a high molecular weight reagent e.g. a commercial hydroxyoxime the reaction site may well be at or near the 'molecular' interface.

An important feature of this model is that it can be used to describe situations where the reaction zone thickness on the aqueous side of the interface can vary.

In the model, the hydrodynamic parameters such as the mass transfer coefficients are separated from the chemical and diffusion terms, so that the model can be applied to contactors with different geometry but using the same chemical systems. The model also incorporates precise descriptions of the equilibria so that its application at positions near equilibrium (industrial contactors) and far away from equilibrium (initial rates) is possible. A computer program was used to model the experimental data, i.e. the flux against variables such as the concentrations of the extractant in the organic phase, C<sub>HR</sub>, the metal ion, C<sub>M</sub><sup>2+</sup>, and the hydrogen ion, C<sub>H</sub><sup>+</sup>, in the aqueous phase. Satisfactory fits were obtained where the controlling chemical step was:



Note that the undissociated form of the hydroxyoxime was identified as the active species in this case because of their low acid dissociation constants in water.



The dissociated form of the dimer molecule is the active species in this case.

The model equation for the flux is of the form,  $J = f(\theta_1, \theta_2, D, k_i, K_{\text{ex}}, C_i)$ , where  $J$  is the extraction flux,  $\text{kmol/m}^2\text{sec}$  and  $\theta_1$  is a grouped kinetic parameter. For hydroxyoximes,  $\theta_1 = k_{\text{R}}D_{\text{HR}}$ , whilst for dialkylphosphoric acids  $\theta_1 = k_{\text{R}}D_{\text{HR}}K_{\text{A}}$  where,  $k_{\text{R}}$  is the chemical rate constant,  $D_{\text{HR}}$  is the extractant diffusion constant in the aqueous phase and  $K_{\text{A}}$  is the extractant dissociation constant.  $\theta_2$  is a grouped physical property parameter,  $\theta_2 = \frac{D_{\text{HR}} P_{\text{MR}_2}}{D_{\text{MR}_2} P_{\text{HR}}}$ , where

$P_{\text{MR}_2}$  and  $D_{\text{MR}_2}$  are the partition coefficient and the diffusion coefficient of the 1:2 metal complex respectively.  $D$  is the distribution coefficient of the extractant between the aqueous and organic phases,  $k_i$  is the mass transfer coefficient of the reacting species in both the organic and aqueous phase diffusion layers,  $K_{\text{ex}}$  is the extraction constant of the overall reaction for the extraction of a metal ion by an acidic extractant and  $C_i$  is the aqueous phase interfacial concentration of the reacting species. The models of Hughes and Rod were improved by replacing the partition coefficient for the extractant with a distribution coefficient which gives a better approach to the distribution of the active extractant species between the two phases. In particular the variation of the flux with pH is now explained fully because of the known variation of the distribution coefficient with pH.

The model employed enables the estimation of the reaction zone thickness. Thus the reaction zone thicknesses for the  $\text{Cu}^{2+} - \text{SO}_4^{2-} / \text{D2EHPA} / \text{heptane}$  system and the  $\text{Cu}^{2+} - \text{SO}_4^{2-} / \text{P50} / \text{heptane}$  system were estimated to be  $0.7\mu\text{m}$  and  $1.3 \times 10^{-3}\mu\text{m}$  respectively. The diffusion layer thickness was calculated from the Levich theory of a rotating disc to be  $33\mu\text{m}$  thick. It can be seen that the reaction zone thickness is well within the diffusion zone.

The model allows for two extremes. At one extreme, when the solubility of the extractant in the aqueous phase is very low the film thickness approaches zero and a true molecular surface involving a monolayer of molecules is involved. On the other hand, when the reaction rate is slow and the extractant is very soluble in the aqueous phase the film thickness with approach 'infinity' and the reaction will occur in the bulk of the aqueous phase. The latter situation is not true of the extractants studied in this work as their solubility in water is limited and their extraction rates are fast, i.e. a thin reaction zone is involved. Recent measurement by Neuman and co-workers (1993) has revealed that the interface for commercial liquid-liquid systems is indeed diffuse in nature ranging from  $7 \times 10^{-3}$  to  $30 \times 10^{-3}\mu\text{m}$  thick for the extraction of nickel with D2EHPA.

**The dependence of the extraction flux on both the extractant solubility in the aqueous phase and the interfacial tension of the liquid-liquid system.**

The interfacial tension of the liquid-liquid system increases as the alkyl chain length of a homologous series of extractant molecules decreases. Such a trend in the interfacial tension was also observed by Miyake et al (1986) and Al-Diwan et al (1977) for hydroxyoximes of the type studied in this work. The extraction rates were found to be higher for shorter chain molecules.

The changes in length of the alkyl chain length is parallel to the changes in the aqueous phase solubility. Overall, the extraction flux increases with an increase in the aqueous phase solubility of the extractant and an increase in the interfacial tension (see Figures 1 and 2).

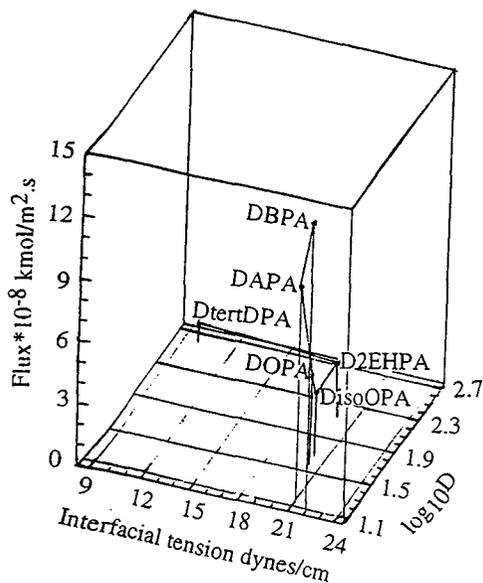


Figure 1: The dependence of the metal extraction flux on the extractant distribution coefficient and the interfacial tension of the  $\text{Cu}^{2+} - \text{SO}_4^{2-}$  /dialkylphosphoric acid/heptane system.  $[\text{Cu}^{2+}] = 0.01\text{M}$ ,  $[\text{HR}] = 0.05\text{M}$   $\text{pH} = 4.5$

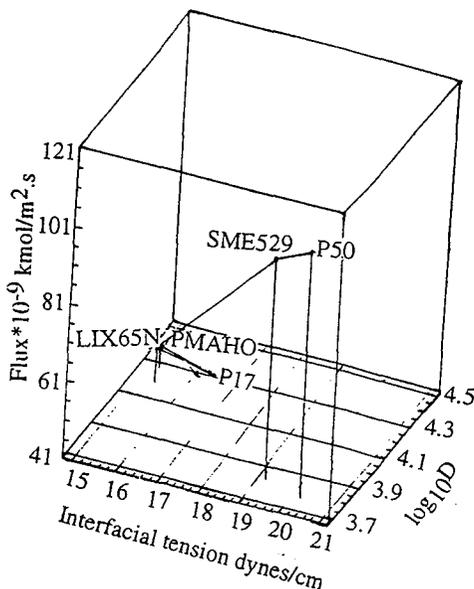


Figure 2: The dependence of the metal extraction flux on the extractant distribution coefficient and the interfacial tension of the  $\text{Cu}^{2+} - \text{SO}_4^{2-}$  /hydroxyoxime/heptane system.  $[\text{Cu}^{2+}] = 0.01\text{M}$ ,  $[\text{HR}] = 0.05$ ,  $\text{pH} = 4.5$

The data from Figures 1 and 2 can be correlated by an equation of the form,  $J = AD^{-1}T^b$ , where  $J$  is the metal extraction flux ( $\text{kmol}/\text{m}^2 \cdot \text{sec}$ ),  $D$  is the extractant distribution coefficient,  $T$  is the interfacial tension of the liquid-liquid system ( $\text{N}/\text{m}$ ) while  $A$  and  $b$  are constant for a homologous series of extractant molecules. The values of  $A$  and  $b$  for the systems shown in Figures 1 and 2 were found to be:-

- (i) For the  $\text{Cu}^{2+} - \text{SO}_4^{2-}$  /dialkylphosphoric acid/heptane system,  $A = 1.029 \times 10^{-3}$  and  $b = 1.68$
- (ii) For the  $\text{Cu}^{2+} - \text{SO}_4^{2-}$  /hydroxyoxime/heptane system,  $A = 2.6980 \times 10^{-5}$  and  $b = -0.81215$

From Figures 1 and 2 it can be seen that aqueous phase solubility effects seem to play a more important rule in the extraction process than the interfacial tension of the liquid-liquid system. However it is expected that for those molecules which are 'completely' insoluble in water, interfacial activity (reflected through the interfacial tension) will then become a dominant feature in the extraction kinetics.

## CONCLUSIONS.

The rate of metal extraction is in part a function of the extractant aqueous phase solubility (reflected in the extractant distribution coefficient between the aqueous and organic phases). Within a homologous series the rate of metal extraction at a particular pH increases with an increase in the aqueous phase solubility (depth of the aqueous reaction zone) and an increase in the interfacial tension (sharper phase boundary).

The interfacial tension of the system will be more important for those situations where the extractant is virtually insoluble in the aqueous phase. In this instance the reaction zone thickness approaches zero and molecular organisation at the interface (reflected by the interfacial tension) is now more important.

## CHEMICAL SYMBOLS

Table 1. The list of chemical symbols that were used in the text and diagrams.

1. Hydroxyoximes		2. Di-alkylphosphoric acids
P50	5-nonylsalicylaldoxime	DBPA dibutylphosphoric acid
SME529	1-hydroxy-5-nonylacetophenone oxime	DAPA diamylphosphoric acid
PMANC	2-hydroxy-5-tert-octylbenzophenone oxime	DOPA di-n-octylphosphoric acid
LIX65N	2-hydroxy-5-nonylbenzophenone oxime	DisoOPA di-iso-octylphosphoric acid
P17	2-hydroxy-5-tert-dodecylbenzophenone oxime	D2EHPA di-2-ethylhexylphosphoric acid
PMAHO	2-hydroxy-5-tert-dodecylbenzophenone oxime	DtertDPA di-dodecylphosphoric acid

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## EFFECT OF LONG-CHAIN ALKYL SUBSTITUENTS OF 8-QUINOLINOL DERIVATIVES ON EXTRACTION AND BACK-EXTRACTION OF PALLADIUM(II)

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### ABSTRACT

The extraction and back extraction behaviors of palladium(II) were investigated with long-chain alkylated 8-quinolinol derivatives such as 5-dipropylaminomethyl-8-quinolinol (HN<sub>3</sub>Q), 5-dibutylaminomethyl-8-quinolinol (HN<sub>4</sub>Q), 5-propyloxymethyl-8-quinolinol (HO<sub>3</sub>Q), 5-octyloxymethyl-8-quinolinol (HO<sub>8</sub>Q), and 2-methyl-5-octyloxymethyl-8-quinolinol (HMO<sub>8</sub>Q) (Fig. 1) in some organic solvents were investigated. The extractability of palladium(II) with HN<sub>3</sub>Q and NH<sub>4</sub>Q from an acidic solution is lower than that with HO<sub>3</sub>Q, HO<sub>8</sub>Q and HMO<sub>8</sub>Q. The extraction constant, K<sub>ex</sub> (=  $\frac{[\text{Pd}(\text{Q})_2]_{\text{org}}[\text{H}^+]^2}{[\text{Pd}^{2+}][\text{HQ}]^2_{\text{org}}}$ ) of palladium(II) with 8-quinolinol derivatives (HQ) increased in the following order of HMO<sub>8</sub>Q < 8-quinolinol < HO<sub>8</sub>Q < Kelex 100. Above pH 1 (HCl), Pd(MO<sub>8</sub>Q)<sub>2</sub> in chloroform containing free HMO<sub>8</sub>Q was not back-extracted at all with SCN<sup>-</sup>, but was completely back-extracted with 0.3 mol dm<sup>-3</sup> SCN<sup>-</sup> in the pH range of 2.0 - 3.0. On the other hand, the back extraction percentage of Pd(O<sub>8</sub>Q)<sub>2</sub> was only 19% even in the presence of 0.3 mol dm<sup>-3</sup> SCN<sup>-</sup> at pH 3.0. The steric effect of the 2-methyl group of HMO<sub>8</sub>Q enhances the back extraction efficiency of Pd(MO<sub>8</sub>Q)<sub>2</sub>. Palladium(II) can be separated with HMO<sub>8</sub>Q and HO<sub>8</sub>Q from other metal ions by the combined procedures of extraction and back extraction.

### INTRODUCTION

The selectivity of the extraction of metal ions with chelating extractants has been one of the attractive subjects in separation science. We have newly prepared some hydrophobic alkylated 8-quinolinol derivatives and reported the extraction behaviors of molybdenum(V,VI) (Ohashi et al., 1985) and copper(II) (Kokusen et al., 1988). Among 8-quinolinol derivatives, HMO<sub>8</sub>Q showed a higher selectivity toward molybdenum(VI) than HO<sub>8</sub>Q; Molybdenum(VI) was extracted from a strongly acidic solution and the molybdenum(VI)-HMO<sub>8</sub>Q complex was easily back-extracted with a dilute aqueous ammonia solution (Purnawawaty et al., 1994).

Ma and Freiser (1984) have found that Kelex 100 was an effective extractant for palladium(II) from a strongly acidic chloride medium and that the palladium(II)-Kelex 100 complex was easily back-extracted with hydrochloric acid containing SCN<sup>-</sup>.

In this work, the extraction and back extraction of palladium(II) with long-chain alkylated 8-quinolinol derivatives in some organic solvents such as heptane and chloroform were investigated to clarify the effect of alkyl substituents of 8-quinolinol derivatives on the extraction and back extraction behavior of palladium(II).

## EXPERIMENTAL

### REAGENTS

$\text{HO}_8\text{Q}$  was prepared by the reaction of 5-chloromethyl-8-quinolinol (Kolobielski et al., 1966) with 1-octanol and was recrystallized from ethanol three times.  $\text{HMO}_8\text{Q}$  was synthesized similarly to the preparation of  $\text{HO}_8\text{Q}$  by using 2-methyl-5-chloromethyl-8-quinolinol as a starting material.  $\text{HN}_3\text{Q}$  ( $\text{HN}_4\text{Q}$ ) was synthesized by reacting 5-chloromethyl-8-quinolinol with 1-propylamine (1-butylamine) in hexane. These compounds were identified by  $^1\text{H-NMR}$  and elemental analysis. Working solutions of palladium(II) were prepared by diluting a standard solution for atomic absorption spectrometry with  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid. Reagent grade chloroform was washed with deionized water just before use. Benzene and heptane were purified before use. The other reagents were of guaranteed reagent quality.

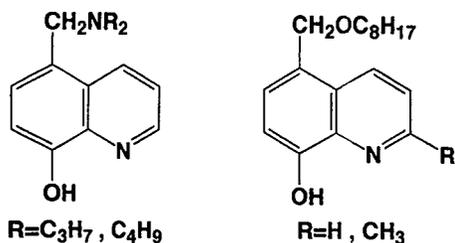


Fig. 1 Structures of 8-quinolinol derivatives

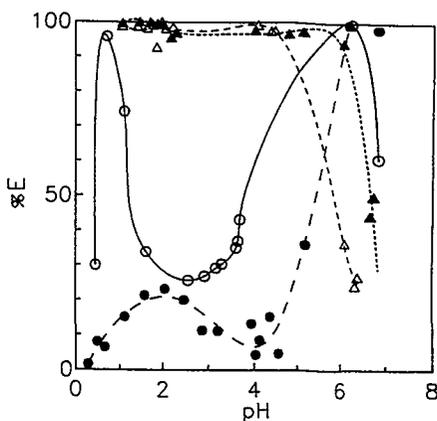


Fig.2. Extraction of Pd(II) with  $0.01 \text{ mol dm}^{-3}$   $\text{HN}_3\text{Q}$  and  $\text{HO}_3\text{Q}$ .  
 ●,  $\text{HN}_3\text{Q}$ -heptane; ○,  $\text{HN}_3\text{Q}$ - $\text{CHCl}_3$ ;  
 ▲,  $\text{HO}_3\text{Q}$ -heptane; △,  $\text{HO}_3\text{Q}$ - $\text{CHCl}_3$ .

### EXTRACTION PROCEDURE

A  $10\text{-cm}^3$  portion of an aqueous solution containing  $(1.1 - 50) \times 10^{-6} \text{ mol dm}^{-3}$  palladium(II) and  $0.1 - 1.0 \text{ mol dm}^{-3}$   $(\text{H}, \text{Na})\text{Cl}$  was placed in a  $50\text{-cm}^3$  glass vial fitted with a glass stopper. A  $10\text{-cm}^3$  portion of chloroform solution containing a given concentration of the extractant was added to the aqueous solution and was shaken vigorously in a thermostated room at  $25^\circ\text{C}$ . The palladium(II) concentration in the aqueous phase was determined using an inductively coupled plasma emission spectrometer (ICP-AES). The extracted palladium(II)-HQ complex was back-extracted with a  $0.01 \text{ mol dm}^{-3}$   $\text{HCl}$  containing  $0.3 \text{ mol dm}^{-3}$   $\text{SCN}^-$  and determined by ICP-AES. The distribution ratio ( $D$ ) of palladium(II) was calculated from the palladium(II) concentration in the aqueous and organic phases.

The pH was adjusted with an acetate buffer (pH 3.5 - 5.8). The pH value of the aqueous phase was immediately measured with a glass electrode using an Orion Research model 701A digital IONALYZER after phase separation. The higher concentration of hydrogen ion ( $2 \text{ mol dm}^{-3}$  - pH 3.3) was adjusted by hydrochloric acid. The ionic strength was kept constant with sodium chloride solution.

## RESULTS AND DISCUSSION

### EXTRACTION BEHAVIOR OF PALLADIUM(II) WITH $\text{HN}_n\text{Q}$

Figure 2 shows the pH dependence of the extractability of palladium(II) with  $\text{HN}_3\text{Q}$  and  $\text{HO}_3\text{Q}$  in chloroform and heptane. Though palladium(II) is completely extracted with  $\text{HO}_3\text{Q}$  in chloroform and heptane in an acidic region of  $1 \text{ mol dm}^{-3} \text{ HCl}$  - pH ca. 4 in chloroform and heptane,  $\text{HN}_3\text{Q}$  shows a lower extractability.  $\text{HN}_4\text{Q}$  provides similar extraction curves to those of  $\text{HN}_3\text{Q}$  for chloroform and heptane. Thus,  $\text{HN}_n\text{Q}$  shows very different extraction behavior from that of  $\text{HO}_3\text{Q}$ .

### EXTRACTION BEHAVIOR OF PALLADIUM(II) WITH $\text{HMO}_8\text{Q}$ AND $\text{HO}_8\text{Q}$

As will be mentioned below,  $\text{HMO}_8\text{Q}$  is a superior extractant to  $\text{HO}_8\text{Q}$  owing to easy back extraction of the  $\text{Pd}(\text{MO}_8\text{Q})_2$  complex. Consequently, the detailed extraction equilibrium of palladium(II) with  $\text{HMO}_8\text{Q}$  in chloroform has been investigated and compared with the palladium(II) extraction with other 8-quinolinol derivatives such as  $\text{HO}_8\text{Q}$ .

It was ascertained that the equilibrium of the forward and back-extraction of  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$  palladium(II) with  $0.01 \text{ mol dm}^{-3} \text{ HMO}_8\text{Q}$  in chloroform from  $0.2 \text{ mol dm}^{-3} \text{ HCl}$  containing  $0.5 \text{ mol dm}^{-3} \text{ Cl}^-$  was established by shaking for 25 h. Under the experimental conditions, the major species of palladium(II) is  $\text{PdCl}_4^{2-}$  and very small amounts of  $\text{PdCl}_3(\text{H}_2\text{O})^-$  exist. Therefore, the overall extraction reaction of palladium(II) with  $\text{HMO}_8\text{Q}$  can be expressed as follows:



Slope analysis was adopted to determine the composition of the extracted palladium(II)- $\text{HMO}_8\text{Q}$  complex.

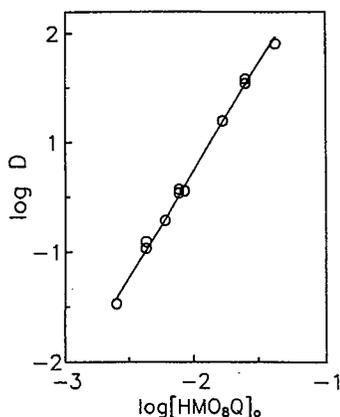


Fig.3. Plots of  $\log D$  vs.  $\log[\text{HMO}_8\text{Q}]_{\text{org}}$ .  
 $0.25 \text{ mol dm}^{-3} \text{ HCl}$ ,  
 $0.5 \text{ mol dm}^{-3} \text{ Cl}^-$ .

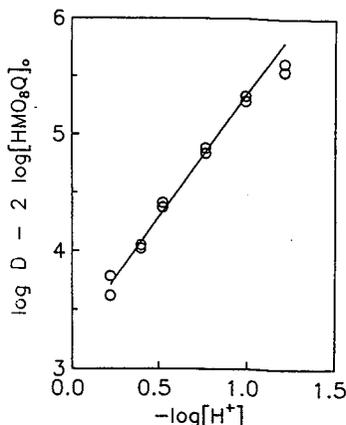
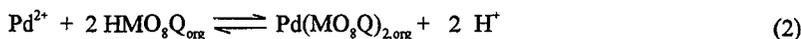


Fig.4. Plots of  $\log D - 2 \log[\text{HMO}_8\text{Q}]_{\text{org}}$  vs.  $-\log[\text{H}^+]$ .  
 $0.01 \text{ mol dm}^{-3} \text{ HMO}_8\text{Q}$ ,  
 $0.4 \text{ mol dm}^{-3} \text{ Cl}^-$ .

The plots of  $\log D - 2 \log[\text{HMO}_8\text{Q}]_{\text{org}}$  vs. pH gave a straight line with a slope of 1.9, as shown in Fig.3. The  $\log D$  vs.  $\log[\text{HMO}_8\text{Q}]_{\text{org}}$  plots provide a straight line having a slope of 2.0 (Fig.4). The  $\text{HMO}_8\text{Q}$  concentration in the organic phase was calculated from the distribution data of  $\text{HMO}_8\text{Q}$  between a hydrochloric acid solution and chloroform. The effect of the chloride ion concentration

on the palladium(II) extraction with  $\text{HMO}_8\text{Q}$  was also examined. The plots of  $\log D - 2\log[\text{HMO}_8\text{Q}]_{\text{org}}$  vs.  $\log[\text{Cl}^-]$  gave a straight line with a slope of -4 (Fig. 5). We concluded that two  $\text{HMO}_8\text{Q}$  molecules, two hydrogen ions and four chloride ions participated in the palladium(II) extraction. The aqueous palladium(II) concentration can be calculated by using the formation constants ( $\beta_n$ ) of  $\text{PdCl}_n(\text{H}_2\text{O})_{4-n}^{(2-n)+}$ . Consequently, the extraction constant ( $K_{\text{ex}}$ ) corresponding to the extraction of aqueous palladium(II) with  $\text{HMO}_8\text{Q}$ , shown by Eq. (2) can be calculated by using Eq. (3).



where the values of  $\beta_3$  and  $\beta_4$  are  $1.58 \times 10^2$  and  $3.16 \times 10^{11}$ , respectively.

$$K_{\text{ex}} = \frac{D [\text{H}^+]^2 (\beta_3 [\text{Cl}^-]^3 + \beta_4 [\text{Cl}^-]^4)}{[\text{HMO}_8\text{Q}]_{\text{org}}^2} \quad (3)$$

The  $K_{\text{ex}}$  values of the palladium(II) complex are listed in Table 1 along with those of the molybdenum(VI)-HQ complex. They increase in the following order of  $\text{HMO}_8\text{Q} < 8\text{-quinolinol} < \text{HO}_8\text{Q} < \text{Kelex 100}$ .

The  $K_{\text{ex}}$  value for  $\text{HMO}_8\text{Q}$  is smallest among these 8-quinolinol derivatives. Of these 8-quinolinol derivatives,  $\text{HMO}_8\text{Q}$  gave the smallest  $K_{\text{ex}}$  value. This may be related to the steric hindrance of the 2-methyl group.

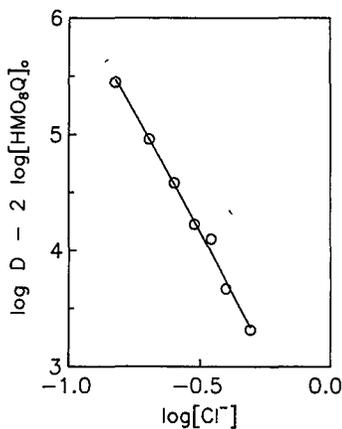


Fig. 5. Plots of  $\log D - 2\log[\text{HMO}_8\text{Q}]_{\text{org}}$  vs.  $\log[\text{Cl}^-]$ .  
 $0.01 \text{ mol dm}^{-3} \text{ HMO}_8\text{Q}$ ,  
 $0.5 \text{ mol dm}^{-3} \text{ H}^+$ .

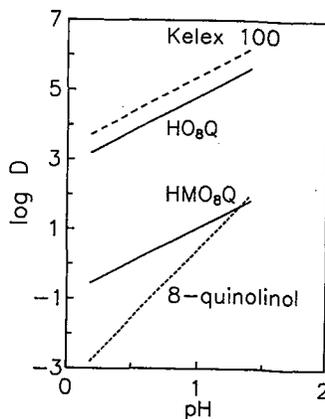


Fig. 6. Comparison of the extraction of Pd(II) at the acidic region.  
 $[\text{HQ}] = 0.050 \text{ mol dm}^{-3}$ ,  $[\text{Cl}^-]_3 = 0.4 \text{ mol dm}^{-3}$ ,  $l = 1 \text{ mol dm}^{-3}$ .

The plots of  $\log D$  vs. pH for the extraction of palladium(II) with  $\text{HO}_8\text{Q}$ , Kelex 100 and 8-quinolinol are also shown in Fig. 6 along with that for the palladium(II)- $\text{HMO}_8\text{Q}$  system. The  $\log D$  - pH curves for  $\text{HO}_8\text{Q}$ , Kelex 100 and 8-quinolinol were obtained from the extraction constants obtained in this work and in the references.

The  $K_{\text{ex}}$  values for the extraction of palladium(II) with  $\text{HO}_8\text{Q}$  in chloroform, benzene, heptane, and isobutylmethylketone were also determined. The  $K_{\text{ex}}$  values are almost independent of the kinds of

organic solvents, suggesting that specific solvation does not occur for both the palladium(II) complex and the chelating ligand.

Palladium(II) is extracted with HMO<sub>8</sub>Q from more strongly acidic solution than with 8-quinolinol in spite of the smaller extraction constant for Pd(MO<sub>8</sub>Q)<sub>2</sub>. The extractability of palladium(II) with 8-quinolinol steeply decreases with a decrement of the pH value below pH 1.0. Such different extraction behavior is due to the difference in the hydrophobicity of both extractants. In an acidic solution, 8-quinolinol is protonated and readily distributed into the aqueous phase. Therefore, the 8-quinolinol concentration in the organic phase decreases with decrease of the pH values of the aqueous phase. On the other hand, the HMO<sub>8</sub>Q concentration in the organic phase does not change so much because the partition coefficient of HMO<sub>8</sub>Q is much higher than that of the 8-quinolinol.

K<sub>ex</sub> values for the molybdenum(VI) extraction with HO<sub>8</sub>Q and 8-quinolinol are reported previously to be almost equal to each other (Table 1). Unlike molybdenum(VI), the K<sub>ex</sub> values for the palladium(II)-8-quinolinol derivatives (HQ) except HMO<sub>8</sub>Q seem to increase in parallel with increase of the hydrophobicity of HQ, though the other effects such as the acid-dissociation constants of HQ cannot be excluded at all.

TABLE 1

Extraction constant of Pd(II) and Mo(VI) with 8-quinolinol derivatives in chloroform

Extractant	log K <sub>ex</sub> <sup>a)</sup>	log K <sub>ex</sub> <sup>e)</sup>
8-quinolinol	15 <sup>b)</sup>	17.6 <sup>b)</sup>
HMO <sub>8</sub> Q	13.2 <sup>c)</sup>	14.9 <sup>d)</sup>
HO <sub>8</sub> Q	16.8 <sup>c)</sup>	17.7 <sup>f)</sup>
Kelex 100	17.4 <sup>d)</sup>	-

- a)  $[Pd(Q)_2]_{org} [H^+]^2 / [Pd^{2+}] [HQ]_{org}^2$ , b) From Stary, 1963, c) This work,  
d) From Ma and Freiser, 1984, e)  $K_{ex} = [MoO_2(Q)_2]_{org} / [MoO_4^{2-}] [H^+]^2 [HQ]_{org}^2$ ,  
f) From Purnawaty, 1994

#### BACK EXTRACTION BEHAVIOR OF PALLADIUM(II) COMPLEXES

The back extraction of Pd(MO<sub>8</sub>Q)<sub>2</sub> and Pd(O<sub>8</sub>Q)<sub>2</sub> complexes with hydrochloric acid containing SCN<sup>-</sup> was examined. Figure 7 shows the pH dependence of the back extraction in the presence of 0.3 mol dm<sup>-3</sup> SCN<sup>-</sup>. Pd(MO<sub>8</sub>Q)<sub>2</sub> in chloroform was completely back-extracted in the pH range of 2 - 3 by shaking for 30 min. Below pH 2, the back extraction efficiency decreases with decrease of the pH value. Pd(MO<sub>8</sub>Q)<sub>2</sub> in chloroform was completely back-extracted with 0.3 mol dm<sup>-3</sup> SCN<sup>-</sup> below pH 2 in the absence of free HMO<sub>8</sub>Q, suggesting that the low back extraction efficiency may be ascribed to the formation of the ion-pair complex, Pd(SCN)<sub>4</sub><sup>2-</sup>·H<sub>2</sub>MO<sub>8</sub>Q<sup>+</sup> in the organic phase. The extraction of palladium(II) as an ion-pair complex was ascertained by the extraction of Pd(SCN)<sub>4</sub><sup>2-</sup> with HMO<sub>8</sub>Q from an acidic solution in chloroform.

As shown in Fig. 7, ca. 90% of Pd(O<sub>8</sub>Q)<sub>2</sub> in chloroform was back-extracted in the presence of 0.3 mol dm<sup>-3</sup> SCN<sup>-</sup> in the pH range of 1.0 - 2.0 at the shaking time of 30 min, but the back extraction of Pd(O<sub>8</sub>Q)<sub>2</sub> was found to increase with increase of the shaking time at pH 2.0 and 3.0. This result

suggests that the back extraction rate of  $\text{Pd}(\text{O}_8\text{Q})_2$  is lower than that of  $\text{Pd}(\text{MO}_8\text{Q})_2$ .

On the other hand, as mentioned above,  $\text{Pd}(\text{MO}_8\text{Q})_2$  is more easily back-extracted than  $\text{Pd}(\text{O}_8\text{Q})_2$ . The enhancement of the back extraction of  $\text{Pd}(\text{MO}_8\text{Q})_2$  may be caused by the steric effect of the methyl group of  $\text{HMO}_8\text{Q}$ .

The back extraction of the palladium(II)- $\text{HN}_4\text{Q}$  complex with  $\text{SCN}^-$  was also examined to compare with those of  $\text{Pd}(\text{O}_8\text{Q})_2$  and  $\text{Pd}(\text{MO}_8\text{Q})_2$ . At pH 2.1, 88% of the palladium(II)- $\text{HN}_4\text{Q}$  complex in an organic phase was back-extracted with  $0.3 \text{ mol dm}^{-3} \text{ SCN}^-$  by shaking for 3 h. The palladium(III)- $\text{HN}_4\text{Q}$  complex was not completely back-extracted even at pH 1.2 by shaking for 4 h.

We previously found that  $\text{MoO}_2(\text{MO}_8\text{Q})_2$  is easily back-extracted with an aqueous ammonia solution compared with that of  $\text{MoO}_2(\text{O}_8\text{Q})_2$ . These facts suggest that the methyl group at the 2-position of  $\text{HMO}_8\text{Q}$  plays an important role in the back extraction of metal complexes of  $\text{HMO}_8\text{Q}$ .

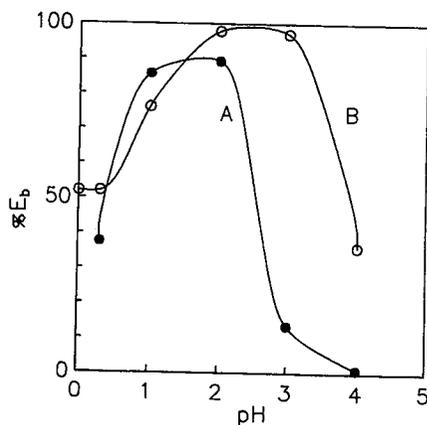


Fig.7. Effect of the acid concentration on the back extraction of Pd(II) with  $0.3 \text{ mol dm}^{-3} \text{ SCN}^-$  in the presence of  $0.01 \text{ mol dm}^{-3} \text{ HQ}$ .

A,  $4.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ Pd}(\text{O}_8\text{Q})_2$ ;  
 B,  $4.9 \times 10^{-5} \text{ mol dm}^{-3} \text{ Pd}(\text{MO}_8\text{Q})_2$ .  
 Shaking time, 30 min.

Palladium(II) is extracted with  $\text{HMO}_8\text{Q}$  from an acidic solution from which many metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Zn}^{2+}$  cannot be extracted. Palladium(II) can be selectively separated from the other metal ions by the combined procedures of extraction and back extraction.

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## EXTRACTION OF COBALT WITH VERSATIC ACID 10 AND STRIPPING-CRYSTALLIZATION OF COBALT UNDER HIGH PRESSURE CARBON DIOXIDE GAS

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### ABSTRACT

Extraction experiment of cobalt with Versatic Acid 10 and stripping-crystallization experiment of cobalt under high pressure  $\text{CO}_2$  gas up to 15 atm at 298K were carried out. Experimental data were analyzed using a thermodynamical model at equilibrium. In this model, it was assumed that cobalt is extracted into the organic phase in the form of a dimer and that carbonate species such as  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  introduced by the application of  $\text{CO}_2$  gas are combined with cobalt. Computed results fit fairly well with the data of the extraction experiment and rather well with the data of the stripping-crystallization experiment. It was suggested from the analysis of the stripping process that the solution under high pressure  $\text{CO}_2$  gas is in the state of a supersaturation for the precipitation of  $\text{CoCO}_3$ .

### INTRODUCTION

One of the important applications of solvent extraction is to obtain fine powders, by using a reverse process of extraction reaction, i.e., stripping reaction. Okuda et al. (1986) obtained powders of  $\text{CoCO}_3$  through the sampling tube of autoclave, in which cobalt extracted in organic solution was stripped into pure water under a high pressure  $\text{CO}_2$  gas. They examined the time variation of the degrees of stripping or crystallization of cobalt and also the change of powder characteristics at various conditions. Wase et al. (1992) investigated a similar process of stripping/crystallization of cobalt in detail, by using Versatic Acid 10 (hereafter referred to as VA10) as solvent and high pressure  $\text{CO}_2$  gas up to 15 atm in autoclave. It was found that, under the condition of  $0.5 \text{ mol/dm}^3$  VA10 concentration,  $0.11 \text{ mol/dm}^3$  cobalt concentration in organic phase and 15 atm  $\text{CO}_2$  gas pressure, the crystallization occurred if the samples were collected through the sampling tube of autoclave, but any crystallization was not observed in autoclave when it was opened after reducing  $\text{CO}_2$  gas pressure from higher to atmospheric one. This implies somewhat a complicated situation in which the manner of crystallization depends sensitively on the method of sampling from the autoclave. In view of the complexity of these processes, thermodynamical considerations may be helpful in investigating the chemical equilibria in the extraction and stripping-crystallization processes.

In this paper, experiments on the extraction of cobalt with VA10 as well as on the stripping of

cobalt and crystallization of cobalt carbonate using high pressure CO<sub>2</sub> gas are carried out and a comparison is made with computations based on a thermodynamical model at equilibrium.

## EXPERIMENTAL METHODS

### Extraction

Organic solution used in this experiment was the solution of VA10, Shell Chemicals Ltd. product, which is a type of carboxylic-acid with chemical formula  $R_1R_2CH_2COOH$  ( $R_1+R_2=C_7H_{10}$ ) (hereafter written as RH (  $R$ ;  $R_1R_2CH_2COO^-$  )). Three initial cobalt (Co) concentrations, 0.005, 0.033 and 0.1 mol/dm<sup>3</sup>, in aqueous phase were used in this experiment. The procedure of the experiment is as follows; 0.015 dm<sup>3</sup> VA10 solution of concentration of 5.2 mol/dm<sup>3</sup> and a certain amount of 6N-NaOH solution ( for the adjustment of pH value ) were taken in a 0.05 dm<sup>3</sup> centrifuge tube, shaken in a recipro shaker at 300rpm for 5 minutes and, after addition of a certain amount of Co(NO<sub>3</sub>)<sub>2</sub> solution, they were shaken again for 30 minutes. The total volume of NaOH, Co(NO<sub>3</sub>)<sub>2</sub> and KNO<sub>3</sub> solutions were fixed to 0.015 dm<sup>3</sup>. Ionic strength has been adjusted to 1.0 using KNO<sub>3</sub> solution.

The solutions were then separated in a centrifuge at 2500 rpm for 15 minutes. From both aqueous and organic phases, samples were taken for analysis of the Co concentration by using an atomic absorption spectrophotometer. The pH value of the aqueous phase was also measured.

### Stripping

VA10 with the concentration of 0.5 mol/dm<sup>3</sup> was used in this experiment. Before the stripping experiment, Co was extracted from aqueous to organic solutions using a similar method as stated above. Organic solutions with various Co concentrations up to maximum 0.216 mol/dm<sup>3</sup> were obtained.

In stripping experiment, with the use of carbon dioxide, a stainless steel autoclave was used. Organic solution containing Co and pure water (0.2 dm<sup>3</sup> each) was placed in the autoclave and stirred at 500 rpm at constant pressure of carbon dioxide. About 30 minutes later, the lid of autoclave was opened and the presence/absence of crystallization was examined. Immediately after that, samples were taken from organic and aqueous phases, and the pH of the aqueous phase was measured. Co concentrations in both aqueous and organic phases were measured.

## RESULTS AND DISCUSSION

### Extraction

Fig.1 shows one of the results on the relationship between pH values in aqueous phase and Co concentrations in aqueous and organic phases, where the initial Co concentration and ionic strength in aqueous phase being 0.1 mol/dm<sup>3</sup> and 1.0 respectively. As the pH value increases, Co concentration in the aqueous phase (open circles) decreases and that in the organic phase (solid

circles) increases, indicating that the degree of extraction increases as the pH value becomes larger. Degrees of extraction of both sodium (Na) and RH, on the other hand, were very small in the same pH region.

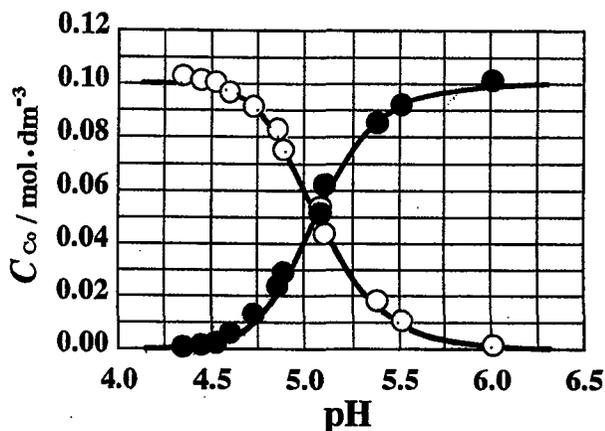


Fig.1 Relation between pH and  $C_{Co}$  concentrations in aqueous and organic phases at 298K.

Initial concentration of cobalt is  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  and ionic strength is 1.0.

Experiment : ○ (in aqueous phase), ● (in organic phase)

Calculation : ———  $K_{ext} = 1.41 \cdot 10^{-21} \text{ dm}^3 / \text{mol}$

### Stripping

The variation of degrees of Co stripping with  $\text{CO}_2$  gas pressure is shown in Fig.2, at initial Co concentration in organic phase of  $0.1 \text{ mol}/\text{dm}^3$ . Degree of stripping (solid squares) increases as  $\text{CO}_2$  gas pressure increases; 50% at 1 atm and close to 100% at 15 atm. No crystallization was observed in this case. The variation of stripping and crystallization with initial Co concentration in organic phase at 15 atm  $\text{CO}_2$  gas pressure is shown in Fig.3. In the region of initial Co concentration below  $0.12 \text{ mol}/\text{dm}^3$ , degree of stripping is almost 100% and crystallization is absent. Above this region, degree of stripping gradually decreases, down to approximately 80% at  $0.22 \text{ mol}/\text{dm}^3$  initial Co concentration. Crystallization (solid triangles) occurs in this region, the degree of which ranges from 20 to 40%.

## THERMODYNAMICAL CONSIDERATIONS

### Thermodynamical Model

Thermodynamical models is used to compute concentrations of various chemical species. In Fig.4 are shown the expected species in the extraction and stripping/crystallization processes at equilibrium.

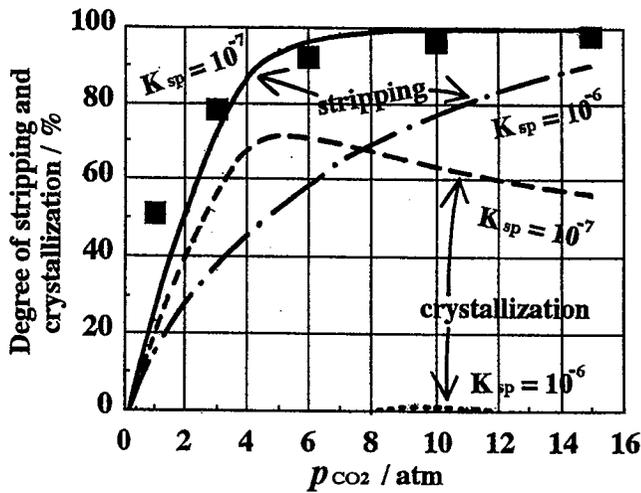


Fig.2 Relation between  $p_{CO_2}$  and degree of stripping and crystallization. Initial concentration of Co in organic phase is  $0.1 \text{ mol} \cdot \text{dm}^3$ . Experiment: ■, Calculation:  $K_{sp} = 10^{-6}$ ,  $K_{sp} = 10^{-7} (\text{mol}/\text{dm}^3)^2$

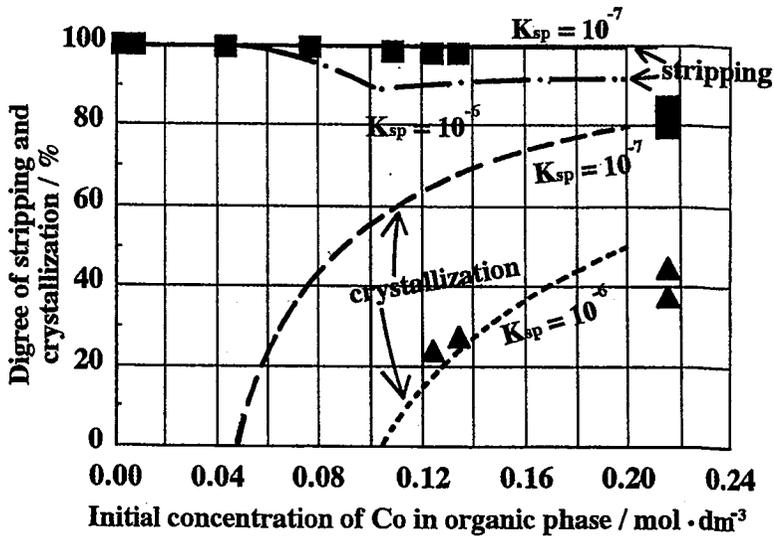
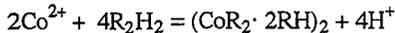


Fig.3 Relation between initial concentration of Co in organic phase and degrees of stripping and crystallization. Experiment: ■ (Stripping), ▲ (Crystallization) Calculation:  $K_{sp} = 10^{-6}$ ,  $K_{sp} = 10^{-7} (\text{mol}/\text{dm}^3)^2$

VA10 in the form of dimer ( $R_2H_2$ ) in organic phase combines with Co ion ( $Co^{2+}$ ) in aqueous phase, lead to the extracted species of Co in the form of a dimer in organic phase through the following reaction;



The equilibrium constant in the above reaction is written as  $K_{ext}$ . In the extraction process, reaction proceeds from left to right in the above equation and, in the stripping process, the reverse reaction proceeds. In the latter case, the additional ions such as  $H_2CO_3$ ,  $HCO_3^-$  and  $CO_3^{2-}$  are introduced by the application of  $CO_2$  gas. The equilibrium constants related to these species are denoted as  $K_1, K_2$  and  $K_3$ . Furthermore, when the crystallization of  $CoCO_3$  occurs, the solubility product  $K_{sp}$  has

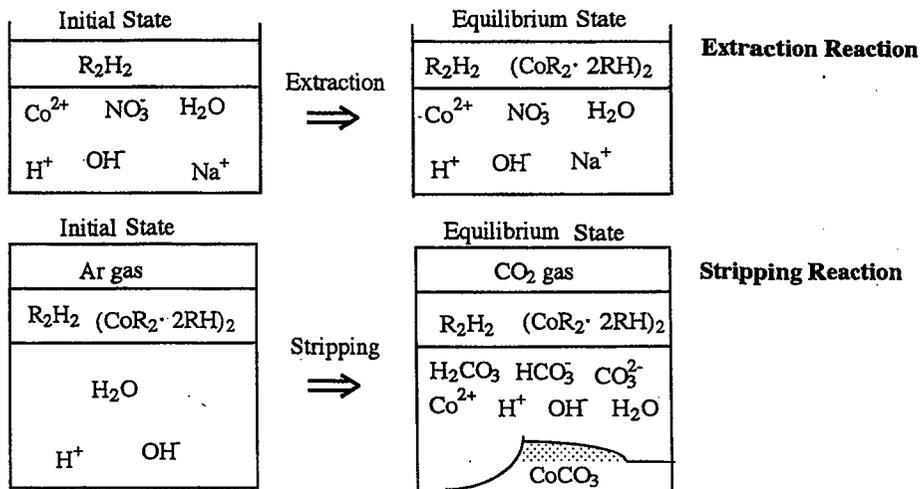


Fig.4 Thermodynamical model for extraction reaction of and stripping reaction of Co under  $CO_2$  gas pressure.

to be accounted for, which was treated as a parameter in this calculation. Combined equations with respect to two independent variables, the concentration of  $H^+$  and  $Co^{2+}$ , can be derived by combining formulae which express the mass action laws on each equilibrium reaction, the material conservation laws and the electric charge conservation laws in aqueous solution. Solving numerically using these combined equations, concentrations of various chemical species shown in Fig.4 were then calculated.

#### Comparison with Experiments

Calculated result showing the relation between pH value and Co concentration in the extraction process is shown in Fig.1 by the solid line. The equilibrium constant of extraction reaction  $K_{ext}$  is set to be  $1.41 \times 10^{-21} \text{ dm}^3/\text{mol}$ , which is 10 times larger than the value determined by Shibata and Nishimura (1975) for the case of dilute solution. Fairly good agreement with the data is obtained.

Fig.2 shows the calculated result on the variation of the degree of stripping and the crystallization with  $CO_2$  gas pressure. Two values of solubility product  $K_{sp}$ ,  $10^{-7}$  and  $10^{-6} (\text{mol}/\text{cm}^3)^2$ , are considered

in the calculation. For  $K_{sp} = 10^{-7} (\text{mol}/\text{dm}^3)^2$ , the calculated degree of stripping fits fairly well to the experimental result. However, it produces a considerable amount of degree of crystallization, which was not observed in the experiment. For  $K_{sp} = 10^{-6} (\text{mol}/\text{dm}^3)^2$ , the degree of crystallization is negligible which is compatible with experiment, though the calculated degree of stripping is somewhat lower than that of the experiment.

Fig.3 shows the calculated result on the variation of the degree of stripping and crystallization with initial Co concentration in organic phase. It should be noted that VA10 concentration must be more than 4 times as large as Co concentration, if extracted species of cobalt would be in the form of dimer in organic phase as was assumed in this work. Therefore 0.5 mol/dm<sup>3</sup> VA10 concentration in the present experiment may be insufficient for obtaining organic loading in the form of dimer for Co concentration above 0.125 mol/dm<sup>3</sup>. Co species with Co concentration above 0.125 mol/dm<sup>3</sup> in Fig. 3 would be extracted in the form of polymer which includes a trimer. Much more complicated analyses including a trimer, therefore, will be required for the stripping and crystallization in the region of higher Co concentration in Fig. 3. As the molecular formula of a trimer has not been known at present, these analyses have not been made in the present paper. Calculated degree of stripping for both  $K_{sp}=10^{-7}$  and  $10^{-6} (\text{mol}/\text{dm}^3)^2$  fit fairly well with the experimental results. Calculated degree of crystallization begins to emerge and becomes larger as initial Co concentration increases. The experimental result is more favorable for  $K_{sp}=10^{-6} (\text{mol}/\text{dm}^3)^2$ . It should be noted that the value of solubility products estimated in Figs.2 and 3 is larger than that reported in the literature, where the  $K_{sp} = 8.0 \times 10^{-13} (\text{mol}/\text{dm}^3)^2$ , suggesting that supersaturation occurs in the process of stripping/ crystallization under a high pressure CO<sub>2</sub> gas.

## CONCLUSIONS

This paper deals with extraction of cobalt with Versatic Acid 10 and stripping- crystallization experiment of cobalt under high pressure CO<sub>2</sub> gas. The main results obtained are as follows;

- 1) Extraction behavior can be predicted by a thermodynamical model by assuming extracted species as a dimer with the extraction equilibrium constant  $K_{ext}=1.41 \times 10^{-21} \text{ dm}^3/\text{mol}$ .
- 2) Stripping-crystallization experiments can be utilized into the thermodynamical model by assuming an equilibrium state under the high pressure CO<sub>2</sub> gas, with solubility product  $K_{sp}=10^{-7}$  or  $10^{-6} (\text{mol}/\text{dm}^3)^2$ .
- 3) It is suggested from the analysis of the stripping process that the solution under a high pressure CO<sub>2</sub> gas is in the state of supersaturation when precipitation of CoCO<sub>3</sub> occurs.

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## INVESTIGATION OF THE EXTRACTION KINETICS OF COBALT AND NICKEL WITH EXTRACTANT 5709

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### ABSTRACT

A modified constant interfacial cell was built and the kinetics of cobalt and nickel extraction with 5709 (Hexyl-Phosphonic Acid Mono-1-Methylheptyl Ester)-heptane system was studied. The parameters investigated include stirring speeds in aqueous and organic phase, interfacial area between two phases in the cell, operation temperature and compositions of the two phases.

The experimental data were treated by a thermodynamic method, and the process controlling regime of extraction kinetics is revealed as the mixed controlling regime. For cobalt at high pH value, the diffusion process is the dominant step, at lower pH value, the complex formation of cobalt is the dominant step. The determination of interfacial tension in these extraction systems and correlation of interfacial excess with extraction rate give evidence which support the proposal that the 1-2 complex formation of cobalt and nickel is the limiting step in the process of chemical reaction.

The apparent activation energy was obtained as 35.9 kJ/mol for cobalt and 36.1 kJ/mol for nickel, which gives an additional evidence for the mixed controlled regime of the cobalt and nickel extraction kinetics.

Based on the experimental results, mathematical models for the extraction kinetics of cobalt and nickel were developed.

### INTRODUCTION

This paper is an extension of the research on the cobalt extraction kinetics with Hexyl-Phosphonic Acid Mono-1-Methylheptyl Ester and is based on the previous work of Li Zhou and Zhou Yong-chuan (1989). The nickel extraction kinetics with 5709 was also previously reported by Li Zhou and She Gao-yao (1992). In contrast to the experimental conditions adopted in the previous work, a new redesigned constant interfacial cell and auxiliaries were constructed for this work. In the feed solution neither normal salt nor buffer reagent was present, and the feed solution flowed continuously to keep its composition constant.

Various technological parameters affecting the extraction kinetics of cobalt and nickel were studied. In addition, the interfacial adsorption characteristics of species were determined by measuring the interfacial tension in 5709-heptane- $\text{CoSO}_4$  (or  $\text{NiSO}_4$ ) and in the more complicated systems. Using a thermodynamic method, the activity of species instead of the concentration was introduced into the mathematic model to describe the extraction kinetics.

## EXPERIMENTAL

### Experimental system

Organic phase: 5709—heptane (5709 is the Chinese trademark of Heptyl—Phosphonic Acid Mono—1—Methylheptyl Ester, the abbreviation is HMHPA, its structure is as follows:

represented as HA in the following).

The delivered 5709 was purified by the method of copper salt crystallization and its purity was up to 99.4%. The heptane was analytically pure and was purified further by distillation.

Aqueous phase:  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  or  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (analytical pure)—deionized  $\text{H}_2\text{O}$ .

In the experiments on interfacial tension measurement, the aqueous solutions of cobalt and nickel were made up with deionized water.

### Equipment

The equipment for studying the extraction kinetics is an improved constant interfacial cell.

Figures 1, 2 show the outline of the improved constant interfacial cell and the experimental installation.

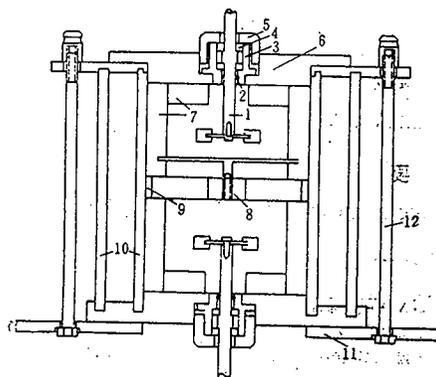


Figure 1 The improved constant interfacial cell

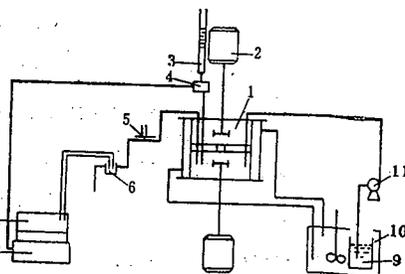


Figure 2 Outline of the experimental installation

The main improvements are as follows:

1. The bottom plates are installed in the constant interfacial cell in order to improve the hydrodynamics inside of the cell (Figure 1).
2. The gravitational leg is installed for keeping the position of interface between the two phases fixed (Figure 2).

The tensiometer CBVP—A3 made in Japan was used for the measurement of interfacial tension.

## EXPERIMENTAL RESULTS AND DATA TREATMENT

### 1. Extraction kinetics experiments

The extraction flux of cobalt or nickel is defined as follows:

$$\bar{J}_M = \frac{\bar{V}}{A} \cdot \frac{d\bar{c}}{dt} \quad (1)$$

where, subscript M represents cobalt or nickel,  $\bar{V}$ —the volume of organic phase in the constant interfacial cell, A—the interfacial area between the two phases.

The experimental results show that the extraction rate  $\bar{J}_M$  is almost proportional to the stirring speed N in aqueous phase, but the stirring speed in organic phase  $\bar{N}$  has almost no effect on  $\bar{J}_M$ . The experimental results also show that  $\bar{J}_M$  is proportional to the interfacial area A.

There is a linear relationship between  $\ln \bar{J}_M$  and  $1/T$ , where T is the temperature in K. The apparent activation energies were determined to be 35.9 kJ/mol for cobalt and 36.1 kJ/mol for nickel by the Arrhenius equation.

The experimental results show that  $\bar{J}_M$  increases as the metal concentration M, in aqueous phase increases, but there is no linear relationship between them as shown in Figs 3,4. Both the extraction flux of cobalt and nickel increases against the increasing of pH value, and there is a linear relationship for nickel, but it is nonlinear for cobalt. The relationship of 5709 concentration in organic phase,  $\bar{C}_{HA}$  with  $\bar{J}_M$  is nonlinear for cobalt but is linear for nickel.

The experimental data was treated by a thermodynamic method. For the aqueous phase, the Debye—Huckel and Pitzer's relations were adopted to compute the activity of cobalt and nickel ions under various experimental conditions, and the computer results are very similar. The activity coefficients of 5709 in organic phase were computed from Scatchard—Hilderbrand model.

The computation results obtained were very interesting. The  $\bar{J}_M$  values responds linearly with  $a_M$  and  $[\bar{a}_{(HA)_2}]^{1/2}$ . Obviously, these are very valuable for revealing the controlling regime of the extraction kinetics for cobalt and nickel.

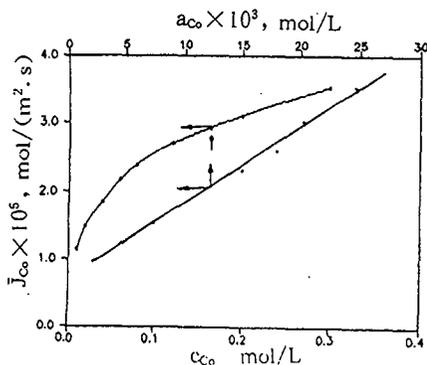


Figure 3  $\bar{J}_{Co}$  versus  $C_{Co}$  and  $a_{Co}$   
 Experimental conditions: pH=5.0,  
 $\bar{C}_{HA}=0.3438 \text{ mol/l}$ ,  $A=25.54 \times 10^{-4} \text{ m}^2$ ,  
 $N=150 \text{ min}^{-1}$ ,  $\bar{N}=120 \text{ min}^{-1}$ ,  $t=25.0^\circ \text{C}$

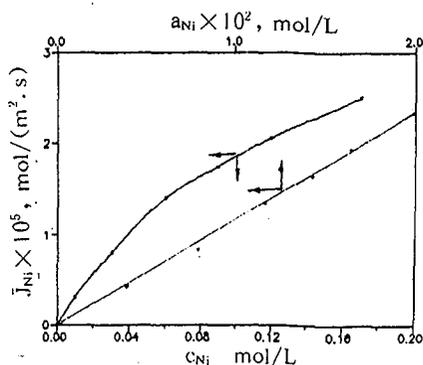


Figure 4  $\bar{J}_{Ni}$  versus  $C_{Ni}$  and  $a_{Ni}$   
 Experimental conditions: pH=6.0,  
 $C_{Ni}=0.17 \text{ mol/l}$ ,  $\bar{C}_{HA}=0.32 \text{ mol/l}$ ,  
 $N=\bar{N}=150 \text{ min}^{-1}$ ,  $A=36.9 \text{ cm}^2$ ,  $t=25.0^\circ \text{C}$

## 2. Determination of interfacial characteristics of species

In this paper the effect of one variable on the interfacial tension was studied while other variables were fixed.

The change of interfacial tension against increasing the 5709 concentrations in  $\text{H}_2\text{O}$  and 5709 in heptane system shows that 5709 is a strong surfactant. The same trends are observed in other systems. The interfacial tension data in  $\text{H}_2\text{O}$  and 5709 in heptane system was first treated by the

Szyszkowski isotherm (1992):

$$\gamma_{S_z} = \gamma_0 \left[ 1 - \text{Bln} \left( \frac{\bar{C}_{HA}}{A'} + 1 \right) \right] \quad (2)$$

where,  $A' = 6.65 \times 10^{-5}$ ,  $B = 8.94 \times 10^{-2}$ , and the average deviation of the computed values from the experimental values is 2.04%.

The derivative of  $\gamma_{S_z}$  with respect to  $\ln \bar{C}_{HA}$  is as follows:

$$\frac{\partial \gamma_{S_z}}{\partial \ln \bar{C}_{HA}} = -\frac{B \gamma_0 \bar{C}_{HA}}{\bar{C}_{HA}} + A' \quad (3)$$

The calculated results of  $\frac{\partial \gamma_{S_z}}{\partial \ln \bar{C}_{HA}}$  are tabulated in Table. 1.

TABLE 1

$\frac{\partial \gamma_{S_z}}{\partial \ln \bar{C}_{HA}}$  in H<sub>2</sub>O—5709 in heptane system

$\bar{C}_{HA}$ , mol/L	$\gamma$ , mN/m	$\frac{\partial \gamma_{S_z}}{\partial \ln \bar{C}_{HA}}$	n
$1 \times 10^{-1}$	14.0	-3.3704	1.1320
$1 \times 10^{-2}$	21.0	-3.3482	1.1245
$5 \times 10^{-3}$	28.7	-3.3265	1.1172
$1 \times 10^{-3}$	29.45	-3.1617	1.0619
$5 \times 10^{-4}$	33.15	-2.9774	1
$1 \times 10^{-4}$	36.15	/	/
0	37.7	/	/

where n is calculated by adopting  $\frac{\partial \gamma_{S_z}}{\partial \ln \bar{C}_{HA}} = -2.9774$  as the reference number.

Yu Qiang (1987), reported that in a similar extraction system (where the extractant is 2-Ethylhexyl-Phosphonic Acid Mono-2-Ethylhexyl Ester, and abbreviated by EHEHPA) it was found that for  $\bar{C}_{HA} < 0.125 \text{ mol/L}$ ,  $\frac{\partial \gamma_{S_z}}{\partial \ln \bar{C}_{HA}} = -2.506$ ; for  $\bar{C}_{HA} > 0.15 \text{ mol/L}$ ,  $\frac{\partial \gamma_{S_z}}{\partial \ln \bar{C}_{HA}} = -4.937$  where,  $n = 1.97$  was obtained, and a change of the adsorbed form at the interface was proposed.

From Table 1 it can be seen that the  $\frac{\partial \gamma_{S_z}}{\partial \ln \bar{C}_{HA}}$  is almost a constant, and  $n \approx 1$ , thus the adsorbed form of 5709 is monomolecular at the interface.

The other possible adsorbed form of 5709 is its ionic form  $A^-$ . The interfacial tensions in H<sub>2</sub>O + H<sub>2</sub>SO<sub>4</sub> (H<sub>2</sub>SO<sub>4</sub> is for regulating the pH value in aqueous phase) and 5709 in heptane system under various pH values were measured. The experimental results show that there is a linear relation ship between interfacial pressure,  $\pi$ , and  $\bar{C}_{HA}$  at a certain pH value, and in the experimental pH range, the lines are approximately coincident.

If HA and  $A^-$  are adsorbed at the interface simultaneously,

$$\Gamma \approx [HA_{ad}] + [A^-_{ad}], \text{ where, } \Gamma \text{ is interfacial excess.} \quad (4)$$

Substituting equation (4) into the Gibbs equation, gives:

$$[HA_{ad}] + [A^-_{ad}] = \frac{[HA]}{RT} \cdot \frac{\partial \pi}{\partial [HA]} \quad (5)$$

Substituting the following equations

$$K'_a = \frac{[H^+][A^-_{ad}]}{[HA_{ad}]}, \quad \text{and defining } m = \frac{\partial \pi}{\partial [HA]} \quad (6), (7)$$

into equation (5), and rearranging, gives;

$$m = RT \frac{[HA_{ad}]}{[HA]} \left(1 + \frac{K'_a}{[H^+]}\right) \quad (8)$$

Since  $m$  is independent of  $pH$ , and  $K'_a \rightarrow 0$ ,  $[H^+][A_{ad}] \rightarrow 0$ , but  $[H^+] \neq 0$ , thus  $[A_{ad}] \rightarrow 0$ , this means that  $A^-$  is not adsorbed at the interface. This interfacial tension measurements further proved that the extracts of cobalt and nickel showed positive adsorption at the interface, but  $H^+$ ,  $CO^{2+}$ ,  $Ni^{2+}$  were shown to have characteristics of negative adsorption.

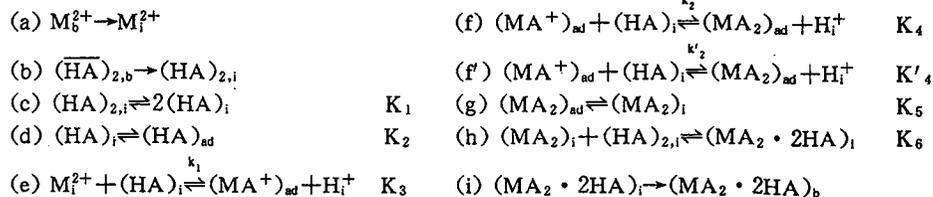
## ASSESSING THE CONTROLLING REGIME FOR THE EXTRACTION KINETICS OF COBALT AND NICKEL

### Preliminary view

From the experimental results it was observed that the extraction flux of cobalt and nickel were related to the stirring speed of the aqueous phase. The flux was also nearly proportional to the interfacial area between the two phases, and are related to the compositions of the two phases. Thus, it is concluded that the extraction kinetics are controlled by mixed controlling regime. The values of the apparent activation energy further present evidence for this controlling regime.

### Extraction mechanism

According to the experimental results the following steps are proposed:



and suppose that step (f) is the controlling step in the extraction chemical reaction process. then, the extraction reaction rate becomes;

$$\rho = k_2 K_3 (a_M)_i (a_{HA})_{ad} (\overline{a_{HA}})_i / (a_H)_i, \text{ where } \rho \text{ represents the extraction reaction rate.}$$

Considering  $(a_{HA})_{ad} = \text{constant}$  in the experimental range of  $(\overline{HA})$ , and introducing  $(a_M)_i = (a_M)_b - (\overline{J}_M/k_w)$ ,  $(a_{(\overline{HA})_2})_i = (a_{(\overline{HA})_2})_b$ ,  $(a_H)_i = (a_H)_b$ ,  $k_w = KN^{-1/2}$ , then:

$$\overline{J}_M = \frac{K' \cdot (a_M)_b [(a_{(\overline{HA})_2})_b]^{1/2} \cdot N^{1/2}}{K'' \cdot (a_H)_b \cdot N^{1/2} + [(a_{(\overline{HA})_2})_b]^{1/2}} \quad (9)$$

where,  $K'$   $K''$  were determined by Marquardt's method and for cobalt:  $K' = 1.43 \times 10^{-3}$ ,  $K'' = 2.55 \times 10^3$ , for nickel:  $K' = 9.43 \times 10^{-4}$ ,  $K'' = 3.82 \times 10^3$ .

Determination of interfacial tensions and the correlation of extraction reaction rate with interfacial excess, Symanowski and Prochaska (1988), offered additional evidence for the proposed mechanism.

## CONCLUSIONS

The extraction kinetics of cobalt and nickel with 5709 were studied using an improved Lewis Cell. The extraction kinetics of cobalt and nickel are controlled by mixed controlling regime, i. e., diffusion in aqueous phase and formation of complex of cobalt or nickel ions through an interfacial

chemical reaction. The pH value in the aqueous phase is an important factor in extraction kinetics. The apparent activation energies determined are  $E = 35.9 \text{ kJ/mol}$  for cobalt and  $36.1 \text{ kJ/mol}$  for nickel. These are the additional evidence for the controlling regime of the extraction kinetics for cobalt and nickel.

### NOMENCLATURE

A	sectional area between two phases ( $\text{m}^2$ )
A'	constant
a	activity (mol/L)
B	constant
c	concentration (mol/L)
K, K', K''	coefficients
$K_i$	equilibrium constants (i: 1-6)
$K'_a$	dissociation constant
$k_w$	subdividual mass transfer coefficient in aqueous phase (m/s)
N	stirring speed in aqueous phase (r/min)
$\bar{N}$	stirring speed in organic phase (r/min)
$\bar{J}_M$	extraction flux ( $\text{mol/m}^2 \cdot \text{s}$ )
n	ratio
T	temperature (K)
t	temperature ( $^{\circ}\text{C}$ )
$\pi$	interfacial pressure ( $\text{mN/m}$ ) ( $\pi = \gamma_0 - \gamma$ )
$\gamma$	interfacial tension ( $\text{mN/m}$ )
$\gamma_0$	interfacial tension with $\bar{C}_{HA} = 0$ in the organic phase ( $\text{mN/M}$ )
$\rho$	extraction reaction rate
$\Gamma$	interfacial excess ( $\text{mol/cm}^2$ )
Subscripts	
b	in bulk phase
i	at interface
ad	in adsorbed form

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## SOLVENT EXTRACTION OF TRIVALENT LANTHANIDES WITH CYANEX 302 FROM ACIDIC AQUEOUS CHLORIDE SOLUTIONS

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### ABSTRACT

The solvent extraction of trivalent lanthanides (except Pm) with Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid, hereafter abbreviated as HL) in heptane from acidic aqueous chloride solutions has been studied systematically. The effects of the equilibrium aqueous pH and extractant concentration on the extraction were observed. The separation of the lanthanides by Cyanex 302 and Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) has been contrasted. The extraction stoichiometry was studied with the method of slope analysis. The extraction of the lanthanides proceeds by a cation exchange reaction, which can be expressed as follows:  $\text{Ln}^{3+} + 2.5(\text{HL})_{2(aq)} \rightleftharpoons \text{LnL}(\text{HL}_2)_{2(aq)} + 3\text{H}^+$ . Purified Cyanex 302 (H(BTMPTP)) exhibited significantly lower extracting power for the lanthanides than Cyanex 302 used as received, and the Yb(III) extraction stoichiometry with purified Cyanex 302 was also studied, the extraction equilibrium constant was calculated. The IR and NMR spectra of the Yb(III) extracted complexes with purified Cyanex 302 were measured. The role of the different components of Cyanex 302 in the Sm(III) extraction have been discussed.

### INTRODUCTION

The extraction separation of the lanthanides with organophosphorus reagents such as di(2-ethylhexyl)phosphoric acid (HDEHP) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester has been studied extensively and applied in the hydrometallurgical process (Peppard, et al., 1957; Li, et al., 1980). Musikas, et al. (1983) found that americium(III) and europium(III) could be extracted fairly well with di(2-ethylhexyl)phosphorodithioic acid (HDEHPDT). Motomizu and Freiser (1985) explored the extraction behavior of lanthanides with di(2-ethylhexyl)phosphorodithioic acid, and found that ytterbium(III) and europium(III) could be extracted quite well with HDEHPDT, used as received. However, careful work led them to the finding that the results must be attributed to HDEHP impurities. More recently, Cyanex 302 has been made commercially available by Cyanamid Canada, Inc. It is the monothiosubstituted derive of Cyanex 272. The study of extraction with Cyanex 302 mainly focussed on the first row transition metals, and Cyanex 302 has shown fairly good behavior for the extraction separation of Zn(II), Fe(III), Co(II), and Ni(II) (Sole, et al., 1992; Tait, et al., 1993). So far the extraction and separation of lanthanides with Cyanex 302 has not been reported. The pKa of Cyanex 302 (5.63) decreases significantly below that of Cyanex 272 (6.37) by substituting the oxygen atom in the P=O group with a sulfur

atom, but the P-OH group remains. This led us to thinking it would possibly show favorable behavior in the extraction of the lanthanides. The results of preliminary experiments indicate that Cyanex 302 can extract lanthanides fairly well.

The extraction of the lanthanides with Cyanex 272 has been reported in previous work (Zhang, et al., 1994). This paper concentrates on the extraction separation properties of Cyanex 302 and compares them with those of Cyanex 272.

## EXPERIMENTAL

### Reagents

Cyanex 302 was kindly supplied by Cyanamid Canada, Inc. The extractant was purified by precipitation of the cobalt salt (Bart, et al., 1991). Cyanex 302 was used as received, except in the study of the extraction stoichiometry. The extractant was diluted with n-heptane of reagent grade. Stock solutions (pH3-5) of lanthanides were prepared from their chlorides. Other reagents were analytical grade.

### Extraction and analytical procedures

The extraction procedure was as described previously (Wang, et al., 1994). The pH values were measured by pH meter (Orion Model SA720). The aqueous concentrations of the lanthanides were determined spectrophotometrically (Shimadzu Model UV-365) by the Arsenazo III method. The metal ion concentration in the organic phase was obtained by difference.

### IR and NMR spectra measurements

IR spectra of organic extracts were determined on a BIO-RAD-7 IR Fourier spectrometer. NMR spectra were obtained using an NMR spectrometer, Varian Model Unity-400.  $^1\text{H}$ -NMR spectra were measured with tetramethyl silane as an internal reference and  $^{31}\text{P}$ -NMR spectra with 85% phosphoric acid as an external reference.

## RESULTS AND DISCUSSION

### Effect of equilibrium aqueous pH

The results shown in Figure 1 indicate that the distribution ratios (D) of the lanthanides increase with increasing pH with constant concentrations of extractant and metal ion. The extractability of the lanthanides increases with increasing atomic number or decreasing atomic radius in the order:  $\text{La}^{3+} < \text{Ce}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+} < \text{Eu}^{3+} < \text{Gd}^{3+} < \text{Tb}^{3+} < \text{Dy}^{3+} < \text{Ho}^{3+} < \text{Y}^{3+} < \text{Er}^{3+} < \text{Tm}^{3+} < \text{Yb}^{3+} < \text{Lu}^{3+}$ . The slopes of the log D versus pH plots (from Lu to Ho) are close to 3, whereas the slopes from Dy to La decrease with decreasing atomic number. This means that the extraction of these metals may exhibit some other reaction stoichiometry, which may be partly due to the presence of intermediate water-soluble complexes at higher aqueous pH.

The separation factors ( $\beta$ ) of lanthanide extraction with Cyanex 302 and 272 were calculated. It has been found that the average separation factor ( $\bar{\beta}_{x+1/2}$ ) (La-Lu, except for Y) for the adjacent lanthanides with Cyanex 302 is 2.95. This is smaller than that in the Cyanex 272-octane-chloride system ( $\bar{\beta}_{x+1/2}=3.6$ ) (La-Lu, except for Y) (Zhang, et al., 1993). However, the average separation factor of the adjacent heavy lanthanides (Gd-Lu) with Cyanex 302 was 3.42, i. e. higher than that in the Cyanex 272 system ( $\bar{\beta}_{x+1/2}=2.24$ , Gd-Lu). This means that the selectivity towards heavy lanthanides with Cyanex 302 is better than that with Cyanex 272.

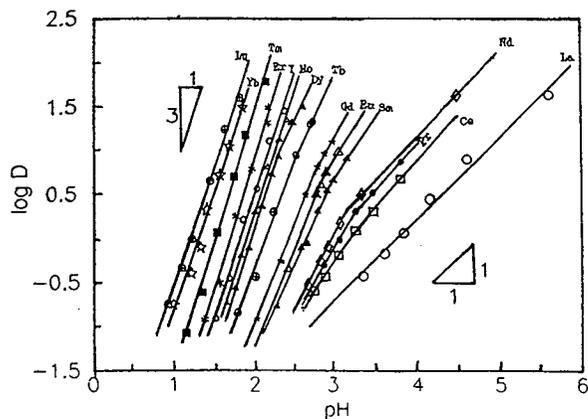


Figure 1. Effect of equilibrium aqueous pH on the extraction with raw Cyanex 302  
 $[\text{Cyanex 302}]_{(o)} = 5.58 \times 10^{-2} \text{ mol/L}$   
 $[\text{Ln}^{3+}] = 3.00 \times 10^{-4} \text{ mol/L}$   
 $[(\text{Na}, \text{H})] = 0.20 \text{ mol/L}$

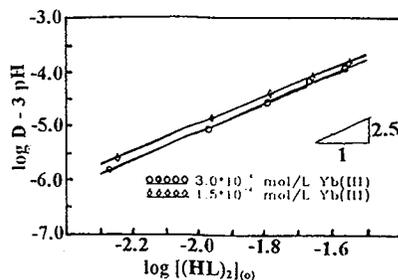
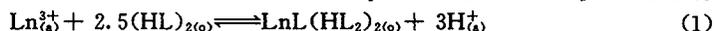


Figure 2. Effect of extractant concentration on the Yb(III) extraction  
 $\text{pH} = 1.78$   
 $[(\text{Na}, \text{H})] = 0.20 \text{ mol/L}$

#### Effect of extractant concentration on the Yb(III) extraction

The effect of the extractant concentration was shown in Figure 2. Cote and Bauer (1986) have reported that the monothiophosphoric acids are usually dimeric. Tait (1993) in his recent work assumed that Cyanex 302 is dimeric in solvents of lower polarity by the method of the vapour pressure osmometry. The slope of  $\log D - 3\text{pH}$  plotted vs.  $\log [(\text{HL})_2]_o$  is close to 2.5, whereas it can be inferred from the results shown in Figure 1 that three moles of hydrogen ions are released per mole of extracted metal ion such as Yb(III). Therefore, it can be assumed that the Yb(III) extraction with Cyanex 302 can be expressed as follows:



where subscripts (a) and (o) refer to the aqueous and organic phase, respectively.  $(\text{HL})_2$  refers to the dimer of Cyanex 302.

#### Extraction of lanthanides with purified Cyanex 302 (H(BTMPPTP))

The  $^{31}\text{P}$ -NMR spectra of Cyanex 302 and purified Cyanex 302 are shown in Figure 3. The

dominant feature of the Cyanex 302 spectrum (Fig. 3a) is the triplet centered at 94.2 ppm assigned to the species  $R_2PSOH$ . Phosphine oxide impurities were detected at 38.6 ppm and 34.3 ppm. In contrast to the  $^{31}P$ -NMR spectrum of purified Cyanex 302 (Fig. 3b), the triplet at 94.2 ppm and the peak at 63.4 ppm remained, whereas the peaks at 38.6 ppm and 34.3 ppm disappeared. This indicates that phosphine oxide impurities were removed from purified Cyanex 302. Compared with raw Cyanex 302, purified Cyanex 302 exhibits significantly poorer extracting power for the lanthanides (see Figure 4). Cyanex 302 can extract lanthanides such as  $Yb(III)$ ,  $Sm(III)$  much more strongly than  $H[BTMPTP]$  under similar conditions. A similar result was obtained by Freiser, et al. (1985), who reported the extraction of  $Eu(III)$  with di(2-ethylhexyl)dithiophosphoric acid (HDEHDTP) and attributed the result to HDEHP contamination. We discuss below the role of different components of Cyanex 302 in order to understand why purified Cyanex 302 exhibits significantly lower extracting power to lanthanides than raw Cyanex 302.

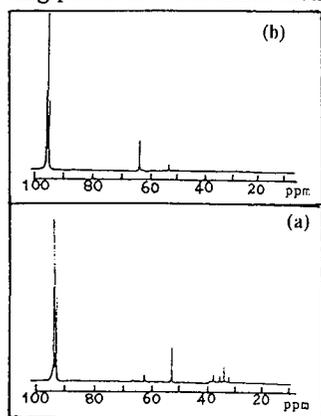


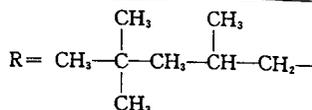
Figure 3.  $^{31}P$ -NMR spectra of raw Cyanex 302 and purified Cyanex 302

(a). raw Cyanex 302

(b). purified Cyanex 302

TABLE 1  
Composition of raw Cyanex 302  
(Sole, et al., 1992)

Extractant	Species	Concentration (%)
Cyanex 302	$R_2PSOH$	78~80
	$R_3PO$	10~12
	$R_2PO_2H$	2~3
	$R_2PS_2H$	2
	Unknowns	~8



According to the composition of Cyanex 302 reported by Sole, et al. (1992) (see Table 1), n-heptane solutions of purified Cyanex 272 ( $H[BTMPP]$ ), tri-n-octylphosphine oxide, purified Cyanex 302 ( $H[BTMPTP]$ ), and mixed solutions of the above three components were prepared. A series of distribution experiments was carried out and the results are shown in Figure 5. It has been found that TOPO extracts  $Sm(III)$  weakly in the pH studied.  $H[BTMPP]$  has a significantly lower extracting power than raw Cyanex 302 and is close to purified Cyanex 302. The distribution ratio of  $Sm(III)$  increases slightly when TOPO is added to the solution of purified Cyanex 302. However, the extractability of  $Sm(III)$  is still significantly weaker than that with raw Cyanex 302 when TOPO and  $H[BTMPP]$  are added to the solution of purified Cyanex 302. The result indicates that the significant extraction of lanthanides with raw Cyanex 302 is not due to the presence of  $H[BTMPP]$ . This is to be studied extensively in further work.

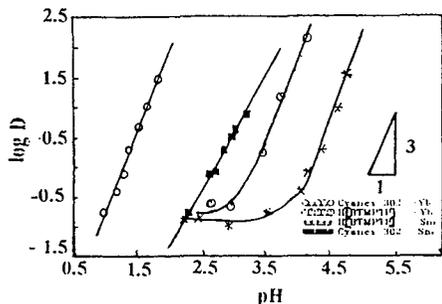


Figure 4. Extraction of Yb(III) and Sm(III) with raw and purified Cyanex 302 (H(BTMPTP))  
 $[Cyanex\ 302]_{(o)} = 5.58 \times 10^{-2}$  mol/L  
 $[H(BTMPTP)]_{(o)} = 5.72 \times 10^{-2}$  mol/L  
 $[Sm^{3+}] = [Yb^{3+}] = 3.0 \times 10^{-4}$  mol/L

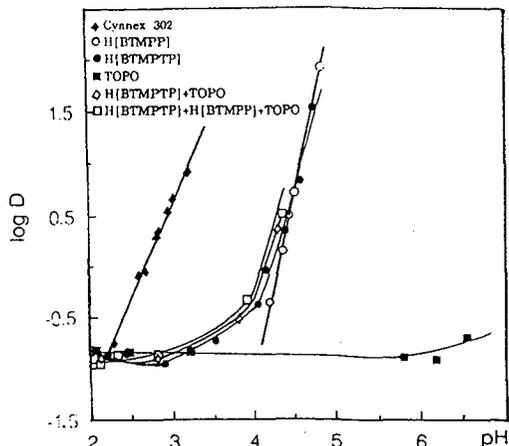
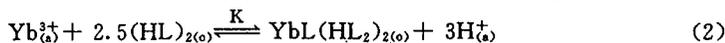


Figure 5. Role of different components of Cyanex 302 on the Sm(III) extraction  
 $[Cyanex\ 302]_{(o)} = 5.58 \times 10^{-2}$  mol/L  
 $[H(BTMPTP)]_{(o)} = 5.61 \times 10^{-2}$  mol/L  
 $[H(BTMPP)]_{(o)} = 8.5 \times 10^{-3}$  mol/L  
 $[TOPO]_{(o)} = 6.0 \times 10^{-3}$  mol/L  
 $[Sm^{3+}] = 3.0 \times 10^{-4}$  mol/L

#### Effect of extractant concentration on the Yb(III) extraction with purified Cyanex 302

The result shows that the slope of  $\log D$ - $3pH$  plots against  $\log [(HL)_2]_{(o)}$  for Yb(III) is about 2.5 and the slope of  $\log D$  plots vs.  $pH$  for Yb(III) is close to 3 (Fig. 4). Therefore, the extraction of Yb(III) can be represented by the following equation:



$K$  represents the extraction equilibrium constant, it was calculated to be  $\log K = -6.27 \pm 0.18$ , independent of the extractant concentration.

#### IR and NMR spectra for Yb(III) extract with H(BTMPTP)

The saturated extract of Yb(III) with H(BTMPTP) in *n*-heptane was examined by IR and NMR. The IR spectrum of H(BTMPTP) shows a P=S stretching band at  $605.8\text{ cm}^{-1}$ ; a P-O stretching band at  $917.0\text{ cm}^{-1}$  and P-O-H stretching and bending bands at  $2950$ ,  $2250$  and  $1650\text{ cm}^{-1}$ . In the spectrum of the extract, the P-O-H stretching and bending bands all disappear, the P-O absorption band shifts to the higher frequency  $1021\text{ cm}^{-1}$  and the P=S stretching band shifts to the lower frequency  $590\text{ cm}^{-1}$ . Therefore, the IR results indicate that the hydroxy proton of the P-OH group is substituted by Yb(III) in the extraction with H(BTMPTP). In contrast to the  $^{31}\text{P}$ -NMR spectrum of H(BTMPTP) which centred at  $95.615\text{ ppm}$ , the  $^{31}\text{P}$ -NMR spectrum of the Yb(III) extract shifts to a higher field at  $36.557\text{ ppm}$  and becomes wide. Obviously, the paramagnetic function of Yb(III) decreases the relaxation time of the phosphorus atom and generates a local field. These results proved that

the hydroxy proton of P-OH group was substituted by Yb(III). The <sup>1</sup>H-NMR spectrum for H(BTMPPTP) shows hydroxy proton peak at 8.02 ppm. The hydroxy proton peak in the Yb(III) extracts disappeared. Therefore, the results of NMR spectra are consistent with those of IR.

### CONCLUSION

In contrast with Cyanex 272, Cyanex 302 exhibited favourable behavior in the extraction separation of heavy lanthanides (Gd-Lu). Purified Cyanex 302 extracted lanthanides less efficiently than raw Cyanex 302. This cannot be ascribed to the presence of H(BTMPP) and must be studied extensively in further work.

### ACKNOWLEDGEMENTS

The authors wish to thank Dr. W. A. Rickelton of Cyanamid Canada, Inc., for samples of the Cyanex extractants. This work was supported by the National Program "The Basic Research of Rare Earth" of China.

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## A CONSTANT INTERFACIAL CELL WITH LAMINAR FLOW

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### ABSTRACT

A technique had been developed to study mass transfer and interfacial reactions in two phase systems. This constant interfacial area cell with laminar flow was made into a cubic structure. The two fluids were continuously recycled and mixed. The concentration of each liquid can be monitored by two different methods. This kind of structure made both flows near the interface parallel to the interface. The interface was smooth and steady. The mass transfer rate could be judged by the linear velocity of the flows. The technique can be used for the analysis of the controlling step in both phases. A preliminary hydrodynamics and mass transfer study using the cell is presented, which ensures the distinction between a diffusion controlled process and a chemical reaction controlled one. A simplified mass transfer equation was derived.

$$N^* = 0.5303D^{\frac{1}{2}} \cdot (C_i - C) \cdot \left(\frac{V}{B}\right)^{\frac{1}{2}}$$

### INTRODUCTION

Mass transfer and kinetics relate not only to the design of a reactor with two phases (such as a mixture-settler, extraction tower, mixture reactor) but also to the knowledge of the mechanism of the two phase reaction. In order to solve these problems, researchers in this field have mainly developed several kinds of techniques, for example, the moving drop method, the growing drop method, the short-time phase contacting method, the LLJR method, and the constant interfacial method (Lewis cell) without a membrane or with a membrane or with a grid. (Danesi P. R. and Chiarizia R., 1980) It was obvious, from the substantial reports in recent years, that extraction mass transfer and chemical reaction kinetics studies in two phases mainly employed a constant interfacial cell. Some different developments have been made on the cell. On the basis of the reports, it was known that the hydrodynamics in the cell was still poorly defined and many developments were made to improve the stability of the interface. Because of the restrictions of a round structure of the cell, four drawbacks resulted. The first one was that the stirring of the upper phase and the lower one at the same rate produced different Reynolds numbers in each compartment. The second one was that the stirrers pushed the fluids against the interface directly, which resulted in an unsteady interface. The third one was that the change of the stirrers' size, shape and level could produce different rate curves judged by the stirring speed, and the worse was that the diffusion film near the interface did not change or changed very little when the stirring speed increased, which led to a wrong result. The last one was that the velocity of the flow changed along the direction of the diameter near the interface, and that made the analysis of the process difficult.

In this work, a new apparatus and experimental technique are described in detail. The cell was made into a cubic shape, and the linear velocity of flows was employed to judge the mass transfer and

chemical reaction rate. The interface was stable as the result of no flow towards the interface, and the operation was carried out under laminar flow. The diffusion theory and hydrodynamics were employed to analyze the cell.

### APPARATUS

Figure 1 shows a schematic diagram of the apparatus. Stirrers 1 and 2 mixed and pushed the lighter phase and the heavier phase in each compartment, respectively. Their maximum rotation speed was limited such that the interface was steady. Flow deflectors 1 and 2 made the lighter phase and the heavier phase circulate in each chamber and the flow near the interface was laminar, respectively. The interfacial plate was a rectangle plate with a rectangle hole at the center of it. The thickness of the plate was 2 mm. The distance from the interface to the flow deflectors was less than 6 mm. Samples of the heavier phase and the lighter phase were drawn from sampling holes 1 and 2, respectively.

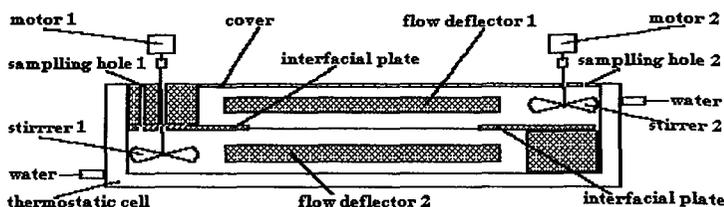


Fig. 1 The schematic diagram of the apparatus

### THEORY

The analysis of the cell using hydrodynamic and diffusion theory is carried out below.

#### Prerequisites

The following prerequisites were needed in solving the equations given below.

(1) isothermal operation; (2) constant densities; (3) constant viscosities; (4) constant diffusivities; (5) negligible diffusion along the interfacial plate direction; (6) steady state operation; (7) negligible flow in the direction along the Y and Z axes; (8) the flows near the interface are completely relaxed (negligible stagnant flow near the edge of the interface plate).

#### Hydrodynamics

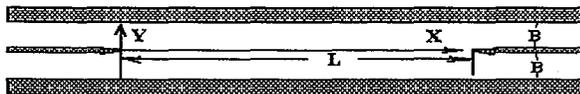


Fig. 2 The coordinates of the cell

Figure 2 shows the coordinates of the cell. According to the conditions above, the Navier-Stokes equations can be reduced to

$$\frac{dp}{dx} = \mu \frac{d^2 u_x}{dy^2} \quad (1)$$

Provided an infinitely thin plate is at the interface, when  $V_i$  is constant. Thus the forces acting on both faces of the plate are equal.

$$\mu^a \frac{dV^a}{dy} = \mu^o \frac{dV^o}{dy} \quad (2)$$

From equations (1), (2), the interfacial velocity is derived.

$$V_i = \frac{3(\mu^a V^a + \mu^o V^o)}{2(\mu^a + \mu^o)} \quad (3)$$

The organic phase velocity function is derived

$$y \geq 0; \quad V^o = \left( \frac{3y^2}{B^2} - \frac{4y}{B} + 1 \right) V_i - \left( \frac{6y^2}{B^2} - \frac{6y}{B} \right) \bar{V}^o \quad (4)$$

The aqueous phase velocity function is derived

$$y \leq 0; \quad V^a = \left( \frac{3y^2}{B^2} + \frac{4y}{B} + 1 \right) V_i - \left( \frac{6y^2}{B^2} + \frac{6y}{B} \right) \bar{V}^a \quad (5)$$

### Mass Transfer

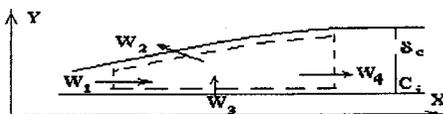


Fig. 3 The unit of concentration boundary

By assuming that a concentration boundary layer provides the main resistance to the mass transfer existing at the interface, the conservation equations below can be derived. Figure 3 is a unit in the concentration boundary layer with length equal to 1, width equal to  $dx$ , and height equal to  $\delta_c$ .

$$W_1 = \int_0^{\delta_c} C \cdot V \cdot 1 \cdot dy \quad (6)$$

$$W_2 = C_b \left[ \frac{\partial}{\partial x} \int_0^{\delta_c} V \cdot 1 \cdot dy \right] dx \quad (7)$$

$$W_3 = -D_{AB} \left( \frac{\partial C}{\partial y} \right)_{y=0} \cdot 1 \cdot dx \quad (8)$$

$$W_4 = \int_0^{\delta_c} C \cdot V \cdot 1 \cdot dy + \frac{\partial}{\partial x} \left[ \int_0^{\delta_c} C \cdot V \cdot 1 \cdot dy \right] dx \quad (9)$$

$$W_4 = W_1 + W_2 + W_3 \quad (10)$$

Then equation 11 was derived

$$\frac{d}{dx} \int_0^{\delta_c} (C_0 - C) \cdot V \cdot dx = D \cdot \left( \frac{\partial C}{\partial y} \right)_{y=0} \quad (11)$$

For a simple solution of the mass transfer equation, another assumption was made. We postulated that the concentration distribution is given by equation (12).

$$C - C_i = a + by + cy^2 + dy^3 \quad (12)$$

And the boundary prerequisites below are satisfied

$$\begin{aligned} \text{when } Y=0; \quad C-C_i=0, \quad \frac{\partial^2}{\partial y^2}(C-C_i)=0 \\ \text{when } Y=\delta; \quad C-C_i=C_b-C_i, \quad \frac{\partial}{\partial y}(C-C_i)=0 \end{aligned}$$

From equation (12) and the boundary prerequisites, equation (13) was derived.

$$\left(\frac{dc}{dy}\right)_{y=0} = \frac{3(C_b - C_i)}{2\delta_c} \quad (13)$$

From equations (4), (11)~(13), an equation involving the thickness of the diffusion film and the diffusivities was derived.

$$\frac{3V_i - 6V_b^o}{32B^2} \delta_c^4 - \frac{4V_i - 6V_b^o}{15B} \delta_c^3 + \frac{3}{16} \delta_c^2 - \frac{3}{2} D \cdot A = 0 \quad (14)$$

$A$  is the length of the contacting interface,  $B$  is the distance from the interfacial plate to the flow deflectors.  $V_b^o$  is the organic phase flow velocity.

The mass transfer equation is

$$N = -D \left(\frac{\partial C}{\partial y}\right)_{y=0} = -\frac{3}{2} D \frac{C_b - C_i}{\delta_c} \quad (15)$$

In order to understand the relationship between the extraction rate and the velocity of flows in the diffusion controlled step, a negligible velocity change of flows in the  $Y$  axial direction was proposed. And a typical mass transfer equation is derived.

$$N^* = 0.5303D^{\frac{1}{2}} \cdot (C_i - C) \cdot \left(\frac{V}{B}\right)^{\frac{1}{2}} \quad (16)$$

Equation (16) is similar to that which was derived using the LLJR method (Sciven I. E. and Pigford R. L., 1959). From equation (16), it is known that the diffusion controlled step between the two phase mass transfer takes place when the extraction rate has a direct ratio to the square root of the mean velocity of the flow.

## EXPERIMENTAL

The equipment used here was made and designed by ourselves. The distances from the interface to the flow deflector plates were 6 mm. It was easy that the flows become turbulence because of the large distances. In the experiment the velocity of the flows ranged from 1.7cm/s to 7.5cm/s. The interface area was 3.5×6.0 cm<sup>2</sup>. The shortest contacting time between the two phase was 0.53s. The interface obviously became unsteady when the velocity of the flows exceeded 8cm/s, or the direction of the two phases was opposite in a small velocity of flows. The test was carried out in the same direction of the flows. The volume of organic phase and aqueous phase was 94 ml (not including the sample volume). The volume of the phase was very important, and it was determined through the extraction rate, the interfacial area per unit volume ( $S/V$ ), the lowest limit of the analysis, and the sampling interval. The larger  $S/V$  value, the shorter was the interval of sampling, and the smaller was the volume of the two phases. Usually, a large  $S/V$  value is expected. The range of the  $S/V$  value related to the structure of the cell and the characteristics of the two phase (such as the viscosities of the two phase, the densities of the the two phase and the strength of the interfacial film). On other hand, the limitation to the  $V$  (volume of the phases) was the cost of the chemicals used in the test. A low consumption of chemicals with more test results is expected, but the operation of the cell becomes worse when the volume of the phases becomes too small. For example, sampling and sample mixing could disturb the interface when the volume of the phases is too small when a sample

consuming method is employed. Therefore, many factors should be thought about when the structural parameters are determined.

The viscosities of the two phase used in the test were measured with a Ubbelohde viscosity meter. The  $\text{ErCl}_3$  was made from  $\text{Er}_2\text{O}_3$  with purity 99.99%. The 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH/EHP) was purified by the published method. (Kamatsu Y., and Freiser H., 1989) The kerosene was distilled from 175°C to 230°C using sulfonated kerosene as a raw oil. The concentration of the  $\text{Er}^{3+}$  in aqueous phase was analyzed by EDTA titration.

## RESULTS AND DISCUSSION

There are three possibilities to control the extraction mass transfer rate. They are a homogeneous chemical reaction controlled step, an interfacial chemical reaction controlled step, and a diffusion controlled step. These three control steps relate to the volume of the phases, the area of the interface, and the velocity of the flows near the interface. This relationship can be used to distinguish the control step. In the control step of a homogeneous chemical reaction, the extraction rate only relates to the volume of the phase. But the Reynolds number changes, in other words, the thickness of the diffusion film changes in a diffusion controlled step, in a round cell, when the volume of the phase changes. Therefore, the extraction rate changes with the change of the volume, and a wrong result which is believed to be a homogeneous reaction controlled step can result. In the control step of an interfacial chemical reaction, the extraction rate only relates to the area of the interface. But the tangential velocity of the flows near the interface changes in the direction of the diameter in a round cell, and which makes the thickness of the diffusion film change in the direction of the diameter. Therefore, a different extraction rate is obtained after the area of the interface is switched because of the mean film thickness change, and a wrong result which is believed to be a chemical reaction controlled step can result. In the control step of a diffusion the extraction rate only relates to the velocity of the flows near the interface. But, sometimes, the tangential velocity of the flow near the interface does not change or changes in a non-linear fashion with the rotational speed of the stirrers. Then, a wrong result which is believed to be a chemical reaction controlled step is produced. Because of the differences of the structure of the stirrers, the size of the stirrers, the level of the stirrers and the structure of the cell, the tangential velocity of the flows near the interface does change even when the rotational speed of the stirrers does not change. Then, a different extraction rate dependence on the rotational speed of the stirrers is produced. To employ the extraction rate dependence on the mean velocity of the flows near the interface can eliminate the differences between different runs and even different cells. The cubic constant interfacial cell employed laminar flows near the interface and eliminated all the above disadvantages. The interface was steady, and the hydrodynamics was well defined.

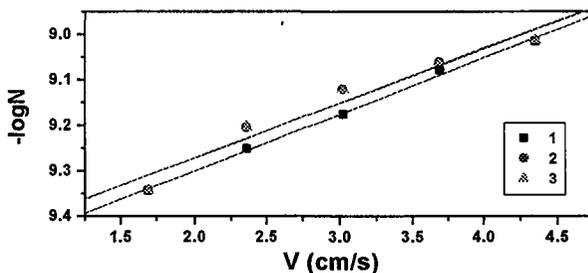


Fig. 4 The effect on the extraction rate of the flow velocity

The control step in this system was shown to be the diffusion process which was the key step. During the test, the evidence of interfacially active material could be found on the interface. At the beginning of the test, the interface looked bright under inclined light, and then it gradually became dim. According to the reports, (Hughes M. A., 1978; Aizheng Ma 1988) the unsaturated lanthanide complexes can form a sticky, soft and wax like material, and its copper compound can exist at the interface between the two phases. Therefore, it was obvious that the unsaturated erbium complex compound could form and exist at the interface, and resisted mass transfer.

Fig. 4 shows the effect on the extraction rate changes in the two phase flow rate. The extractant is HEH/EHP and the extracted ion  $\text{Er}^{3+}$ . Line 1 is the result from the test, line 2 is the result from equation 4 with the condition that  $D$  and  $C-C_i$  are unchanged, and line 3 is the result from equations (3), (14) and (15) with the same condition as line 2. It is known that  $D$  and  $C-C_i$  have no effect on the shape of the curve from equation (16), and it is known that  $D$  has little effect on the shape of the curve from equations (3), (14) and (15). Line 1, 2 and 3 are approximately linear with respect to the diffusion control process. Therefore, equation (16) is adopted as the simplified equation for the diffusion control process.

### ACKNOWLEDGMENTS

The authors gratefully acknowledge the support provided for this work by the National Science Committee on "The Basic Research of Rare Earth Science".

### NOMENCLATURE

B: The distance between flow deflectors and the interface (m).

C: Concentration ( $\text{mol/dm}^3$ ).

L: The interfacial length along the direction of flows (m).

N: Mass transfer rate ( $\text{mol/s cm}^2$ ).

V: Mean linear velocity of the phase flow ( $\text{cm/s}$ ).

W: Mass transfer speed ( $\text{mol/s}$ ).

Superscript

o: Organic phase.

a: Aqueous phase.

Subscript

i: Interface.

b: Bulk phase.

c: Concentration.

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## SIMULTANEOUS CORRELATION OF LIQUID-LIQUID EQUILIBRIA AND LIQUID DENSITIES WITH AN EQUATION OF STATE

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### ABSTRACT

Liquid-liquid equilibria and liquid densities for three binary systems made of methanol with n-hexane, cyclohexane, or n-heptane were simultaneously correlated with an equation of state (EOS). The EOS successfully gave satisfactory correlation results on solubility and liquid density behaviors; furthermore good prediction results on vapor-liquid and vapor-liquid-liquid equilibria.

### INTRODUCTION

Liquid-liquid equilibria and liquid densities of fluid mixtures are required in the design and operation of extraction equipments.

In general, conventionally, liquid-liquid equilibria are correlated with activity coefficient equations. Anderko *et al.* (1989, 1990) proposed a new EOS, and successfully applied it to liquid-liquid, solid-liquid, and vapor-liquid equilibrium behaviors of mixtures.

In the previous study (Kato *et al.*, 1992), liquid-liquid equilibria and liquid densities were measured for three binary systems made of methanol with n-hexane, cyclohexane, or n-heptane. The experimental liquid-liquid equilibrium and liquid density data obtained were simultaneously correlated with an EOS, using five temperature-independent and two temperature-dependent binary interaction parameters. The authors (Yoshikawa *et al.*, 1994) previously measured the solubility and liquid density behavior for binary systems of 2,2,4-trimethylpentane with methanol or nitroethane. The experimental solubility and liquid density data obtained were simultaneously correlated with an EOS, using three temperature-independent binary interaction parameters.

In the present study, liquid-liquid equilibria and liquid densities previously measured (Kato *et al.*, 1992) for the three binary systems made of methanol with n-hexane, cyclohexane, or n-heptane were simultaneously correlated with the pseudocubic EOS previously proposed (Kato *et al.*, 1986, 1988), using three temperature-independent binary interaction parameters to keep the simplicity. The EOS furthermore gave satisfactory prediction results on vapor-liquid and vapor-liquid-liquid equilibria.

### CORRELATIONS

The liquid-liquid equilibria and liquid densities were correlated with the following pseudocubic EOS previously proposed (Kato *et al.*, 1986, 1988), which introduced an apparent volume to the van der Waals equation. Combining a cubic EOS for the apparent volume and a quadratic relation between the actual volume and apparent volume, the pseudocubic equation was obtained. Given temperature and pressure, the EOS has at most three real roots for the volume. The largest and smallest volumes correspond to the vapor and liquid phases, respectively. The distinction between vapor and liquid phases is as easy as that with the conventional cubic EOS. The EOS is therefore called a pseudocubic EOS.

The pseudocubic EOS strictly satisfies the critical point requirements.

$$P = \frac{RT}{V^* - b} - \frac{a}{V^{*2}} \quad (1)$$

$$V^* = \frac{(V - \varepsilon b)(V + \sigma b)}{V} \quad (2)$$

where,

$$\varepsilon = (1 - \theta)(\xi - 2), \quad \sigma = (1 - \theta)(\xi + 2) \quad (3)$$

$$\xi = \sqrt{(4 - \theta)/(1 - \theta)} \quad (4)$$

$$\theta = Z_c / Z_{cs}, \quad Z_{cs} = 3/8 \quad (5)$$

The temperature dependencies of the parameters "a" and "b" were introduced to expand the applicable temperature range of the EOS.

$$a = K_a a_c, \quad b = K_b b_c \quad (6)$$

where,

$$a_c = \Omega_a \frac{(RT_c)^2}{P_c}, \quad b_c = \Omega_b \frac{RT_c}{P_c} \quad (7)$$

$$\Omega_a = 27/64, \quad \Omega_b = 1/8 \quad (8)$$

in which,  $K_a$  and  $K_b$  denote temperature correction factors, and the subscript "c" denotes the values at the critical temperature.

The following empirical temperature dependencies of the two correction factors were introduced in this study:

$$\ln K_a = S_a (1 - \sqrt{T_r}), \quad \ln K_b = S_b (1 - \sqrt{T_r}) \quad (9)$$

where,

$$S_a = \frac{\ln K_{a0}}{1 - \sqrt{T_{r0}}}, \quad S_b = \frac{\ln K_{b0}}{1 - \sqrt{T_{r0}}} \quad (10)$$

In these equations,  $T_r$  represents the reduced temperature and the subscript zero denotes the value at 298.15K. The values of  $K_{a0}$  and  $K_{b0}$  were determined from the saturated vapor pressure obtained from the data book of Boublík *et al.* (1984) and experimental liquid density of the pure substances at 298.15K. Values of these correction parameters are listed in TABLE 1. In the present calculations, the critical values of methanol, n-hexane, cyclohexane, and n-heptane were obtained from the works of Reid *et al.* (1977).

The following mixing rules were used in the present study, similar to the previous study (Yoshikawa *et al.*, 1994).

$$a = \sum_i \sum_j \sum_k y_i y_j y_k a_{ijk} \quad (11)$$

$$b = \sum_i \sum_j y_i y_j b_{ij} \quad (12)$$

$$\theta = \sum_i \sum_j y_i y_j \theta_{ij} \quad (13)$$

The parameters  $a_{112}$ ,  $a_{122}$ ,  $b_{12}$ , and  $\theta_{12}$  of unlike molecules are expressed by

$$a_{112} = (1 - k_{112}) a_1^{2\beta} a_2^{1-\beta} \quad (14)$$

$$a_{122} = (1 - k_{122}) a_1^{1-\beta} a_2^{2\beta} \quad (15)$$

$$b_{12} = (b_1 + b_2)/2 \quad (16)$$

$$\theta_{12} = (1 - c_{12})(\theta_1 + \theta_2)/2 \quad (17)$$

where,  $k_{112}$ ,  $k_{122}$ , and  $c_{12}$  denote the binary interaction parameters.

The interaction parameters,  $k_{112}$ ,  $k_{122}$ , and  $c_{12}$ , were treated as independent on temperature in the present study, to keep the simplicity. In the liquid-liquid equilibrium calculations, the fugacities of both phases were calculated from the EOS. TABLE 2 gives the binary interaction parameters obtained and the correlation accuracy on liquid densities.

In Figures 1 to 3, the continuing lines indicate the calculation results of solubility curves with the EOS for three binary systems, methanol-n-hexane, methanol-cyclohexane, and methanol-n-heptane, respectively.

The continuing lines in Figure 4 show the calculation results of the liquid densities for the methanol-n-heptane system at 298.15K, giving satisfactory agreement with the experimental values. The broken lines in Figure 4 give the ones calculated by the EOS in the two liquid phase separation regions.

Figures 5 and 6 show the vapor-liquid equilibrium composition curves for methanol-cyclohexane system at 323.15K and methanol-n-heptane system at 298.15K, respectively.

**TABLE 1**  
Critical properties and correction parameters for pure components

Materials	$T_c$ , K	$P_c$ , atm	$V_c$ , cm <sup>3</sup> ·mol <sup>-1</sup>	$K_{a0}$	$S_a$	$K_{b0}$	$S_b$
Methanol	512.6 <sup>a</sup>	79.9 <sup>a</sup>	118.0 <sup>a</sup>	2.0202	2.9628	0.9786	-0.0911
n-Hexane	507.4 <sup>a</sup>	29.3 <sup>a</sup>	370.0 <sup>a</sup>	1.6451	2.1324	0.9813	-0.0809
Cyclohexane	553.4 <sup>a</sup>	40.2 <sup>a</sup>	308.0 <sup>a</sup>	1.6320	1.8414	0.9800	-0.0760
n-Heptane	540.2 <sup>a</sup>	27.0 <sup>a</sup>	432.0 <sup>a</sup>	1.7440	2.1634	0.9554	-0.1775

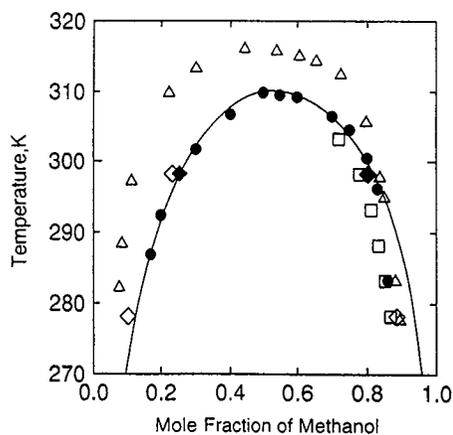
<sup>a</sup> From Reid *et al.* (1977).

**TABLE 2**  
Parameters obtained in mixing rules

Systems	$k_{112}$	$k_{122}$	$c_{12}$	$ \Delta\rho_{L,av} $
I	-0.02087	0.07180	-0.08705	5.4
II	0.04143	0.10763	-0.11031	3.5
III	-0.01583	0.07747	-0.10065	4.9

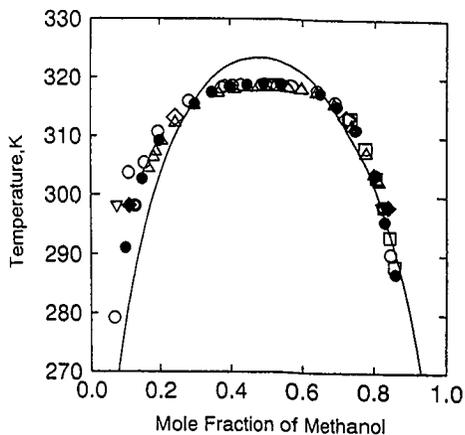
I : Methanol-n-Hexane, II : Methanol-Cyclohexane, III : Methanol-n-Heptane.

$|\Delta\rho_{L,av}| : \sum |\rho_{L,calc} - \rho_{L,exp}|/I$ , [kg·m<sup>-3</sup>], I : Number of data points.



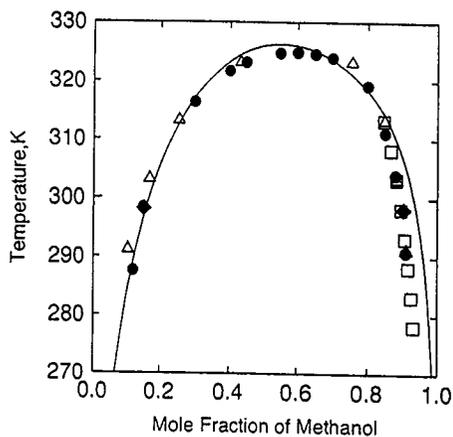
●, ◆:Kato *et al.*(1992), △:Rothmund(1898), □:Kiser *et al.*(1961), ◇:Radice *et al.*(1975), —:Calculated by EOS

Fig.1 Solubility Curve for Methanol-n-Hexane System



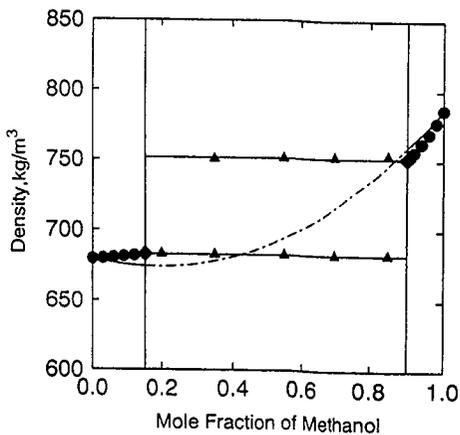
●, ◆:Kato *et al.*(1992), ○:Jones *et al.*(1930), △:Eckfeldt *et al.*(1943), □:Kiser *et al.*(1961), ◇:Sergeeva *et al.*(1969), ▽:Sergeeva *et al.*(1971), ⊙:Takeuchi *et al.*(1975), —:Calculated by EOS

Fig.2 Solubility Curve for Methanol-Cyclohexane System



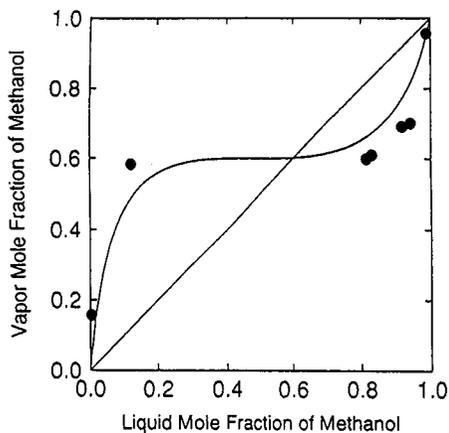
●, ◆:Kato *et al.*(1992), △:Tagliavini *et al.*(1958), □:Kiser *et al.*(1961), —:Calculated by EOS

Fig.3 Solubility Curve for Methanol-n-Heptane System



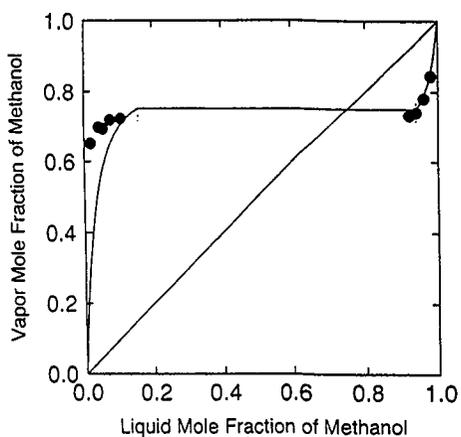
●, ▲, ◆:Kato *et al.*(1992), —:Calculated by EOS

Fig.4 Liquid Densities for Methanol-n-Heptane System at 298.15K



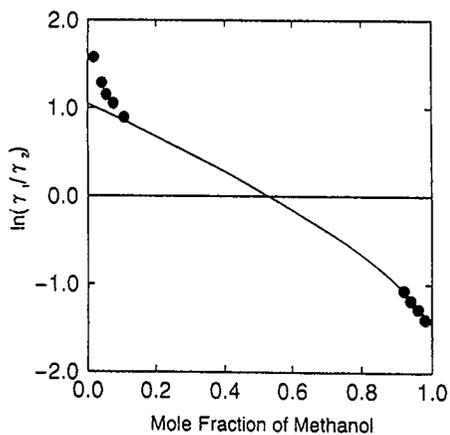
●:Strubl *et al.*(1970), —:Calculated by EOS

Fig.5 Vapor-Liquid Equilibria for Methanol-Cyclohexane System at 323.15K



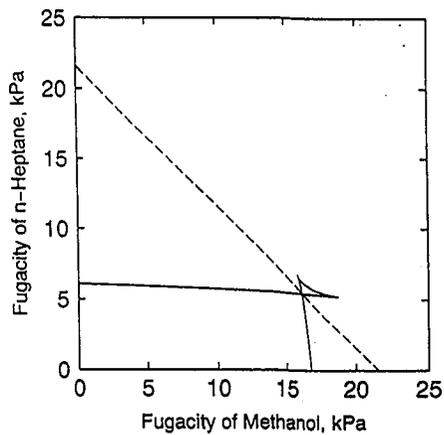
●:Yasuda *et al.*(1975), —:Calculated by EOS

Fig.6 Vapor-Liquid Equilibria for Methanol-n-Heptane System at 298.15K



●:Yasuda *et al.*(1975), —:Calculated by EOS

Fig.7 Liquid Phase Activity Coefficients for Methanol(1)-n-Heptane(2) System at 298.15K



--:Vapor, —:Liquid

Fig.8 Fugacities for Methanol-n-Heptane System at 298.15K and 21.61 kPa

Figure 7 gives the liquid activity coefficient curves for the methanol-n-heptane system at 298.15K. The activity coefficient  $\gamma_i$  was evaluated with the following equation.

$$\gamma_i = \phi_i / \phi_i^0 \quad (18)$$

where, the effective fugacity coefficient in mixture  $\phi_i$  and the one of pure component  $\phi_i^0$  were calculated with the EOS.

Figure 8 shows the calculation results of fugacities at the vapor-liquid-liquid equilibrium temperature and pressure for the methanol-n-heptane system. The continuous and dotted lines indicate the liquid and vapor, respectively. The intersection point gives the vapor-liquid-liquid equilibrium state.

## CONCLUSIONS

Liquid-liquid equilibria and liquid densities for three binary systems made of methanol with n-hexane, cyclohexane, or n-heptane were simultaneously correlated with the EOS, including good prediction on vapor-liquid and vapor-liquid-liquid equilibria.

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## THERMODYNAMICS OF DISTRIBUTION OF CARBOXYLIC ACIDS BETWEEN ORGANIC SOLVENTS AND PERCHLORATE SOLUTION

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### ABSTRACT

The distribution of acetic and propionic acids and their phenyl derivatives between carbon tetrachloride and octanol and 0.1 mol dm<sup>-3</sup> (Na<sup>+</sup>, H<sup>+</sup>)ClO<sub>4</sub><sup>-</sup> solution has been determined at five different temperatures (10-30 °C) and the thermodynamic parameters for the process evaluated from the van't Hoff isochore. The free energy change for the transfer of the methylene group from water to organic solvent was entropically controlled. The effect of perchlorate concentration on the distribution constant of propionic acid has also been measured at 25 °C. The distribution constant increased with increase in salt concentration as described by a modified Setschenow's equation.

### INTRODUCTION

The distribution behaviour of various solutes between different organic solvents and aqueous solution has been studied widely by many workers. The value for the free energy of transfer of methylene group from water to organic solvent has been used to examine the hydrophobic effect and interactions (Davis et al. 1974; Beezer et al. 1983; Tanford, 1973). On the basis of the thermodynamics of distribution, the free energy, enthalpy and entropy changes for the transfer of methylene group from aqueous salt solution to organic solvents have been considered (Anderson et al., 1983; Riebesehl and Tomlinson, 1983; Kojima and Davis, 1984; Davies et al., 1951; Charykov and Pavlovskaya, 1981). In a previous paper (Kojima and Davis, 1984), we described the thermodynamics of distribution of para-substituted phenols between organic solvents and sodium chloride solution.

This paper examines the temperature dependency of the distribution and dimerization constants of carboxylic acids between 0.1 mol dm<sup>-3</sup> (Na<sup>+</sup>, H<sup>+</sup>)ClO<sub>4</sub><sup>-</sup> solution and octanol and carbon tetrachloride and also the effect of perchlorate concentration on distribution was also studied.

## EXPERIMENTAL

### APPARATUS

Equilibrium studies were carried out using a shaking water bath (Altec, Persomal Lt-10) thermostated at a given temperature ( $\pm 0.1^\circ\text{C}$ ). A Shimadzu Model UV-2100 spectrophotometer was used for the determination of concentration of phenyl derivatives in aqueous solution at their maximum wavelength (257.2 nm) with 10 cm silica cell.

### CHEMICALS

Carboxylic acids from Wako were purified by distilling twice and collecting a middle fraction distillate at constant temperature. Organic solvents were purified by washing first with dilute sodium hydroxide solution, then with dilute hydrochloric acid solution and finally with distilled water. They were used without dehydration. Deionized water of specific resistivity of  $18.1 \text{ M ohm cm}^{-1}$ , obtained with a Milli-Q purification system, was used throughout.

### PROCEDURE

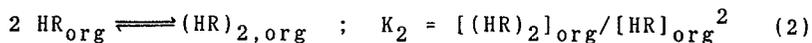
All experiments were carried out in a room thermostated at  $25 \pm 1^\circ\text{C}$ . Phenolphthalein was used as an indicator in the acid-base titration. Stock solutions of acids were prepared by dilutions of the acids with  $0.01 \text{ mol dm}^{-3}$  perchloric acid containing  $0.09 \text{ mol dm}^{-3}$  sodium perchlorate. Phenyl derivatives were dissolved in octanol for the aqueous-octanol system. The aqueous and organic phases were contacted in a stoppered centrifuge glass tube of  $50 \text{ cm}^3$  capacity. After equilibrium, phase separation was achieved by standing the system. The concentration of acids in the aqueous phase was determined by measuring their absorbance at their maximum wavelength of absorption of phenyl derivatives or titrimetrically for aliphatic acids.

## RESULTS AND DISCUSSION

The distribution of an acid between the aqueous and organic phases can be written as :



where HR denotes the acid molecule and the subscripts aq and org refer to the aqueous and organic phases, respectively. The dimerization of the acid molecule in the organic phase can be written as :



The distribution ratio of the acid is given by :

$$\begin{aligned}
 D &= C_{HR,org}/C_{HR,aq} \\
 &= ([HR]_{org} + 2[(HR)_2]_{org})/([HR]_{aq} + [R^-]_{aq}) \\
 &= (K_d + 2 K_d^2 \cdot K_2 \cdot [HR]_{aq})/(1 + 1/K_{HR}[H^+]) \quad (3)
 \end{aligned}$$

where  $C_{HR,org}$  and  $C_{HR,aq}$  denote the total concentration of the acid in the organic and aqueous phases, respectively, and  $K_{HR}$  the formation constant of the acid monomer in the aqueous phase. When the dissociation of the acid monomer is negligible in the aqueous phase,  $[HR]_{aq}$  is equal to  $C_{HR,aq}$ . Then eqn. (3) is rewritten as :

$$D = K_d + 2 K_d^2 \cdot K_2 \cdot C_{HR,aq} \quad (4)$$

Under the present experimental condition, i.e.,  $[H^+] = 10^{-2}$  M, the distribution ratio is given by equation (4). Comparing the plot of  $\log D$  against  $\log C_{HR,aq}$  with a normalized function  $Y = \log(1+x)$ ;  $X = \log x$ , the distribution and dimerization constants can be easily obtained, respectively. The results obtained were summarized in Tables 1 and 2.

Table 1 Distribution and Dimerization Constants of Acids in the Carbon Tetrachloride-Perchlorate System at Different Temperatures

Temp. °C	CH <sub>3</sub> COOH		C <sub>2</sub> H <sub>5</sub> COOH		PhCH <sub>2</sub> COOH		PhC <sub>2</sub> H <sub>5</sub> COOH	
	log K <sub>d</sub>	log K <sub>2</sub>	log K <sub>d</sub>	log K <sub>2</sub>	log K <sub>d</sub>	log K <sub>2</sub>	log K <sub>d</sub>	log K <sub>2</sub>
10	-2.71	3.13	-1.95	3.19	-0.86	3.56	-0.25	3.68
15	-2.68	3.11	-1.89	3.10	-0.81	3.46	-0.20	3.55
20	-2.60	2.94	-1.84	3.01	-0.78	3.35	-0.15	3.42
25	-2.55	2.88	-1.78	2.89	-0.73	3.24	-0.12	3.29
30	-2.49	2.76	-1.73	2.84	-0.70	3.14	-0.07	3.17

Table 2 Logarithmic Distribution Constants (log K<sub>d</sub>) of Acids in the Octanol-Perchlorate System

Temp. (°C)	CH <sub>3</sub> COOH	C <sub>2</sub> H <sub>5</sub> COOH	PhCH <sub>2</sub> COOH	PhC <sub>2</sub> H <sub>5</sub> COOH
10	-0.33	0.29	1.44	1.99
15	-0.30	0.30	1.45	1.99
20	-0.30	0.31	1.44	1.96
25	-0.29	0.30	1.45	1.98
30	-0.28	0.30	1.44	1.98

The thermodynamics of distribution of monomeric carboxylic acid are given by equations (5) and (6).

$$\Delta G = -RT \ln K_d^X \quad (5)$$

$$\ln K_d^X = -\Delta H/R T + \Delta S/R \quad (6)$$

where  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are the partial free energy change, enthalpy change and entropy change of monomer transfer, respectively, and  $R$  and  $T$  are the gas constant and absolute temperature.  $K_d^X$  and  $K_2^X$  defined by the distribution constant and dimerization constant in terms of mole fraction, respectively, can be calculated by means of equations (7) and (8).

$$K_d^X = K_d \cdot V_{org}/V_{aq} \quad (7)$$

$$K_2^X = K_2 \times 1000 / V_{org} \quad (8)$$

where  $V_{org}$  and  $V_{aq}$  are the molar volumes of the organic and aqueous solution, respectively. The molar volumes of solvent at different temperatures are calculated from density values at the corresponding temperature from the knowledge that the density changes linearly with temperature (Weast, 1974). By applying equation (6) to the data for the distribution constants obtained over a temperature range of 10-30°C,  $\Delta H$  and  $\Delta S$  are calculated from the slope and the intercept of the plot of  $\ln K_d^X$  against  $1/T$ , respectively, provided the enthalpy remains constant irrespective of the temperature range studied. Figs. 1 and 2 show the van't Hoff plots obtained for all data. The distribution constant increases with increase in temperature for all of the solutes

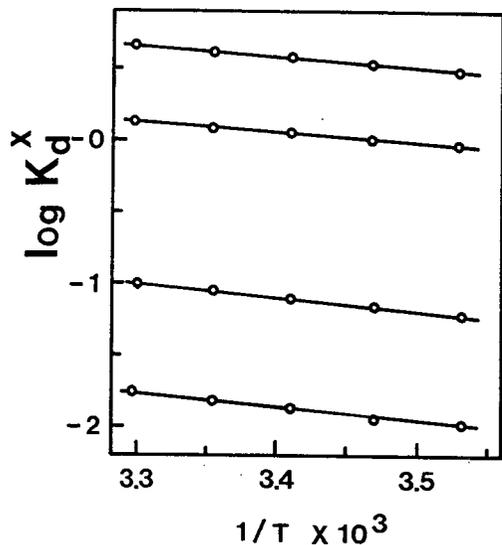


Fig. 1 van't Hoff plots for carbon tetrachloride perchlorate system

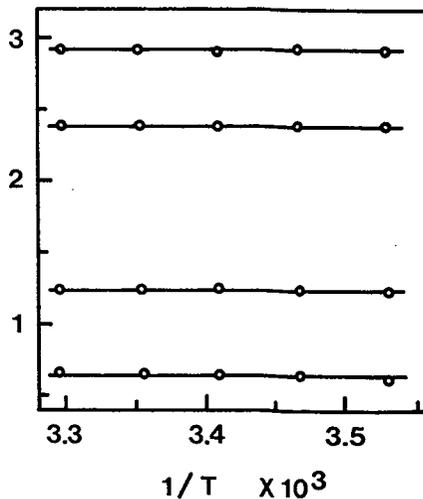


Fig. 2 van't Hoff plots for octanol-perchlorate system

Lines show phenylpropionic, phenylacetic, propionic and acetic acids from the top.

studied in the present work for carbon tetrachloride-perchlorate system, while the distribution constant for octanol-perchlorate system is constant. Excellent linearity was obtained between  $\ln K_d^x$  and  $1/T$ . The results obtained are summarized in Table 3. This indicates that the enthalpy of transfer for a given solute is constant over the temperature range studied in all cases. The entropy of transfer increases with increasing methylene group. The change of  $\Delta G$  of transfer per methylene group is almost entirely entropically controlled. From these data, it may be concluded that

Table 3 Thermodynamic constants for distribution of acids between organic solvents and perchlorate system at 25 °C

Solute	Carbon Tetrachloride				Octanol	
	Distribution		Dimerization		Distribution	
	H kJ/mol	S J/mol K	H kJ/mol	S j/mol K	H kJ/mol	S J/mol K
CH <sub>3</sub> COOH	17.8	25.1	-29.5	-24.7	0	12.2
C <sub>2</sub> H <sub>5</sub> COOH	18.3	41.2	-30.3	-26.6	0	23.7
PhCH <sub>2</sub> COOH	13.2	44.2	-35.0	-35.8	0	45.6
PhC <sub>2</sub> H <sub>5</sub> COOH	14.4	60.5	-42.2	-59.2	0	55.9

the increment in free energy ( $\Delta G$ ) per methylene group does not arise from a change in  $\Delta H$  but from  $\Delta S$ , i.e.  $\Delta\Delta H \approx 0, \Delta\Delta G \approx (T\Delta\Delta S)$ . This incremental value arises from the decrease in the entropy of solution of the methylene group in water (Tanford, 1973). On the other hand, the enthalpy and entropy of dimerization for aliphatic acids is constant over the temperature range studied (Fig. 3 and Table 3). For phenyl derivatives, the estimation of the dimerization constant in carbon tetrachloride is relatively incorrect, owing to the high distribution ratio and relatively large estimation error from equation (4). Thus nothing is discussed here for phenyl derivatives.

Effect of NaClO<sub>4</sub> concentration on the distribution ratio of propionic acid between carbon tetrachloride and aqueous perchlorate solution was also studied. From the plot of  $\log D$  against  $\log C_{HR,w}$ , the distribution and dimerization constants were also obtained by the same manner. The distribution constant increased with increase in NaClO<sub>4</sub> concentration. The plot of  $\log K_d$

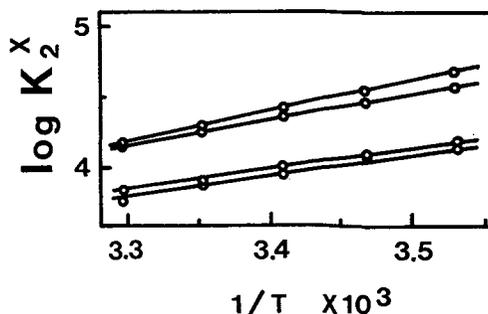


Fig. 3 van't Hoff plot of dimerization constants

Lines show the same in Fig. 1

against  $\text{NaClO}_4$  concentration gave a straight line with the correlation coefficient of 0.996 :

$$\log K_d = 0.0689 [\text{NaClO}_4] - 1.78$$

The well-known Setschenow's equation holds for this system. This can be explained by a salting out effect of  $\text{NaClO}_4$  on the solubility of propionic acid in an aqueous solution. On the other hand, dimerization constant is almost constant irrespective of  $\text{NaClO}_4$  concentration. This can be expected from the point that dimerization reaction occurs in the carbon tetrachloride solution (Sekine et al., 1969).

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# SOLVENT EXTRACTION OF METAL PERCHLORATES WITH TRIOCTYLPHOSPHINE OXIDE IN HEXANE

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## ABSTRACT

Metal ions in aqueous  $1 \text{ mol dm}^{-3}$  sodium perchlorate solution have been extracted with trioctylphosphine oxide (TOPO) in hexane at 298K. The magnitude of the extraction constants is compared with the Gibbs free energy of hydration and the formation constants of chelate complexes in order to find the relation between the hydration in the aqueous phase and the solvation with TOPO in the organic phase. It is concluded that the hydration of the extracted species should impair the extraction and it will be stronger among transition metal ions in the order of ions which form more stable complexes.

## INTRODUCTION

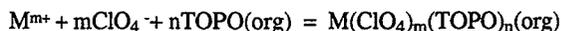
When a metal ion in an aqueous solution is extracted with a solvating type extractant into an inert organic solvent, the hydration of the ion in the aqueous phase should impair the extraction, and solvation by the extractant should enhance the extraction. It is of interest that the hydration and solvation should be an analogous chemical affinity of a metal ion but they play opposite roles in this type of extraction. In order to contrast these two, metal ions in aqueous sodium perchlorate solution have been extracted with trioctylphosphine oxide (TOPO) in hexane. The specific properties of the perchlorate ion such as poor interaction with the metal ions in the aqueous phase, poor hydrophilic tendency in the organic phase and good extraction of ion pairs are convenient for this ion to be used as the counter ion. TOPO is a strong solvating reagent often used in solvent extraction systems.

The extraction of metal perchlorates can be regarded as the ion-pair extraction of a large cationic solvate of TOPO and perchlorate ion(s) even though the solubility of TOPO in the aqueous phase is very low. The solvation number of TOPO in the extracted species can be obtained from the slope analysis of the distribution data and the extractability can be expressed by the extraction constants. The experimental results have already been reported -Kusakabe(1983,1995). The results are re-examined here from the above standpoint especially for transition metal ions in relation to the mechanism of synergistic extraction.

## EXPERIMENTAL

An aliquot of the metal perchlorate solution in aqueous  $1 \text{ mol dm}^{-3}$   $(\text{Na,H})\text{ClO}_4$  and the same volume of hexane solution containing TOPO were placed in a stoppered glass tube of  $20\text{cm}^3$ . The two phases were agitated mechanically in a thermostated room at 298K. After centrifugation, the metal concentration in both phases was measured by atomic absorption spectrometry, flame emission spectrometry, with an ion-selective electrode, or by colorimetry. The extraction

equilibrium can be written as;



$$K_{ex} = [M(ClO_4)_m(TOPO)_n]_{org} / [M^{m+}][ClO_4^-]^m [TOPO]_{org}^n \quad (1)$$

$$D = [M^{m+}]_{org, total} / [M^{m+}]_{total} = K_{ex} [ClO_4^-]^m [TOPO]_{org}^n \quad (2)$$

where the subscript "org" denotes the chemical species in the organic phase. Measured distribution ratios of the cation  $M^{m+}$  were treated by using a least squares program. The concentration of perchlorate ion was regarded as unity but that of TOPO was calculated considering the decrease caused by the coextraction of sodium perchlorate and perchloric acid.

## RESULTS AND DISCUSSION

The extraction constants and solvation numbers are listed in Table 1. Since the extraction of trivalent metal ions has been discussed elsewhere-Kusakabe(1995), discussion is focussed on the divalent metal ions.

**Table 1** Extraction constant of perchlorates from 1 mol dm<sup>-3</sup> (Na,H)ClO<sub>4</sub> with TOPO in hexane at 298K and the solvation number of TOPO in the extracted species.

M <sup>m+</sup>	logK <sub>ex</sub>	n	ref.	M <sup>m+</sup>	logK <sub>ex</sub>	n	ref.	M <sup>m+</sup>	logK <sub>ex</sub>	n	ref.
H <sup>+</sup>	3.15	2	a	Ca <sup>2+</sup>	6.39	4	g	UO <sub>2</sub> <sup>2+</sup>	10.1	4	f
Li <sup>+</sup>	2.29	3	b	Sr <sup>2+</sup>	5.13	4	g	Sc <sup>3+</sup>	11.83	4	k
Na <sup>+</sup>	1.01	3	c	Ba <sup>2+</sup>	4.92	4	g	Y <sup>3+</sup>	8.64	4	k
K <sup>+</sup>	0.59	3	b	Mn <sup>2+</sup>	6.14	4	f	La <sup>3+</sup>	8.2	4	f
Rb <sup>+</sup>	1.68	4	b	Fe <sup>2+</sup>	5.5	4	f	Cr <sup>3+</sup>	7.1	5	k
Cs <sup>+</sup>	1.50	4	b	Co <sup>2+</sup>	4.91	4	f	Fe <sup>3+</sup>	11.86*	4	l
NH <sub>4</sub> <sup>+</sup>	1.78	3	d	Ni <sup>2+</sup>	4.54	4	f	Ga <sup>3+</sup>	7.1	4	f
Ag <sup>+</sup>	7.32	4	e	Cu <sup>2+</sup>	5.81	4	f	In <sup>3+</sup>	9.57	4	f
Tl <sup>+</sup>	2.01	3	f	Zn <sup>2+</sup>	5.41	4	h	Tl <sup>3+</sup>	nil		
Be <sup>2+</sup>	8.01	4	g	Cd <sup>2+</sup>	6.35	4	i	Eu <sup>3+</sup>	8.46	4	k
Mg <sup>2+</sup>	4.99	4	g	Pb <sup>2+</sup>	6.92	4	j				

a) Niitsu, M. and Sekine, T., *J. Inorg Nucl. Chem.*, **37**, 1064 (1975). b) Kusakabe, S. and Sekine, T., *Bull. Chem. Soc. Jpn.*, **53**, 2087 (1980), partly revised in ref e. c) Kusakabe, S. and Sekine, T., *Bull. Chem. Soc. Jpn.*, **53**, 1759 (1980). d) Kusakabe, S., Hishikura, H. and Sekine, T., *Bunseki Kagaku*, **31**, E157 (1982). e) Kusakabe, S., Abe, S. and Sekine, T., "Solvent Extraction in 1990" (Proceedings of ISEC'90) A123, Elsevier, Amsterdam (1992). f) Kusakabe, S. and Sekine, T., Proceedings of ISEC'83, 347 (1983). g) Kusakabe, S. and Sekine, T., *Bull. Chem. Soc. Jpn.*, **54**, 2903 (1982). h) Moriya, H. and Sekine, T., *Bull. Chem. Soc. Jpn.*, **45**, 1626 (1972). i) Murai, R. and Sekine, T., *Bunseki Kagaku*, **31**, E413 (1982). j) Kusakabe, S. and Sekine, T., *Bull. Chem. Soc. Jpn.*, **54**, 2553 (1981). k) Kusakabe, S., Takatsuki, A., and Ebato, N., to be submitted. l) Sekine, T., Honda, H. and Zeniya, Y., *J. Inorg. Nucl. Chem.*, **38**, 1347 (1976). \*) 4 mol dm<sup>-3</sup> (Na,H)ClO<sub>4</sub>.

The degree of hydration of an ion may be measured by the Gibbs standard free energy of hydration. If the hypothetical unit activity of TOPO is taken as the standard, the extractability of a metal perchlorate can be compared by the distribution ratio, as is seen in eq. 2, disregarding the solvation number. This relationship is illustrated in Fig. 1. The abscissa of the figure is taken with a minus sign,  $-\Delta G_h^0$ , after subtracting the equivalent hydration energy of the perchlorate ion,  $-230m/\text{kJ mol}^{-1}$  ( $m$  is the charge of cation). This term is necessary when the extractability is compared among differently charged cations. The values of  $\Delta G_h^0$  are taken from Marcus(1991).

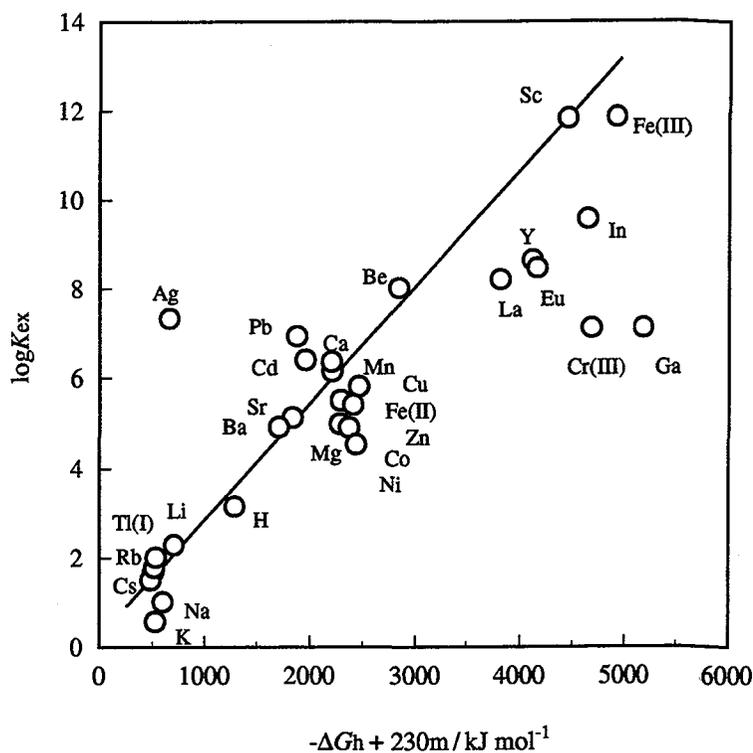


Fig. 1 Correlation of the extraction constants with Gibbs free energy of hydration of the cation.

As is seen in Fig. 1 the relationship between the extractability and hydration energy are linearly correlated as a whole although several ions deviate. The line drawn from the plot for  $\text{Cs}^+$  to that of  $\text{Sc}^{3+}$  has been discussed in a previous paper -Kusakabe (1995) and shows the fundamental relationship between these two parameters. The reason why the plots for several ions deviate from this line is summarized as (1) upward deviation is caused by the strong coordination of TOPO with the metal ion and (2) downward deviation is caused by the hydration of the metal ion in the extracted

species. Most plots for the transition metal ions in Fig. 1 are located below the line although the relationship between them is not clear. This may be because the value of  $\Delta G^0$  is not too different between them.

To find another aspect, the value of  $\log K_{ex}$  is compared with the stability constant of the EDTA complexes in aqueous solution. The EDTA complexes are known to be hardly extractable into organic solvents, however, it should suggest the behavior of metal ions on forming complexes. The stability constants for the 1:1 complexes obtained under similar experimental conditions to the present study, which are defined by the equilibrium  $M^{m+} + L^{4-} \rightleftharpoons ML^{m-4}$ , were selected from the literature and the extraction constants are plotted in Fig. 2 against them.

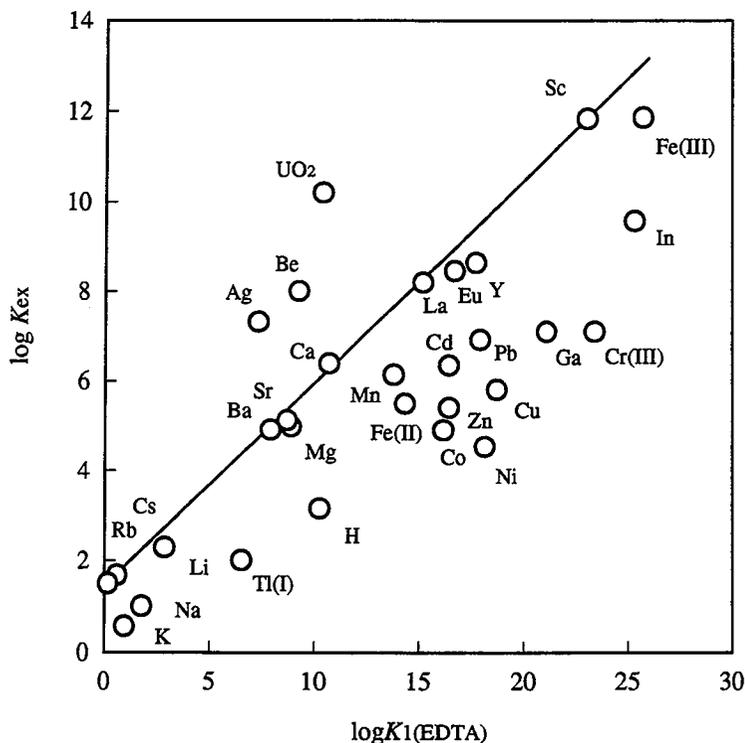


Fig. 2 Extraction constants of perchlorates with TOPO in hexane and stability constants of EDTA complexes of the cations in aqueous solutions.

At a glance, the points in Fig. 2 seem to be scattered, however, some information can be obtained. Although the size of the metal ion in general affects the stability of EDTA complexes, it should not be very important for the transition metals because the radius is not too different among them. It is reported from an NMR study of the structure of EDTA complexes in aqueous solutions that the

Mn(II) and Fe(III) complexes are both mostly monoaquapentadentate form and Co(II), Ni(II), and Cu(II) are in an equilibrium between monoaquapentadentate form and anhydrating hexadentate form - Oakes(1983). If a metal complex transferred from an aqueous solution contains water in a non-polar solvent, the hydration might be stabilized by leaving the water molecules of the second hydration sphere in the aqueous solution. Therefore, a certain number of waters will possibly remain bound to the extracted metal ions when the coordination sites are not fully occupied by the ligands. Since the solvation number of the transition metal ions with TOPO is generally four, this should be the case. This will be certain for Cr<sup>3+</sup> because the extraction of this perchlorate with TOPO is found to be at equilibrium within a few minutes. Considering the slow substitution of hydrated water on this metal ion, the five TOPO molecules of the extracted species should be regarded to solvate not the metal ion but the hydrated waters. In Fig. 2 the Cs-Sc line suggests a hypothetical relationship between the stability of the EDTA chelate and the extractability with TOPO. Here, we can see that all points for the transition metals scatter below the line, although the hydration in the EDTA complexes may give complicated effects on their stability. This means the transition metals are relatively less extractable than the other ions such as the alkaline earths when the stability of the complexes is taken into account. Furthermore, although the Irving-Williams order is found among the stabilities of EDTA chelates, the magnitude of the extraction constant with TOPO seems to show an opposite tendency. This may become clearer by a comparison with the stability constants of the acetylacetonato-complexes of these metal ions.

The value of  $\log K_{ex}$  is correlated in Fig. 3 with the stability constants of the bis-acetylacetonato-complexes in aqueous solution. The values of the stability constants are those recommended by Stary (1982). In Fig. 3 the opposite tendency between these two constants is seen among the transition metal ions. In other words the metal ion which forms a more stable complex with acetylacetonate, extracted less with TOPO.

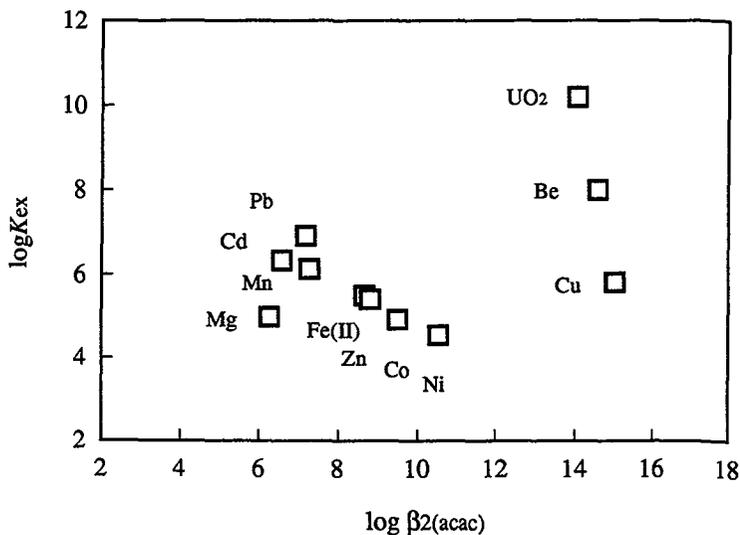


Fig. 3 Extraction constants of divalent metal perchlorates with TOPO in hexane from 1 mol dm<sup>-3</sup> (Na,H)ClO<sub>4</sub> and the stability constants of M(acac)<sub>2</sub> complexes in aqueous solution (*I*=0 at 298K).

From the measurements of the hydration enthalpy-Holmes(1957), it may be possible to say that the hydration is stronger in the order  $Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)$ . The stability of TOPO complexes may also follow a similar sequence. Therefore, the stability of TOPO complexes should be evaluated separately from the extractability and the reason for this opposite tendency will be attributed to the hydration of the extracted species which would be stronger in the order above.

TOPO is often used for the synergistic extraction of metal complexes. As was found in the present study, extraction with only TOPO as the extractant is not always high. This may be because donation of the TOPO molecule is not strong enough to remove all the hydrated water completely and the upper limit of the solvation number of the metal ion seems to be four except when the TOPO donates to the ligand molecules as in the case of Cr(III). The role of TOPO in the synergistic extraction lies in the replacement of hydrated water on the metal complexes-Lis(1991). This substitution can be done more easily in more weakly hydrated complexes. This should be the reason why the less stable complexes are extracted more effectively by the association with the solvating type extractant.

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## STUDIES ON THE MECHANISM OF EXTRACTION OF CARBOXYLIC ACIDS WITH TRI-N-OCTYLAMINE BY CHEMICAL COMPLEXATION

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### ABSTRACT

The probabilities of ion-pair formation and hydrogen-bond formation in the extraction of carboxylic acids by tri-n-octylamine are tested quantitatively by analyzing the FT-IR spectra of the organic phase containing the solutes. The effects of acid concentration, diluent and the acid  $pK_a$  on the probability of ion-pair formation are determined. A new idea on the extraction mechanism based on molecular resonance theory is proposed. Two forms of the product of the complexation reaction, the ion-pair form and the hydrogen-bonded form, resonate. The effect of the probability of ion-pair formation on the equilibrium distribution coefficient  $D$  in an active diluent is discussed.

### INTRODUCTION

Solvent extraction based on reversible chemical complexation can have a high capacity for dilute solutions and also a high selectivity (King, 1987). Studies on the extraction of carboxylic acids from dilute solution with tertiary amines by chemical complexation have been investigated mostly in a batch operation. We have found that the equilibria for chemical complexation depend greatly on the nature of the diluent and the acid at a certain temperature. However, the complexation mechanism has not been understood deeply, with many questions remaining for further investigation. In the extraction of an acid with an amine, the acid-base interaction between them creates selectivity for the acid of interest as opposed to other solutes. Spectroscopic studies of this acid-amine system have shown that the proton of the carboxylic acid group often, but not always, transfers to the amine, making an organic ion-pair composed of a quaternary ammonium cation and a carboxylate anion (King, 1992). From the studies of other authors (Tamada et al., 1989), a controversy remains as to whether the (1,1) complex of weak acids and an amine is an ion-pair or a molecular hydrogen-bonded form. In previous investigations in this research group (Yang, 1990), FT-IR spectroscopic analysis of organic samples (tertiary amine and a diluent) loaded with carboxylic acids showed that the amine ( $R_3N$ ) formed a complex with acids ( $RCOOH$ ) through both hydrogen bonding and ionic association and that the latter was more obvious in more dilute aqueous solutions. Thus, two courses of reaction exist simultaneously in this extraction system, ion association and hydrogen bond complexation. These are expressed as:



Equation (1) represents the ion association process, and equation (2) represents the hydrogen bond complexation.

The objective of this work is to gain more fundamental information about the mechanism of the extraction of acids with tri-n-octylamine by chemical complexation so as to improve the extraction

process. The organic phase (tri-*n*-octylamine and a diluent), containing acids is studied by FT-IR spectroscopy. The probability of ion-pair formation in each system is tested quantitatively. The effects of acid concentration, diluent, and acid  $pK_a$  on this probability are determined. A new idea that the two main forms of the product of chemical complexation, the ion-pair form and the hydrogen-bonded form of the complex, coexist under resonance is proposed. This idea unifies the two-course theory raised by this group before.

## EXPERIMENTAL

### FT-IR Technique

The FT-IR spectra of organic samples containing a series of carboxylic acids of different concentrations were obtained on a Nicolet 5DX Infrared Spectrometer with a 0.01 mm NaCl window at room temperature. In this investigation, two characteristic peaks appear. One corresponds to the carboxylate band  $\nu_{as}(\text{COO}^-)$  at 1550-1620  $\text{cm}^{-1}$ , which denotes the ion-pair form of the complex. Another is the carbonyl band  $\nu(\text{C}=\text{O})$  at 1700-1740  $\text{cm}^{-1}$ , which denotes the hydrogen-bonded form of the complex. In order to quantitatively analyze the FT-IR spectra, a series of standards were prepared containing acetic acid and ammonium acetate in ethanol. The molar ratio of ammonium acetate to acetic acid is thought to be equal to the molar ratio of carboxylate anion ( $\text{COO}^-$ ) to carbonyl group ( $\text{C}=\text{O}$ ). The calibration plots which show the correlation between the molar ratio of (a) the carboxylate anion to the carbonyl group ((b) the carbonyl group to the carboxylate anion) and the ratio of the absorption peak area of (a)  $\nu_{as}(\text{COO}^-)$  to  $\nu(\text{C}=\text{O})$  ((b)  $\nu(\text{C}=\text{O})$  to  $\nu_{as}(\text{COO}^-)$ ) are presented in figure 1. An assumption is made below that the character of the carboxylate band and the carbonyl band in these standards is similar to that in organic samples loaded with acids.

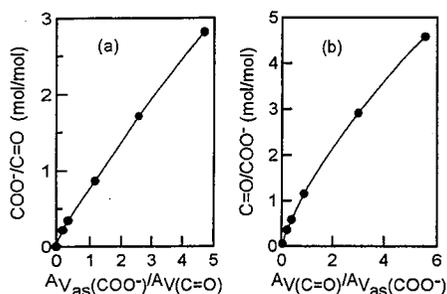


Figure 1 Calibration plots of (a) molar ratio  $\text{COO}^-/\text{C}=\text{O}$  versus ratio of absorption peak area  $A_{\nu_{as}(\text{COO}^-)}/A_{\nu(\text{C}=\text{O})}$  and (b)  $\text{C}=\text{O}/\text{COO}^-$  versus  $A_{\nu(\text{C}=\text{O})}/A_{\nu_{as}(\text{COO}^-)}$

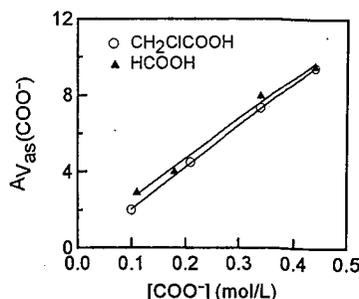


Figure 2 Correlation between absorption peak area of  $\nu_{as}(\text{COO}^-)$  and  $C_{\text{COO}^-}$  for monochloroacetic acid and formic acid in TOA-1-octanol

### Materials

The complexing agent was tri-*n*-octylamine (TOA), a tertiary amine. Carboxylic acids include acetic acid, butanoic acid, hexoic acid, monochloroacetic acid and formic acid. 1-octanol, chloroform and 1-butanol were used as active diluents. Benzene, carbon tetrachloride and *n*-dodecane are used as inert diluents. All of the acids, diluents and amine were of analytical grade.

### Procedure

To investigate the effects of acid concentration, diluent, acid  $pK_a$ , etc., on the probability of ion-pair formation, the spectra of a series of organic samples (30% TOA-70% diluent, volume fraction) loaded with acids were obtained. Based on batch extraction experiments and model simulation, it is

assumed that, in the region of the ratio of acid : amine less than 1:1, only a (1,1) complex between the amine and the acid is formed in these samples. Even though this is not the case when the ratio of acid to amine is slightly higher than 1, the data is also calculated on this assumption in order to give a larger region of description. As the acid concentration increased, the intensities of the carboxylate band at  $1550\text{-}1620\text{ cm}^{-1}$  and the carbonyl band at  $1700\text{-}1740\text{ cm}^{-1}$  underwent a gradual change. The ratio of the absorption peak area of  $\nu_{\text{as}}(\text{COO}^-)$  to  $\nu(\text{C}=\text{O})$  was obtained. The probability of ion-pair formation (I %) was calculated from the calibration plots in figure 1. However, for stronger acids monochloroacetic acid and formic acid, the carboxylate band usually moved to a higher band at around  $1600\text{ cm}^{-1}$ , suggesting a stronger interaction between the acid and the amine. Since in 1-octanol as diluent, monochloroacetic acid and formic acid both have 100 percent probability of ion-pair formation when acid:amine ratio is less than 1:1, they were analyzed quantitatively by their own standards. In this region, the loaded acid concentration is finally equal to the carboxylate anion concentration in these organic samples. Figure 2 shows the correlation between the absorption peak area of  $\nu_{\text{as}}(\text{COO}^-)$  and the carboxylate anion concentration for these two systems. When  $\text{CCl}_4$  is used as diluent, these standards are also used for monochloroacetic acid and formic acid, respectively.

## RESULTS AND DISCUSSION

### Effect of Diluent

Batch experiments show that very large changes in the equilibrium distribution coefficient can be achieved by changing the diluent. A comparison of the probability of ion-pair formation between active diluents and inert diluents has been made for acetic acid. Figure 3 shows the correlation between the probability of ion-pair formation (I %) and the concentration of acetic acid in  $\text{CH}_3\text{COOH}\text{-TOA}$ -active diluent systems. The active diluents used were 1-octanol, chloroform, and 1-butanol. Figure 4 shows the results for the  $\text{CH}_3\text{COOH}\text{-TOA}$ -inert diluent systems. The inert diluents used were benzene, carbon tetrachloride and n-dodecane. It is clear that as the acid concentration decreases, the probability of ion-pair formation decreases a little in inert diluents, but increases appreciably in active diluents. In inert diluents, such as n-dodecane, carbon tetrachloride and benzene, the probability of hydrogen-bond formation is larger than that of ion-pair form. On the other hand, in active diluents, such as 1-octanol, chloroform and 1-butanol, the probability of ion-pair formation is larger than that of hydrogen-bond formation when the acid:amine ratio is less than 1:1, even approaching unity at low acid concentrations. It can be explained that the hydrogen-bond form can happily exist in a nonpolar environment and the interaction of active diluents with the ion-pair form can stabilize the ion-pair form. The active diluents such as 1-octanol, chloroform and 1-butanol probably form hydrogen bonding with the ion-pair form of (1,1) acid-amine complex.

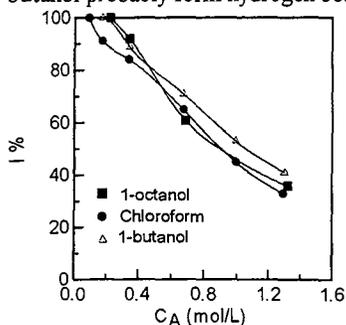


Figure 3 Correlation between I % and  $C_A$  in  $\text{CH}_3\text{COOH}\text{-TOA}$ -active diluent

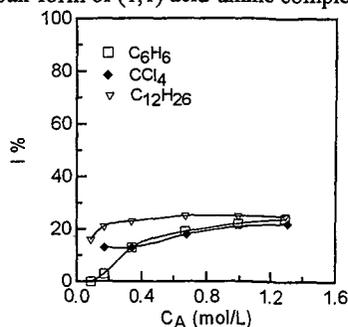


Figure 4 Correlation between I % and  $C_A$  in  $\text{CH}_3\text{COOH}\text{-TOA}$ -inert diluent

### Effect of Acid Type

Extraction ability is expected to increase with increasing acidity and increasing hydrophobicity of the acids (Tamada et al., 1990). Here, probability of ion-pair formation is thought to be related to

TABLE 1

$pK_a$ values of acids and probability of ion-pair form (I %) at 1:1 acid :amine			
Acid	$pK_a$	I % in 1-octanol	I % in $CCl_4$
monochloroacetic acid	2.86	91	23
Formic acid	3.75	84	27
Acetic acid	4.76	61	18
Butanoic acid	4.85	58	21
Hexoic acid	4.88	63	/

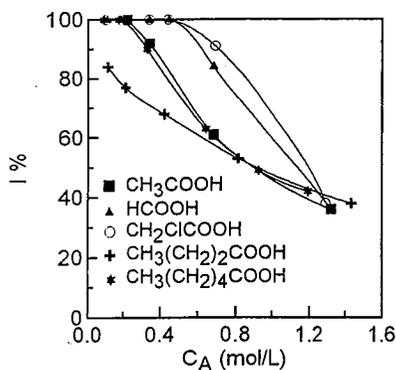


Figure 5 Correlation between I % and  $C_A$  in 1-octanol for different acids

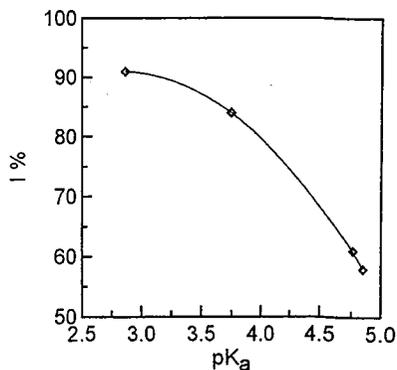


Figure 6 Effect of  $pK_a$  value on I % at 1:1 ratio of acid to amine in 1-octanol

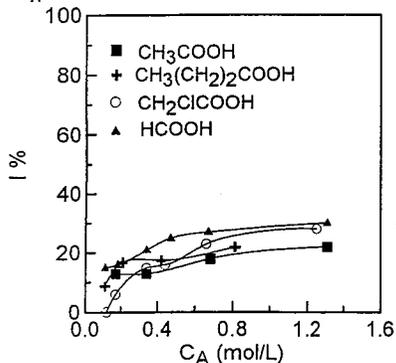


Figure 7 Correlation between I % and  $C_A$  in  $CCl_4$  for different acids

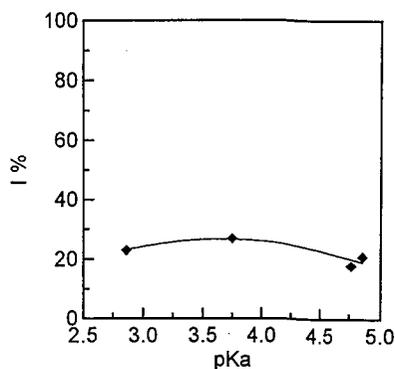


Figure 8 Effect of  $pK_a$  value on I % at 1:1 ratio of acid to amine in  $CCl_4$

acidity and hydrophobicity. Figure 5 shows the effect of acid concentration on the probability of ion-pair formation in 1-octanol as diluent for the different acids. At a 1:1 ratio of acid to amine, the probability of ion-pair formation decreases in the following sequence: monochloroacetic acid > formic acid > hexoic acid > acetic acid > butanoic acid. The  $pK_a$  values of these acids which reflect their acidity, and the probability of ion-pair formation at a 1:1 ratio of acid to amine are listed in Table 1. It is clear that acidity has a stronger influence than hydrophobicity for all these acids

except hexoic acid. Figure 6 shows the effect of  $pK_a$  on the probability of ion-pair formation at a 1:1 ratio of acid to amine except hexoic acid. The probability of ion-pair formation decreases with increase in  $pK_a$ . This result agrees generally with the effect of the  $pK_a$  of the acid on the apparent 1:1 heterogeneous complexation constant,  $K_{11}$  (Tamada et al., 1990). Even though the difference in  $pK_a$  between hexoic acid and butanoic acid is small, the probability of ion-pair formation of hexoic acid is much larger than that of butanoic acid. It is probable that the hydrophobicity of hexoic acid dominates the probability of ion-pair formation and the degree of extraction. The activity coefficients of hexoic acid and butanoic acid in the aqueous phase are 131.12 and 24.83, respectively (Zhao, 1991). These reflect the hydrophobicity of hexoic acid is much larger than that of butanoic acid.

As in the inert diluent  $CCl_4$ , the result is much different from that in 1-octanol. Figure 7 shows the effect of  $C_A$  on the probability of ion-pair formation with the diluent  $CCl_4$  for different acids. At a 1:1 ratio of acid to amine, there is an approximately equal probability of ion-pair formation for all these acids. The correlation of the probability of ion-pair formation and the  $pK_a$  is shown in Figure 8.

### Resonance

From our previous work, a two-course theory is proposed and used for interpreting the complexation reactions. The two-course theory is expressed as:



In this study, the complex is thought to have two forms. One is the ion-pair form  $R_3NH^+ \cdot OOCR$ , and the other is the hydrogen-bonded form  $R_3N \cdots HOOCR$ . Let us assume an equilibrium between the ion-pair form and the hydrogen-bonded form exists, and  $K_3$  is the equilibrium constant.



$$K_3 = \frac{[R_3NH^+ \cdot OOCR]}{[R_3N \cdots HOOCR]} \quad (4)$$

$$\frac{K_3}{K_3 + 1} = \frac{[R_3NH^+ \cdot OOCR]}{[R_3N \cdots HOOCR] + [R_3NH^+ \cdot OOCR]} \times 100 = \text{Ion-pair form \%} \quad (5)$$

From the above results, it can be seen that the probability of ion-pair formation changes with the acid concentration. Thus,  $K_3$  will change simultaneously according to equation (5). The value of  $K_3$  can no longer be a definite constant as expected for an equilibrium system, i.e. that at any given temperature the value of the mass action expression is a constant regardless of the initial concentrations of the reactants. We can conclude that the equilibrium assumption represented in equation (3) does not exist. In order to unify the two-course theory, a new idea of the extraction mechanism based on molecular resonance theory is proposed. It is expressed as:



Where  $K$  is the overall equilibrium constant of the complexation reaction, and the product of this

reaction is  $R_3NHOOCR$ . This product has several possible Lewis structures, which contribute differently to this product. In this study, only two forms, the ion-pair form  $R_3NH^+ \text{ } ^-OOCR$  and the hydrogen-bonded form  $R_3N \cdots HOOCR$  are considered as the stable forms and they contribute mainly to the product. These two forms resonate all the time. Under defined conditions, these two forms of the product have their own probabilities of existence. These probabilities change with the extraction conditions, such as diluent, acid concentration, acid  $pK_a$ , etc.

### Equilibrium Distribution Coefficient

Batch extraction experiments were performed using acetic acid with 30%TOA-70%diluent (volume fraction). The active diluents, 1-octanol and chloroform were used. The correlation of equilibrium distribution coefficient  $D$  and the acid concentration in the organic phase  $C_{A,org}$  has been determined. It is presumed that the nature of the FT-IR organic samples containing the acids is similar to that of the organic phase in batch extraction at equilibrium. Thus, the effect of the probability of ion-pair formation on  $D$  can be determined. The result is shown in figure 9. The larger the value for  $D$ , the higher the probability of ion-pair form, and vice versa. Since the ion-pair

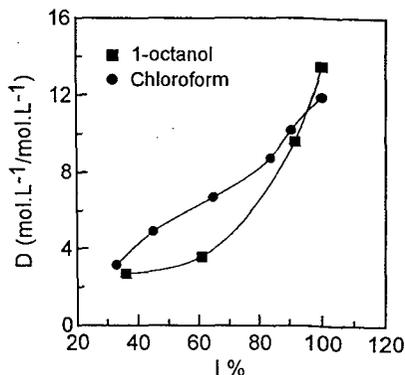


Figure 9 Effect of I % on equilibrium distribution coefficient  $D$

form has a stronger acid-amine interaction than the hydrogen bonded form and the active diluents can raise the stability of the ion-pair form, the ion-pair form is the more stable form in active diluents. Thus, the forward complexation reaction is favored in active diluents at a larger probability of ion-pair formation, resulting in a higher  $D$  value.

### CONCLUSION

A FT-IR spectroscopic method is used to investigate the probabilities of ion-pair formation and hydrogen-bond formation in extraction of carboxylic acids by tri-n-octylamine in active and inert diluents. Factors affecting the probability of ion-pair formation such as acid concentration, diluent, and acid  $pK_a$  are investigated. A resonance concept is proposed to further understand and unify the mechanism of complexation. Since a higher equilibrium distribution coefficient  $D$  has a higher probability of ion-pair formation in active diluents, it is important to study this probability further for enhancing the extraction process.

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## THE MASS TRANSFER OF WATER BETWEEN WATER-IN-OIL MICROEMULSION AND CONJUGATE AQUEOUS PHASE - A KEY TO THE MECHANISM OF REVERSE MICELLAR EXTRACTION

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### ABSTRACT

Kinetic results of the measurement of the water exchange between water-in-oil (w/o) microemulsion phase (salts of Aerosol OT in isooctane) and conjugate aqueous phase (aqueous solution of metal salts) performed in a stirred cell have been presented. For a certain pair of ions the change of water content of micellar phase exhibits a pronounced minimum or maximum (depending on the ion pair), which means changes of micellar sizes occur during ion-exchange. The experimental results lead to a new mechanism of the interactions of reverse micelles with a macroscopic liquid/liquid interface (i. e. extraction or reextraction process) involving the dynamic changes of primary buds induced by ion-exchange.

### INTRODUCTION

In recent years a lot of attention has been paid to the development of a new method of the recovery, separation and concentration of hydrophilic species from an aqueous phase: the so-called reverse micellar extraction (Hatton, 1989 a, b; Dekker et al., 1989). This method represents an interesting alternative to existing methods of separation especially in the case of separation of bioproducts (Schügerl, 1994).

Recently in our group, the kinetics of mass transfer in Winsor II-systems was systematically studied in a stirred cell in order to elucidate the mechanism of the micellar extraction (Nitsch, Plucinski 1990; Plucinski, Nitsch, 1992, 1993, 1994; Bausch et al., 1992). It was shown that extraction and reextraction were interfacial processes and the interactions of reverse micelles with a macroscopic liquid/liquid interface could be described by the so called "Docking mechanism" consisting of three consecutive steps: sticky collision, mass transfer and fusion (Plucinski, Nitsch, 1993, 1994).

In the kinetic experiments mentioned above, the micellar phase on the beginning of the kinetic experiments was always presaturated by injecting pure water to give a concentration corresponding to the equilibrium value.

In this work, special attention has been paid to the measurement of water concentration in the micellar phase (as  $w_o = [H_2O]/[AOT^-]$ ) during ion-exchange for different pairs of ions ( $Me_{mic}$ -AOT and  $Me_{aq}$ ).

### EXPERIMENTAL

The kinetic experiments have been performed in the two-phase stirred cell. The construction and the procedures of the evaluation of experimental data are described elsewhere (Nitsch, Plucinski 1990). The equilibrium results of the process were also obtained using standard methods. The concentrations of metallic species were determined by atomic absorption spectrometry (AAS SP 9 Pye Unicam). Water concentrations in the organic phase were measured using a Karl Fischer titration (633 Karl-Fischer-Automat, Metrohm). The different AOT salts (AOT = bis(2-ethylhexyl)-sulfosuccinate) have been obtained as follows: 0.2 mole of the sodium AOT salt was

dissolved in 600 ml of absolute methanol and added to an aqueous solution (usually 2.0 mol/dm<sup>3</sup>) of metal chloride with a 4 fold Me<sup>n+</sup> excess. The solution was next stored at least 12 hours at a temperature of -15°C. The "liquid crystal"-like lower phase formed was separated, dissolved in n-pentane and washed with pure water until no chloride ions were detected. The surfactant containing phase was then evaporated to dryness. The majority of residual water was removed by distillation as an azeotrope with dry methanol. The product (Me<sub>mic</sub>AOT<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub> salt) was desiccated over P<sub>2</sub>O<sub>5</sub>.

## RESULTS AND DISCUSSION

### Changes of water concentration in the micellar phase

While contacting an aqueous phase with several metal (Me<sub>2</sub>) chlorides with an organic micellar phase containing different salts of AOT (Me<sub>mic</sub>) in the stirred cell diverse changes of water concentration in the micellar phase were observed during the ion-exchange (Me<sub>mic</sub> was replaced by Me<sub>aq</sub>).

**Case 1:** Me<sub>mic</sub> = sodium, Me<sub>aq</sub> = transition element: If the AOT sodium ion was replaced by a transition group element (investigated here: Cd, Cu, Mn, Ni, Zn), characteristic minima of the water concentration in the organic phase were observed (Fig. 1). This means the change of the size of reverse micelles (diameter) is proportional to the water content  $w_0$  (Aveyard et al. 1986) and additional water fluxes between both phases.

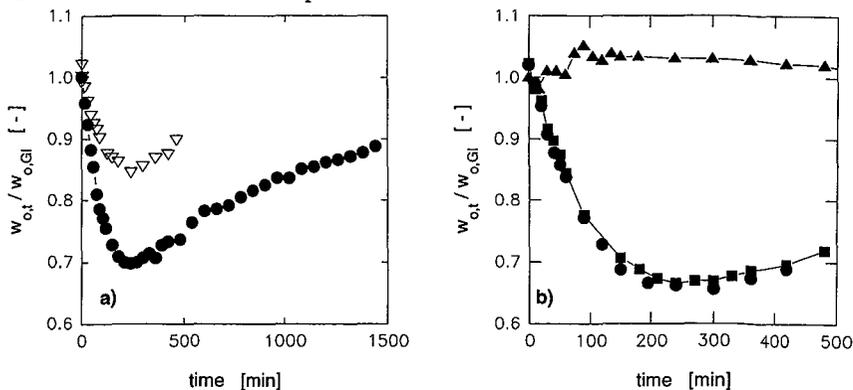


Fig. 1 The change of the water content of the micellar phase during the ion exchange,

[AOT] = 0.050 kmol/m<sup>3</sup>;  $n = 150 \text{ min}^{-1}$

a) influence of zinc concentration

● - [Zn<sup>2+</sup>] = 0.50 kmol/m<sup>3</sup>,  $w_{o,eq} = 30.8$

▽ - [Zn<sup>2+</sup>] = 0.175 kmol/m<sup>3</sup>,  $w_{o,eq} = 35.8$

b) influence of kind of ion

[MeCl<sub>2</sub>]<sub>0</sub> = 0.50 kmol/m<sup>3</sup>,

● - manganese,  $w_{o,eq} = 26.3$

■ - nickel,  $w_{o,eq} = 30.2$

▲ - strontium,  $w_{o,eq} = 9.5$

The course of changes in the water concentration depended both on the metal concentration in the aqueous phase and on the Na-AOT concentration; it did not depend on the kind of transition element (Fig. 1). An increase of Zn concentration in the aqueous phase ( $0.175 \leq [\text{Zn}^{2+}]_0 \leq 0.50 \text{ kmol/m}^3$ ) results in increased water flux ( $o \rightarrow w$ ) and shifts the minimum  $w_0$  to lower values (Fig. 1a).

**Case 2:**  $Me_{mic}$  = sodium,  $Me_{aq}$  = main group element: The replacement of sodium from AOT micelles by a main group element (investigated here: Ca, Sr) does not result in changes of  $w_o$  of the micellar phase (Fig. 1b). This means that micellar size remains unchanged during the ion-exchange.

**Case 3:**  $Me_{mic}$  = transition element,  $Me_{aq}$  = transition element: The exchange of nickel from the reverse micelles via solubilization of zinc does not change the water concentration in the organic phase which means constant micellar sizes (Fig. 2a).

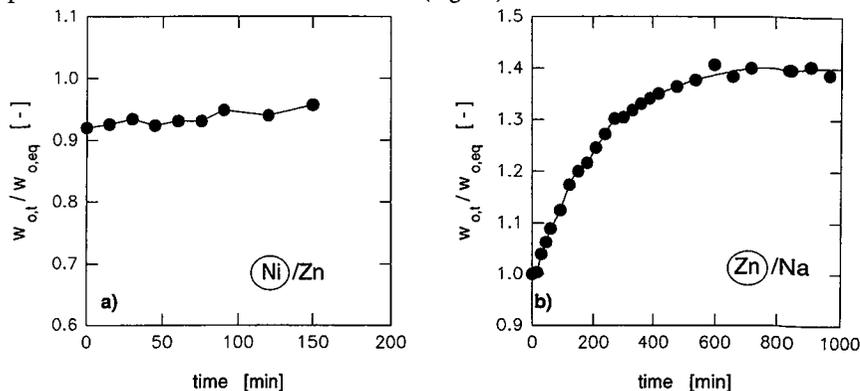


Fig. 2 The change of the water content of the micellar phase during the ion exchange,  $[AOT^-] = 0.050 \text{ kmol/m}^3$ ;  $n = 150 \text{ min}^{-1}$   
a)  $[ZnCl_2] = 0.25 \text{ kmol/m}^3$ ;  $w_{o,eq} = 31.4$  b)  $[NaCl] = 0.50 \text{ kmol/m}^3$ ;  $w_{o,eq} = 17.0$

**Case 4:**  $Me_{mic}$  = transition element,  $Me_{aq}$  = main group element: The substitution of zinc from the reverse micelles by sodium ion transferred from aqueous phase results in a pronounced increase in the water content of micellar phase i. e. an increase of micellar diameter (Fig. 2b). Unfortunately, the micellar phase became turbid at approx. 14 hours. After a further agitation period of 24 hours followed by centrifugation, clear phases obtained, with the expected equilibrium value of the water concentration.

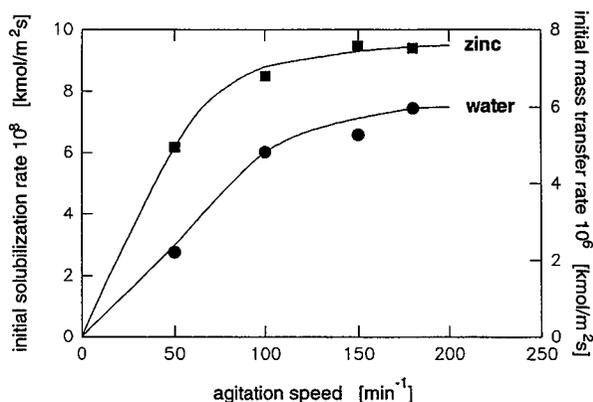


Fig. 3 The influence of the agitation speed on the initial mass transfer of metal ions and water  $[AOT^-] = 0.050 \text{ kmol/m}^3$ ;  $[ZnCl_2]_0 = 0.50 \text{ kmol/m}^3$ ;  $w_{o,eq} = 30.8$

### Limitation of mass transfer

From the measured concentration changes of water and ions during the kinetic experiments the corresponding initial mass transfer rates  $j_0$  were calculated for different hydrodynamic conditions i. e. agitation speeds (Fig 3).

$$j_0 = \frac{d[\text{Sol}]}{dt} \cdot \frac{V}{A} \quad (1)$$

The plateau-like regimes of the independence of mass transfer of the applied convection exclude the limitation of a mass transfer process by the convection. According to results shown in Fig. 3 it can assumed that both water and ion-exchange are limited by the interfacial process for agitation speed  $n \geq 100 \text{ min}^{-1}$  (Nitsch, 1984, Nitsch, Plucinski 1990, Plucinski, Nitsch, 1992, 1993, 1994).

### "Merging mechanism" of the interfacial micellar mass transfer

Two assumptions are essential for the mechanistic considerations: Firstly, based on literature data (Aveyard et al. 1986; Eastoe et al. 1993) it has been assumed, that in the range of the values of  $w_0$  investigated, only spherical micelles are formed. The second assumption is that the AOT molecules stay exclusively at the interfaces, which means the exclusion of AOT desorption.

Sticky collision of reverse micelles with the interface has been proposed as the first step of the mass transfer mechanism (Fig. 4, step 1), due to the always observed increase in the fluxes with the increase of micellar concentration (Plucinski, Nitsch, 1993, 1994).

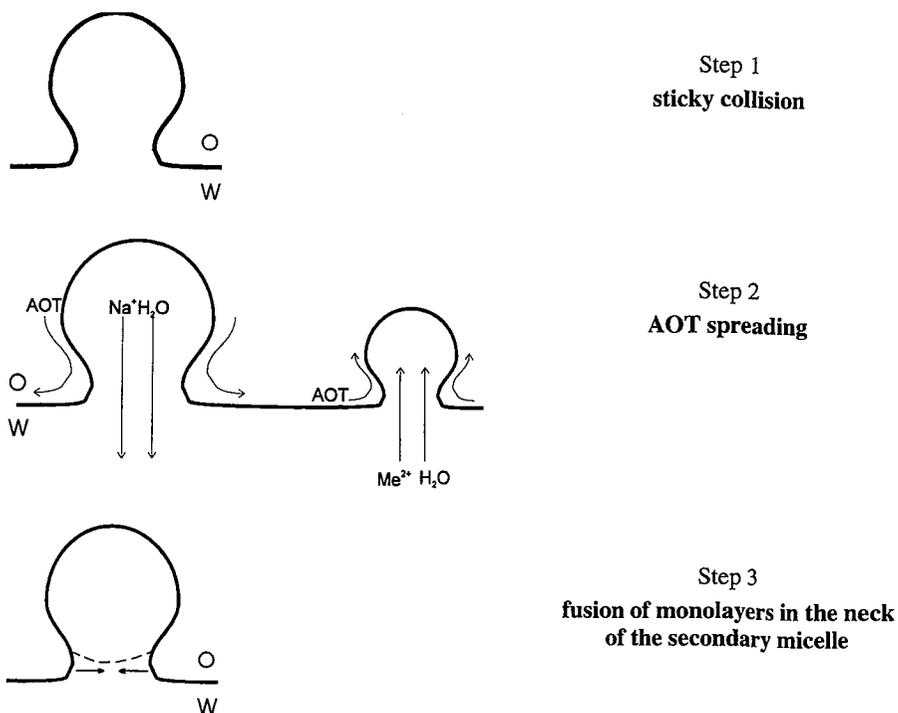


Fig. 4. Schematic view of the "Merging mechanism".

The decrease in water concentration in the micellar phase means shrinking of the micelles after a sticky collision, forcing AOT molecules to spread into the neighbouring macroscopic interface. Because of complete AOT coverage of the macroscopic interface, spreading of surfactant molecules demands the creation of secondary micelles (Fig. 4, step 2). The size of secondary micelles depends on the rate of fusion (Fig. 4, step 3).

The three characteristic features of the mechanism are:

- A driving force has to exist for the AOT spreading.
- The size of the secondary micelle is limited by the surfactant spreading and monolayer fusion.
- The mass transfer through the neck of a primary bud is not relevant in this mechanism, the secondary bud (and micelle) is formed from the macroscopic liquid/liquid interface with previously adsorbed counter ions.

In the first approach it is assumed that similar to the surfactants spreading, the difference of the Gibbs excess concentrations  $\Gamma$  of AOT between the primary bud and the neighbouring macroscopic interface should be the driving force for the lateral movement of AOT molecules. From the results of Eastoe et al. (Eastoe et al., 1992, 1993) it is known that the area occupied by AOT molecules (inversely proportional to  $\Gamma$ ) with main group elements as counter ions is equal to  $f_{\text{AOT}^-} = 84 \pm 8 \text{ \AA}^2$ , and with transition elements results with  $f_{\text{AOT}^-} = 64 \pm 6 \text{ \AA}^2$ . According to these results the difference of Gibbs excess concentrations for the ion pair  $\text{Me}_{\text{mic}} = \text{Na}$  and  $\text{Me}_{\text{aq}} = \text{Zn, Cd, Mn, Ni}$  has a positive value representing the driving force for the measured water flux from the organic towards aqueous phase (Fig. 1). For the ion pair  $\text{Me}_{\text{mic}} = \text{Zn}$  and  $\text{Me}_{\text{aq}} = \text{Na}$  the direction of the driving force is opposite and correspondingly a water flux into the micellar phase was observed experimentally (Fig. 2b). If both values of the Gibbs excess concentrations are practically equal ( $\text{Me}_{\text{mic}} = \text{Me}_{\text{aq}} = \text{main group element}$  or  $\text{Me}_{\text{mic}} = \text{Me}_{\text{aq}} = \text{transition group element}$ ) a driving force does not occur and indeed for the same conditions water fluxes cannot be measured (see Figs 1b, and 2a).

### The course of water concentration in kinetic experiments

The proposed merging mechanism for the interaction of reverse micelles with the macroscopic liquid/liquid interface also explains the time dependent changes of water concentration in the micellar phase after sticky collision (step 1). In the time period before the minimum value of  $w_o$  is reached ( $t < t_{\text{min}}$ ) the reduction of micellar size due to the water delivery ( $o \rightarrow w$ ) dominates the total mass transfer (Fig. 1). The very slow increase of the water concentration in the micellar phase ( $t > t_{\text{min}}$ ) means that water flux is directed into the micellar phase ( $w \rightarrow o$ ), i. e. the growth of buds during their residence time at the interface. Such a growth of the bud can be done only, if at the same time and in the direct neighbourhood of a secondary bud, micelles undergo sticky collisions, delivering AOT molecules necessary for the growth of the secondary bud. This necessity of this time and place coincidence could explain a much slower water uptake into the micellar phase.

### ACKNOWLEDGEMENT

This work has been supported by Deutsche Forschungsgemeinschaft (grant SFB 266).

## NOMENCLATURE

A	m <sup>2</sup>	mass transfer area (cross section area of stirred cell)
f	m <sup>2</sup> /molecule	AOT anion area occupied at the interface
j	kmol/m <sup>2</sup> s	solubilization (or mass transfer) rate
t	s	time
V	m <sup>3</sup>	volume of micellar phase
w <sub>o</sub>	-	water ratio (w <sub>o</sub> = [H <sub>2</sub> O]/[AOT])
Γ	kmol/m <sup>2</sup>	Gibbs excess
aq	aqueous	
eq	equilibrium	
mic	micellar	
o	oil	
t	time	
w	water	
→		direction of mass transfer
0		initial

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## CONCENTRATION PROFILES IN EXTRACTION COLUMNS

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### ABSTRACT

Ternary mass transfer in liquid-liquid extraction was studied in a countercurrent spray column using the ethyl-acetate/acetone/water system. The extraction paths were determined for mass transfer out of the ethyl-acetate phase into the water phase as well as out of the water phase into the ethyl-acetate phase. The extraction paths show an asymptotic behaviour towards the binodal line and are remarkably bent in the area of undersaturation. To describe the observed extraction paths thermodynamic coupling effects must be taken into consideration.

### INTRODUCTION

The mass transfer between the drops of the dispersed phase and the surrounding continuous phase in a countercurrent extraction column is an extremely complex process. Even in the simplest case, when both main components of the extraction system are completely immiscible and when just one solute is transferred from the raffinate phase into the extract phase, we have a combination of several transport mechanisms. The transport of the solute between bulk phases and the phase boundary is caused by molecular diffusion and convective mixing processes. The flux through the phase boundary can be described by equation (1), where the direction of the diffusional flux is determined by the concentration difference between the bulk phase (B) and the phase boundary (I).

$$(1) \quad J = k \cdot A \cdot (c^I - c^B)$$

The type and extent of the convectational flow, especially within the drops, depend on the physical properties of the system as well as on the operating conditions of the extractor, i.e. on the drop size and on the hold-up of the dispersed phase. No well-founded knowledge exists about the influence of the phase boundary on mass transfer. So, nearly all models of mass transfer are based on the assumption that the concentrations of both phases in the phase boundary, which is assumed as two-dimensional, are in equilibrium and that there is no resistance to mass transfer. Actually, compared with the molecular diffusion in the bulk phases, very fast mass transfer was observed in the area of the phase boundary during experiments with quiescent phases (Pertler et al. (1995)). As the slowest of the three transport steps - transport out of the bulk phase, transport across the phase boundary and transport into the bulk phase - determines the speed of the mass transfer, it seems quite reasonable to neglect the influence of the phase boundary. But if interfacial instabilities appear in an extraction system during mass transfer, which cause mixing of both of the bulk phases, the rate of mass transfer is significantly increased. In the mass transfer models this effect is usually taken into account by an enhancement factor (Golovin (1992)) or by the increase of the frequency of surface renewal (Sethy, Cullinan (1975)).

During the practical application of liquid-liquid extraction, in most of the cases, it is not enough to only take into account the mass transfer of one single component. Often the two main components of the extract and the raffinate phase are not completely immiscible or there are several solutes present in the system. The fluxes of the components are not independent from each other any more. For the simplest case of multicomponent mass transfer, i.e. mass transfer in a ternary system, the component fluxes can be described by equation (2).

$$(2) \quad \begin{pmatrix} j_1 \\ j_2 \end{pmatrix} = \begin{pmatrix} k_{11} & k_{12} \\ k_{21} & k_{22} \end{pmatrix} \begin{pmatrix} \Delta c_1 \\ \Delta c_2 \end{pmatrix}$$

The flux of the third component is determined by the conservation equation (3).

$$(3) \quad \sum_{i=1}^3 j_i = 0$$

As a consequence of diffusive interactions, a so-called up-hill transport is possible: especially for both main components, which normally show just small concentration differences between the bulk phase and the phase boundary. They can be dragged along by the transfer of the solute. In this case, we observe the transfer of a component against its composition driving force.

In ternary systems with both main components not completely immiscible, e.g. glycerol/water/acetone or ethyl-acetate/acetone/water, both extraction paths can, in principle, run within the area of undersaturation or along the binodal line. Only phases with compositions which lie on the ends of a common tie line are in equilibrium, but between all other saturated phases a mass transfer can definitely take place. In the unsaturated area we can make conclusions on the structure of the matrix of the mass-transfer coefficients judging by the curvature of the extraction paths. When the tangent of the extraction path coincides with the linking straight line between the bulk concentration and the phase boundary concentration, as explained in fig. 3, the matrix of the mass-transfer coefficients has diagonal form (Equ. 4).

$$(4) \quad k_{12} = k_{21} \quad , \quad k_{11} = k_{21}$$

In this case, there are no diffusive interactions between the component fluxes. An extraction path in this direction can also be caused by a purely fluid dynamically induced transport mechanism like the fluctuation transport proposed by Schermuly and Blass (1991). It assumes an exchange of fluid-elements across the phase boundary, which leads to a mixing process of both bulk phases. But if the direction of the extraction path differs from the linking straight line between the bulk and the phase boundary concentration, the curvature can only be explained by the influence of diffusive interactions. The off-diagonal elements of the matrix of the mass transfer coefficients do not disappear in this case.

Until now only few studies of mass transfer in liquid-liquid extraction have been accomplished in the systems where mutual solubility of the main components cannot be neglected. The equilibration path in unsaturated bulk phases was examined by Sethy and Cullinan (1975) in the acetonitrile/benzene/n-heptane system and by Krishna et al. (1985) in the glycerol/water/acetone system. Both of them used a modified Lewis-cell. Schermuly and Blass (1991) investigated the extraction paths in a countercurrent extraction column in the glycerol/water/acetone system.

## EXPERIMENTS AND RESULTS

To examine the extraction path in the ethyl-acetate/acetone/water system the existing equipment which was set up by Schermuly and Blass (1991) was used, i.e. a spray column with an inner diameter of 25 mm and an active height of 4.3 m, which includes 7 sampling points for the dispersed and the continuous phase. To determine the extraction paths a considerable height of the column is very important to get sufficiently high mass transfer rates. The samples from both phases were analyzed using a Hewlett Packard 5890 Series II gas chromatograph. We obtained the best results using a PoraPLOT Q capillary column with program-controlled values for the oven temperature and the column head pressure. A multi-level calibration was done separately for the ethyl-acetate and water phases, the chromatograms were analyzed by an internal-standard-method.

The ethyl-acetate/acetone/water system shows a considerable area of miscibility at both sides of the miscibility gap, which allows the examination the course of the extraction paths while approaching the binodal line. Equilibrium measurements at the temperatures of 10°C, 20°C and 30°C showed that the binodal line is nearly the same in that range of temperatures. The dependence of viscosity and density on concentration is far less distinctive than in the glycerol/water/acetone system. To give an example, two series of measured data are shown in Fig. 1. Just a small and mainly linear dependence on concentration exists in the ethyl-acetate phase. The physical properties in the water phase change considerably. It is conspicuous that the maximum of the viscosity curve is very distinctive.

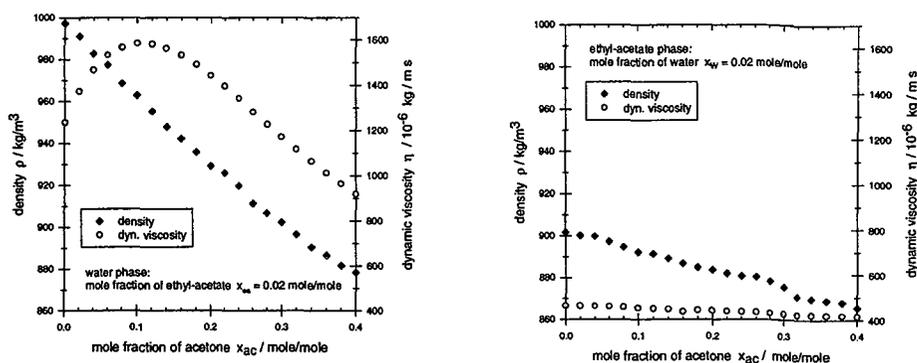
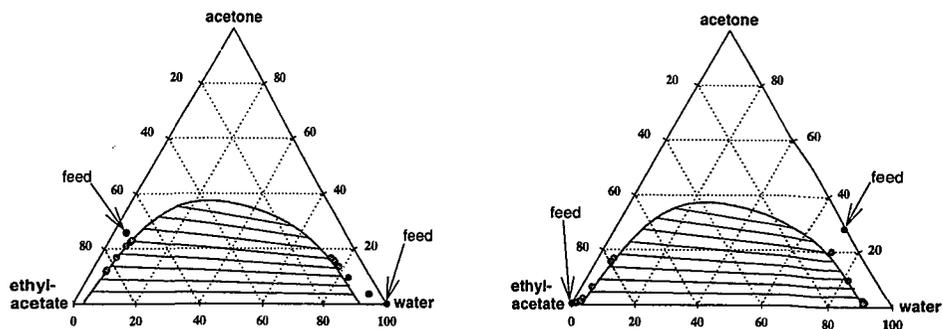
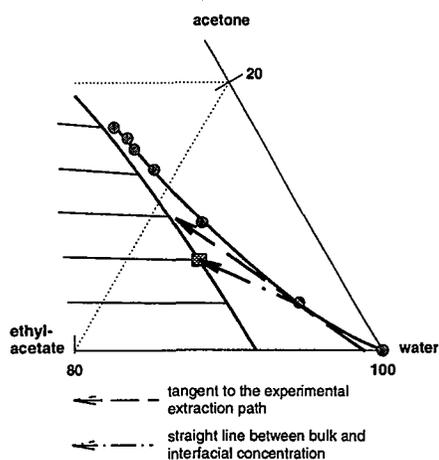


Figure 1. Dependence of density and viscosity on concentration in the water phase (left) and ethyl-acetate phase (right) at a temperature of  $T = 20^\circ\text{C}$



**Figure 2.** Extraction paths during the mass transfer out of the ethyl-acetate phase into the water phase (left) and out of the water phase into the ethyl-acetate phase (right) at a temperature of  $T = 20^\circ\text{C}$

The extraction experiments were done with both directions of mass transfer. Both phases were fed to the extractor in a non-saturated state. According to the criteria of Sterling and Scriven, interfacial instabilities were observed during the mass transfer out of the water phase into the ethyl-acetate phase. The instabilities manifest themselves in an extremely strong tendency to droplet-droplet coalescence. In order to exclude the influence of the coalescence on the mass transfer, very low flow rates of both phases were used in these experiments. Hence the hold-up of the dispersed phase in the extractor was extremely small. During the mass transfer from the ethyl-acetate phase into the water phase the drop

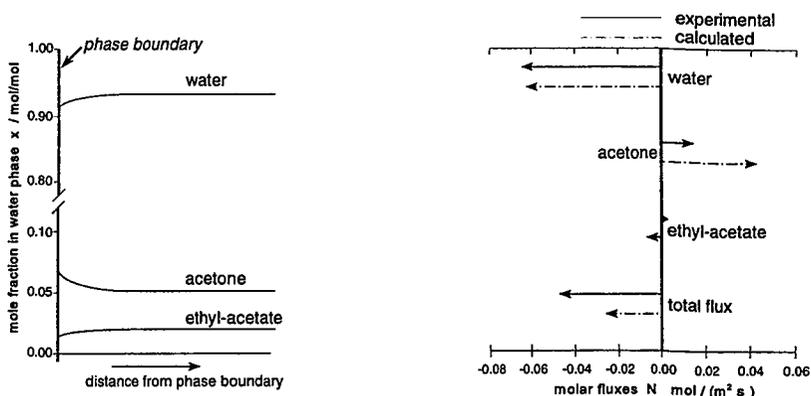


**Figure 3.** Course of the extraction path in the water-phase

size distribution was nearly constant over the whole column height even with a significantly greater hold-up and no indications of interfacial instabilities were registered. Fig. 2 shows the extraction paths for two experiments. Independent of the direction of mass transfer, the extraction paths show a strong tendency towards the binodal line. As soon as the phases reach the state of saturation the extraction paths run along the binodal curve. In the non-saturated area the extraction paths are obviously bent. The tangents to the path deviate considerably from the linking straight line between the bulk concentration and its phase boundary concentration (Fig. 3). This indicates the presence of diffusive coupling effects.

Fig. 4 shows the concentration profiles and the interfacial fluxes of the individual components in the water phase at one sampling point within the

column. The bulk concentrations are directly measured while samples are taken, the concentrations at the phase boundary are determined assuming equilibrium. Comparing the concentration gradients with the direction of the observed fluxes we see that the fluxes of water and acetone follow the direction of the gradients, in contrast to the up-hill transport of ethyl-acetate. This result is reflected qualitatively by our simulation. The calculation was made analogously to the method proposed by Taylor and Krishna (1993). The dependence of the ternary diffusion coefficients on concentration was taken into consideration and the mass-transfer coefficients were calculated using a penetration model.



**Figure 4.** Concentration gradients and calculated local fluxes in the water phase

## CONCLUSION

The extraction paths in a countercurrent spray column were measured in the ethyl-acetate/acetone/water system. If the feed concentration is within the area of undersaturation, we observe bent extraction paths. The paths approach the binodal line in an asymptotic way. The tangents to the paths do not coincide with the linking straight line between the bulk concentration and the pertinent concentration at the phase boundary. From this course we can conclude that, in the area of undersaturation, diffusive coupling effects do appear. Investigating the local component fluxes at the phase boundary, we frequently observe an up-hill transport against the composition driving force. While calculating mass transfer in extraction columns the diffusive interaction must be taken into consideration when the extraction path is within the area of undersaturation.

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## SOLVENT EXTRACTION OF VANADIUM FROM CAUSTIC LIQUORS

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### ABSTRACT

The extraction of  $\text{VO}_4^{3-}$  ion from caustic solutions containing up to 30g/l NaOH is compared using various Aliquat 336.X salts where X= Cl<sup>-</sup>, OH<sup>-</sup>,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ . The carbonate salt provides the highest extraction, but isotherms exhibit an S-shape, which varies with X. This is attributed to changes in vanadium speciation and extractant aggregation in the organic phase.

### INTRODUCTION

In Western Australia, the Coates deposit near Perth is a relatively low grade vanadium-bauxite ore which contains around 30%  $\text{Al}_2\text{O}_3$  and 1% V. At current market prices, it is uneconomic to process this ore for either alumina or vanadium alone, but there is significant value added if vanadium can be recovered from the caustic solutions used to process the alumina. In India, vanadium is often associated with bauxite ores and in the Bayer Process, about 30% of any vanadium is leached into the hot caustic liquor. Here it is concentrated in the recycled process streams and precipitates as an alumina/ vanadium sludge containing 6-20%  $\text{V}_2\text{O}_5$  which must be further processed to recover vanadium (Mukherjee et al.1990; Pattnaik et al.1983;Thakur and Sant,1975). However, this is not a viable option for ores with significant vanadium values.

Clough Resources Ltd therefore undertook to determine the feasibility of applying the Bayer Process and increasing the recovery of vanadium from its Coates deposit. Following successful laboratory trials, the company is currently piloting a novel adaptation of the Bayer Process in which the ore is salt-roasted to maximise the liberation of vanadium, followed by digestion in hot caustic liquors at 140°C. This procedure solubilises about 90% of the alumina and 70% of the vanadium under optimum conditions. Vanadium then must be solvent extracted from the hot caustic leach liquor prior to alumina crystallisation. The concentration of vanadium in the liquor would vary between 1-10g/l V depending on the extent of recycle in the process.

This paper reports on basic studies with synthetic caustic solutions related to this process which has applications to a wider range of materials requiring alkaline leaching. The extractant chosen was Aliquat 336 (Henkel) in Shellsol 2046 diluent containing 5%v/v iso-decanol modifier. Extraction was carried out by mixing the two phases at 25 or 60°C in a water jacketed glass cell over a period

of 2 minutes. The kinetics of extraction of vanadate ion was determined to be fast and equilibrium was reached within 90 seconds

It is beyond the scope of this paper to discuss the overall process flowsheet development and solvent extraction studies with actual leach liquors.

## SOLVENT EXTRACTION OF VANADIUM

### (a) Present Practice.

Vanadium (V) can be readily solvent extracted from slightly acidic or slightly alkaline leach liquors in the pH range 1-10 using tertiary or quaternary amines. Hence solvent extraction has been applied to the reprocessing of spent catalysts in acid media, and to the extraction of vanadium from alkali salt-roasted ores which are leached with water (Ho et al., 1994). In this pH range, vanadium(V) forms a series of polynuclear anionic oxy-vanadium species like  $[V_{10}O_{28}]^{6-}$  (Figure 1) where the number of vanadium atoms per unit charge exceeds 1, thus allowing high organic loadings of vanadium to be achieved with tertiary and quaternary ammonium extractants. Typically, 10% v/v Aliquat 336 loads between 20-30g/l V depending on the pH and exact species extracted (Ho et al., 1994); and this is readily stripped with ammonia/ammonium chloride at pH 9 to produce water insoluble ammonium metavanadate.

However, there has been only one report of vanadium extraction from caustic liquors at pH >12, where the predominate species is vanadate ion  $[VO_4]^{3-}$ , (Ritcey and Lucas, 1979). In this particular study, a chromium bearing alkaline roast-leach liquor containing about 1g/l V required seven stages of extraction with Aliquat 336 to extract the vanadium at pH 13.

### (b) From Caustic Solutions.

The extraction isotherm for vanadium from 10g/l NaOH solution at pH 13.4 shows much lower loadings of vanadium into 10%v/v Aliquat 336 ( $Cl^-$  form) compared to that from solutions at pH 6-11 (Figure 2). It also displays an S-shaped isotherm similar to those at pH 9 and 11. For example, with 1g/l V in the aqueous phase at pH 13.4, there is 2.5g/l V in equilibrium in the organic phase, and 5 stages are required to extract about 60% of the vanadium. The organic loading is about 8 times lower than that at pH 6, but most of this decrease can be attributed to the species extracted and their charge (Figure 1). At pH 6 the V:charge ratio is 2:1, whilst at pH 13 it is 0.33:1. Although the theoretical loading is about 4g/l V, the measured loading of  $[VO_4]^{3-}$  ion is significantly lower due to hydroxide ion competing with vanadate ion. Less than 20% V extraction could be obtained from solutions containing 40g/l NaOH.

Clearly some improvement in this extraction system is required for applications to Bayer liquors which typically contain up to 30g/l free NaOH. Thus the effect of concentration, temperature and counter anion were considered to improve the loading or eliminate the S-shape of the isotherm.

### (c) Effect of Counter Anion with Aliquat 336

The extraction of metals with quaternary ammonium reagents depends on the stability of the ion-pair  $R_4N.X$  and the equilibrium constant for anion exchange. For example, Preston (1982) showed that different anions displaced  $SCN^-$  ion from Aliquat 336 thiocyanate in the order  $SCN^- > NO_3^- > Cl^- > SO_4^{2-} > CH_3COO^-$ .

In this work, the extraction of vanadate ion was measured with various Aliquat 336.X salts, prepared by repeated shake-outs with concentrated Na.X salt solutions. Hence it was found that  $VO_4^{3-}$  was displaced in order by  $X = NO_3^- > VO_4^{3-} > OH^- > Cl^- > SO_4^{2-} > CO_3^{2-}$ . Figure 3 shows the extraction isotherms determined for vanadate ion at 60°C using these Aliquat 336.X salts. It is notable that the S-shape is more significant when  $X = Cl^-$  than when  $X = CO_3^{2-}$  or  $OH^-$ . Thus, although less vanadium is loaded into the organic phase when  $X = OH^-$ , multiple extractions with Aliquat 336 hydroxide leads to better vanadium extraction due to the shape of the isotherm. Overall, however, it is concluded that Aliquat 336 carbonate is the preferred extractant in caustic liquors. For 20%, 10% and 5%v/v Aliquat 336 carbonate, the distribution coefficient for  $VO_4^{3-}$  ion extraction from 10g/l NaOH solution is about 6, 4 and 2 respectively.

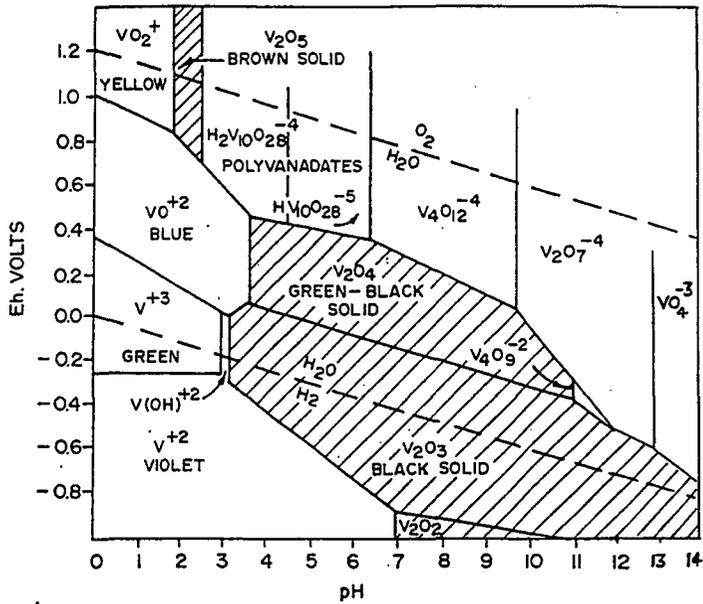


Figure 1. Stability Regions of Vanadium Oxides and Ions at 25°C and 10<sup>-2</sup>M. V. (Adapted from Mukherjee et al. 1990).

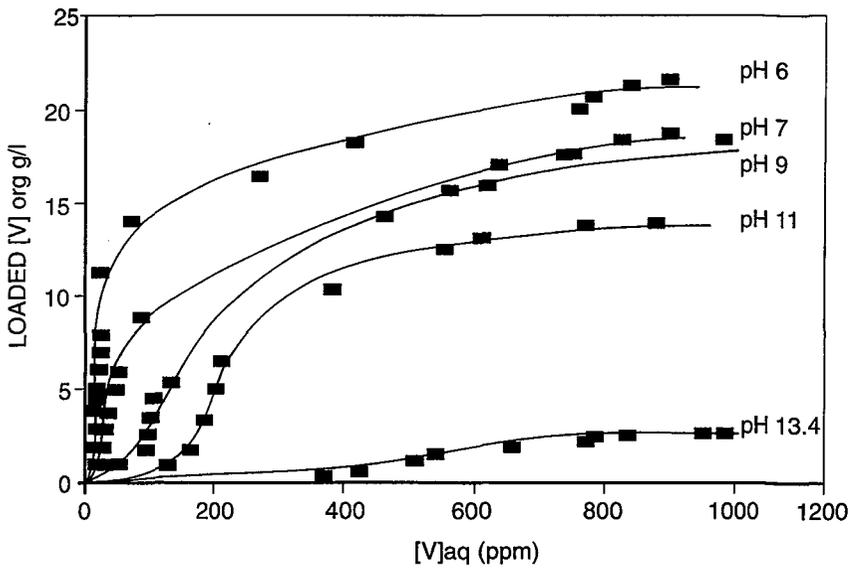


Figure 2. Extraction Isotherms for Vanadium at pH 6-13 using 10%v/v Aliquat 336.Cl. (Ho et al. 1994)

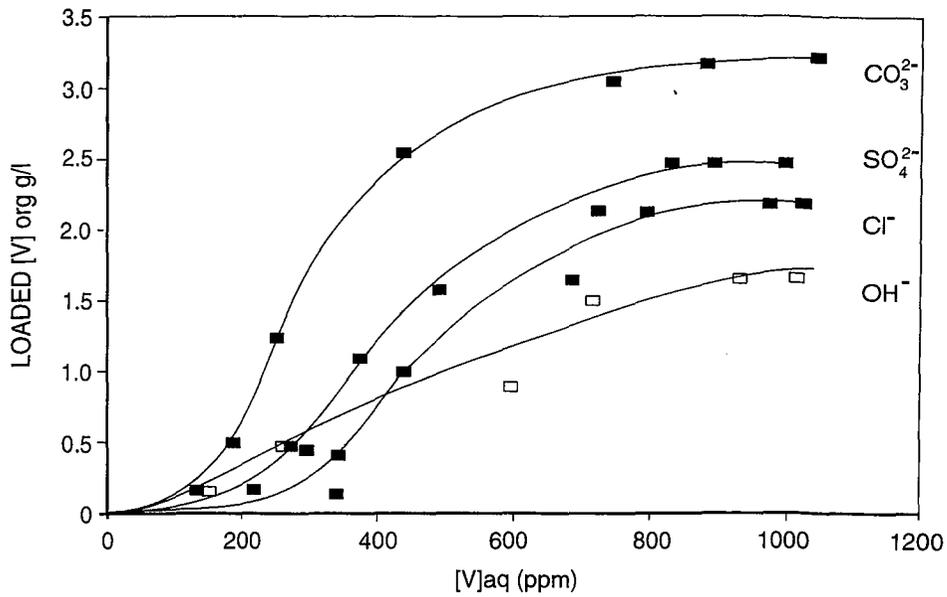


Figure 3. Extraction Isotherms for Aliquat 336.X. at 60°C in the presence of 10g/l NaOH.

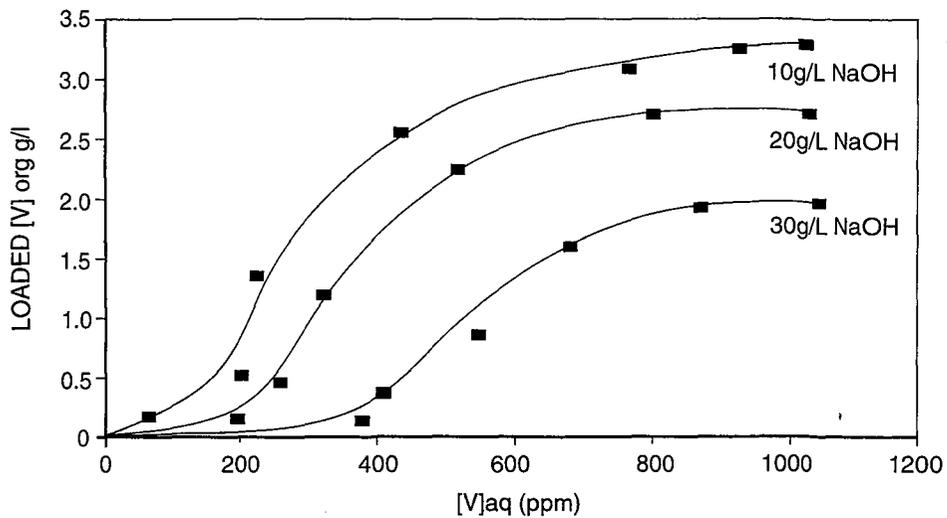


Figure 4. Effect of NaOH Concentration on Vanadium Extraction with 10%v/v Aliquat 336. $\text{CO}_3$  at 60°C.

#### **d) Effect of Caustic Concentration**

The extraction isotherms for vanadium using 10% v/v Aliquat 336 carbonate in the presence of increasing concentrations of free NaOH, are presented in Figure 4. Clearly, competition with OH<sup>-</sup> significantly affects the organic loading of VO<sub>4</sub><sup>3-</sup>, and higher concentrations of Aliquat 336 would be required to readily extract vanadium from liquors containing >30 g/l NaOH. However, even more significant is the increasing S-shape of the isotherm as more OH<sup>-</sup> displaces CO<sub>3</sub><sup>2-</sup>, which restricts the fraction of vanadium which can be extracted in a few stages.

### **DISCUSSION**

The S-shaped isotherm, accounts for the low distribution coefficient and large number of stages required for vanadium extraction. Ritcey and Ashbrook (1979) attributes the shape to either polymerisation of the metal ion species or agglomeration of the extractant in the organic phase. Recent work by Preston (1994) found a similar S-shaped isotherm for cadmium extraction with carboxylic acids and alkane thiol mixtures, which was attributed to an oligomer of six cadmium atoms with bridging organic ligands. The distribution coefficient was shown to increase with a higher concentration of Cd in the aqueous phase. In this work, it would appear that the [VO<sub>4</sub>]<sup>3-</sup> ion in the aqueous phase is extracted into the Aliquat 336 phase as [V<sub>2</sub>O<sub>7</sub>]<sup>4-</sup>.

However agglomeration of the extractant cannot be ruled out. Belaustegi et al.(1993), recently showed that long chain quaternary ammonium salts were strongly or weakly associated in the organic phase depending on the size of the anion. Thus more agglomeration can be expected when the anion is Cl<sup>-</sup> or OH<sup>-</sup> than when it is CO<sub>3</sub><sup>2-</sup> or VO<sub>4</sub><sup>3-</sup>. It follows that as vanadium is loaded into the Aliquat 336, the extractant becomes less aggregated. Likewise there would be more aggregation when OH<sup>-</sup> displaces CO<sub>3</sub><sup>2-</sup> from Aliquat 336 in strong caustic liquors (Figure 5); or when the concentration of Aliquat 336 is increased. During shake-out tests with Aliquat 336 to replace Cl<sup>-</sup> with other anions, it was noted that whilst complete exchange was achieved with 3 contacts using 5%v/v Aliquat 336, only 60% exchange was achieved using 20%v/v indicative of strong extractant association. It is believed that both metal ion polymerisation and extractant association affect the extraction isotherm of this system.

### **CONCLUSIONS**

The extraction of vanadium can be carried out from caustic liquors containing up to 30g/l NaOH using Aliquat 336 carbonate or hydroxide. However, due to competition with hydroxide ion and the S-shaped extraction isotherm complete extraction of vanadium is difficult. Solvent extraction of vanadium from the Bayer Process is best applied to recycled caustic liquors where partial extraction can maintain the vanadium balance.

### **ACKNOWLEDGEMENTS**

Clough Resources Ltd. is thanked for providing a scholarship to S.L. and for its interest in this work which relates to a thesis study at Murdoch University.

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## KINETICS OF EXTRACTION IN TYPICAL AND MICELLAR SYSTEMS

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### ABSTRACT

Kinetics of extraction is discussed and the effect of various chelating ligands and surfactants on metal complexation in aqueous micellar systems is presented. Anionic surfactants accelerate the complexation of metal cations, while nonionic and cationic surfactants retard the process. Depending upon complexing agent hydrophobicity and surfactant type, the complexation can occur mainly in the aqueous pseudophase or micellar pseudophase.

### INTRODUCTION

The kinetics of metal extraction in typical and micellar systems have some similarities and differences discussed in previous works (Szymanowski, 1993, 1994). The both processes can be compared when extraction is kinetically controlled. In typical extraction of metal ions the complexation can occur in the bulk of the aqueous phase or at the interface. The latter mechanism seems dominant for strongly hydrophobic extractants.

Micellar aqueous solutions of various surfactants can be considered as composed from the aqueous pseudophase containing metal ions and the pseudomicellar phase containing an extractant and being able to solubilise the extracted complex. They can also solubilise low molecular alcohols (butanol, pentanol) and hydrocarbons forming O/W microemulsions. The aqueous micellar phase can be treated as the reservoir of extractant and complex and used for separation of trace components, including metal ions. The complexation can occur in the bulk of the aqueous pseudophase or at the micelle border. The latter is, however, less defined than the interface between two extraction phases. The micelles are in dynamic equilibrium with individual molecules with the residence time and the micelle lifetime of the order of  $\mu\text{s}$  and  $\text{ms}$ , respectively.

### DISCUSSION

The rate of metal extraction depends significantly on the hydrophobicity of extractants and can be significantly changed by surfactants as the result of phase transfer catalysis, micelle and reverse micelle formation in the aqueous and organic phase, respectively, microemulsion formation in the organic phase and the interface modification by adsorbed surfactant molecules (Szymanowski, 1994). Similar effects are observed in micellar systems (Table 1) (all references cited in the paper). The rate of complexation falls when the hydrophobicity of the complexing agent increases. Anionic surfactants increase the rate of metal complexation, while nonionic and cationic surfactants retard strongly complexation.

Complexing agent hydrophobicity and type of extractant affect also the location of the complexation step. In micellar media containing anionic surfactants metal cations are attracted by anionic micelles and the complexation can occur both in the bulk of the aqueous pseudophase and in the micellar

pseudophase; the former mechanism becomes dominant for less hydrophobic chelating agents, e.g., 8-hydroxyquinoline, which can be distributed between both phases considered. The hydrophobic extractants are located almost completely in micelles and even mainly in their cores. Thus, there is a high barrier not only for metal cations entering the micelle but also for extractant molecules leaving the micelle, like in the case of 7-(ethyl-1-methyloctyl)-8-hydroxyquinoline. The complexation occurs mainly in the micellar pseudophase. The same concerns the complexation with other hydrophobic compounds given in Table 1.

Cationic micelles repel metal cations and the rate of complexation falls. The complexation occurs mainly in the aqueous pseudophase. Nonionic micelles do not affect the rate of complexation by electrostatic forces but they give a strong resistance to ionic species entering micelles and those of extractant leaving them.

The kinetic model for metal extraction with chelating and acidic extractants must at least take into account the partitioning of complexing agent molecules HL between both pseudophases considered (aqueous, W and micellar, M) (eq. 1), the dissociation of the complexing agent (eq. 2) with partitioning of the ionic species (eq. 3) and the complexation of the metal cations with both forms of chelating agent (eqs 4 and 5). The complexation can occur in the both pseudophases. Moreover the hydrophobic extractants are probably located in the micelle core C and additional equilibrium for the partitioning of the reagent between two pseudophases and the micelle core must be considered. The latter equilibrium becomes especially important when O/W microemulsion is considered, i.e., when the system contains additionally a hydrocarbon and a low molecular alcohol as a co-surfactant.



The double subscript (W,M) means that the reaction can occur in any one of the pseudophases.

Thus, the appropriate constants must be independently determined to model correctly the complexation/extraction in micellar media.

The considered model is very similar to the one in solvent extraction. However, it is impossible at this stage to tell whether the interfacial reaction takes place at the surface of the micelles or in a small volume close to the micellar surface. The latter hypothesis is commonly considered. Thus, this hypothesis is similar to the one in classical solvent extraction which assumes that complexation occurs in a thin aqueous film near the interface. However, in that case the use of adsorption equations (Gibbs, Langmuir, Szyszkowski, etc.) to evaluate the interfacial concentration of extractant is not possible.

TABLE 1  
Complexation in Micellar and Microemulsion Systems. Kinetic studies

Reagent	Metal	Micellar media	Remark	Ref
2,2'-Bipyridyl and 4,4'-dimethyl-2,2'-bipyridyl	Ni(II) pH 7.8- 8.1	Sodium dodecyl sulphate (SDS)	Complexation in micellar pseudophase. Rate enhancement	Reinsbo-rough 1979

Pyridine 2-aza- <i>p</i> -dimethylaniline (PADA)	Ni(II) pH 6.5- 7.7	SDS Sodium decylsulfate AOT/Water/Heptane Microemulsion	Complexation in micellar pseudophase. Concentration of Ni(II) in Stern layer	James 1978, Robinson 1978, Diekmann 1979 Fletcher 1983
Pyridine 2-aza- <i>p</i> -dimethylaniline (PADA)	Co(II)	SDS	Complexation in micellar pseudophase. Enhancement of complexation rate	Fletcher 1984
Pyridine 2-aza- <i>p</i> -dimethylaniline (PADA)	Ni(II) pH 7.9- 8.1 $\mu$ = 0.03M	SDS	Complexation in micellar pseudophase. Enhancement of complexation rate in cmc region	Carbone 1986
Pyridine 2-aza- <i>p</i> -dimethylaniline (PADA)	Ni(II) pH 7.9- 8.1 $\mu$ = 0.03M	Hexadecyltrimethyl ammonium nitrate (CTAN) Ethoxylated octylphenol (Triton X-100)	Complexation in aqueous pseudophase. Stronger inhibition in the presence of CTAN than Triton caused by the stronger hydrophobic binding of PADA to CTAN than to Triton micelles	Carbone 1986
Pyridine 2-aza- <i>p</i> -dimethylaniline (PADA) Ni(dien) <sup>2+</sup>		SDS	Complexation in micellar pseudophase but unfavourable reagent orientation in micelle for quick reaction	Fletcher 1984
Pyridine 2-aza- <i>p</i> -dimethylaniline (PADA) Ni(phen) <sup>2+</sup>		SDS	Complexation in micellar pseudophase but unfavourable reagent orientation in micelle for quick reaction	Fletcher 1984
PAP	Ni(II) pH 7	SDS AOT/Water/Heptane Microemulsion	Complexation in micellar pseudophase. Rate enhancement	Fletcher 1984
1-(2-Pirydylazo)-2-naphthol (PAN)	Ni(II) Zn(II) pH 7.5	SDS AOT/Water/Heptane	Complexation in micellar pseudophase but unfavourable PAN binding into micelle/microemulsion core. Small enhancement or retardation	Fletcher 1984

Murexide	Ni(II) pH 4.0- 7.3	SDS	Murexide anions are repelled from anionic micelles. Complexation in aqueous pseudophase	Fischer 1978, 1980
4-((Alkylcarbonyl)-amino)-2-hydroxybenzoic acid R=C <sub>2</sub> H <sub>5</sub> and C <sub>4</sub> H <sub>9</sub>	Fe(III)	Ethoxylated dodecanol (Brij-35)	Complexation in aqueous pseudophase	Cavasino 1989
8-Hydroxyquinoline (HQ)	Ni(II) pH 6-9	SDS Triton X-100, Brij 35 CTAN	Concurrent complexation by neutral and anionic species in micellar and aqueous phase	Muralidharan 1990
8-Hydroxyquinoline (HQ)	Ni(II) pH 8	Hexadecyltrimethyl ammonium bromide (CTAB)	Complexation in aqueous pseudophase	Kim 1989
8-Hydroxyquinoline (HQ)	Ni(II) pH 7.2- 9.4	SDS/Pentanol/ Dodecane	Complexation mainly in aqueous pseudophase, much quicker than with C <sub>11</sub> -HQ	Tondre 1989
8-Hydroxyquinoline (HQ)	Ni(II) pH 6.5-9	Direct microemulsions in water: - SDS/Pentanol/ Dodecane - SDS/Pentanol/ Toluene - C <sub>12</sub> EO <sub>6</sub> /Decane CTAB/Butanol/ Hexadecane Reverse Microemulsions in Toluene: SDS/Pentanol/Water SDS/Butanol/Water	Complexation much quicker (20-60 times) than with C <sub>11</sub> -HQ and dependent upon nature of microemulsion components and pH	Boumezouid 1989a
7-4-(Ethyl-1-methyloctyl)-8-hydroxyquinoline (C <sub>11</sub> -HQ)	Ni(II) pH 8	CTAB	Complexation much slower than with HQ, mainly in micellar pseudophase	Kim 1989
7-4-(Ethyl-1-methyloctyl)-8-hydroxyquinoline (C <sub>11</sub> -HQ)	Ni(II) pH 7.2- 9.4	SDS/Pentanol/ Dodecane	Complexation much slower than with HQ, mainly in micellar pseudophase	Tondre 1989

7-4-(Ethyl-1-methyloctyl)-8-hydroxyquinoline (C <sub>11</sub> -HQ)	Ni(II) pH 6.5-9	Direct micro-emulsions in water: - SDS/Pentanol/ Dodecane - SDS/Pentanol/ Toluene - C <sub>12</sub> EO <sub>6</sub> /Decane CTAB/Butanol/ Hexadecane Reverse microemulsions in toluene: SDS/Pentanol/Water SDS/Butanol/Water	Complexation much slower (20-60 times) than with HQ and dependent upon nature of microemulsion components and pH	Boumez-ioud 1989
7-4-(Ethyl-1-methyloctyl)-8-hydroxyquinoline	Cu(II) pH 6.5	CTAB/Butanol	Slow kinetics	Tondre 1991
6-(Hexadecylamino)-methyl-2-hydroxy-methylpyridine	Cu(II) pH 3.5	SDS C <sub>12</sub> EO <sub>6</sub> CTAB	Slow kinetics, especially in CTAB	Tondre 1991
6-(Alkylamino)methyl-2-hydroxymethyl-pyridines, R=C <sub>1</sub> -C <sub>16</sub>	Cu(II) pH 2- 5	Aqueous solution without surfactant	Apparent rate constants are weakly dependent on alkyl chain length	Hébrant 1992
6-(Alkylamino)methyl-2-hydroxymethyl-pyridines, R=C <sub>1</sub> -C <sub>16</sub>	Cu(II) pH 3.5	SDS C <sub>12</sub> EO <sub>6</sub> CTAB CTAB/Butanol CTAB/Butanol/ Alkane (C <sub>8</sub> -C <sub>12</sub> )	Apparent rate constants are strongly dependent on alkyl chain length in CTAB and C <sub>12</sub> EO <sub>6</sub> and weakly dependent in SDS	Son 1992
1-(2'-Hydroxy-5'-alkylphenyl)-1-alkanone (E)-oximes (two isomers)	Cu(II) pH 7.2	CTAB	Rate of complexation is higher for 1-(2'-hydroxy-5'-methylphenyl)-1-dodecanone (E)-oxime than for 1-(2'-hydroxy-5'-nonylphenyl)-1-ethanone (E)-oxime	Richmond 1995
6-(Alkylamino)methyl-2-hydroxymethyl-pyridines, R=C <sub>8</sub> -C <sub>16</sub>	Cu(II) pH 3.5	C <sub>12</sub> EO <sub>6</sub> CTAB	Complexation in bulk aqueous phase dominant for CTAB and concurrent complexation in micellar and aqueous phase for SDS	Tondre 1992

## CONCLUSIONS

Micellar systems containing solubilised extractants/complexing agents can be used to transfer metal ions into micelles. The rate of such process depends upon extractant hydrophobicity and surfactant type. Anionic surfactants accelerate the complexation of metal cations, while nonionic and cationic surfactants retard the process. Depending upon complexing agent hydrophobicity and surfactant type the complexation can occur mainly in the aqueous pseudophase or micellar pseudophase. Such process followed by microfiltration can be used to recover and separate metal ions from diluted aqueous solutions.

## ACKNOWLEDGEMENTS

The work was supported by KBN donation for Institute activity DS PP No 32/221.

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## Hydrolysis of TBP AND its EFFECT ON EXTRACTION PROCESS

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### ABSTRACT

The main products of tri-*n*-butylphosphate (TBP) hydrolysis in acid medium are dibutylphosphoric acid (HDBP) and butanol. The investigation of HDBP accumulation in TBP in the presence of various acids and water has shown that the type of acids according to their catalytic effect on TBP hydrolysis, is the following:  $\text{HCl} \gg \text{HNO}_3 > \text{HF} > \text{H}_2\text{SO}_4$ . The rate of TBP hydrolysis is additive for the mixture of HCl and  $\text{HNO}_3$ , and hydrolysis in the presence of HF and  $\text{H}_2\text{SO}_4$  is much more extensive. The calculation of the coalescence constants on the basis of the measurement of residence time of the isolated drop on the flat interface between TBP and  $\text{HNO}_3$  was carried out.  $\text{C}_4\text{H}_9\text{OH}$  and especially HDBP reduce the drop coalescence. HDBP practically does not affect the mass transfer of Zr and rare earth elements (REE) from the aqueous phase, through the flat interface, to TBP if the ratio  $[\text{HDBP}]/[\text{metal}]$  is very slow.

### INTRODUCTION

Tri-*n*-butylphosphate (TBP) is widely used as individual extractant or in the synergistic mixture for solvent extraction in hydrometallurgy. In spite of the known advantages of TBP, it has a significant shortcoming in its ability to degrade through hydrolysis in an acid medium. Hydrolysis involves the destruction of C-O bond and the formation of dibutyl-, monobutyl- and phosphoric acid (in consecutive order) and butanol. Protons of the mineral acids solvate the TBP and act as a catalyst in the process of TBP hydrolysis. Since the acid is connected with phosphoryl group of TBP, and this proton is positioned at a far distance from the C-O bond, hydrolysis of TBP is not extensive in the acid medium (Belsky, 1977). But after a long period of its use a noticeable amount of HDBP and butanol which are the main products of TBP hydrolysis (Kulikov et al., 1985) are produced. It has been shown that the process of TBP hydrolysis leads not only to the loss of the extractant owing to its degradation but also to the slower separation of the mixed phases, due to the formation of strong complexes of extractable metals with dibutylphosphate anion or insoluble substances accumulating at capable to concentrate on the interface (Solovkin et al., 1969). It was proposed that the presence of such compounds in an extraction system could affect the coalescence of drops and the mass transfer of the extractable substances. In the present work the rate of TBP hydrolysis in the presence of different acids has been investigated and an attempt was made to quantitate the influence of the hydrolysis products on the drop coalescence and the mass transfer.

## EXPERIMENTAL

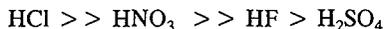
The rate of TBP hydrolysis was estimated from the start of the of hydrolysis. After contacting 100% TBP with aqueous solutions in different acids of various concentration the phases were separated. HDBP concentration in the organic phase was monitored continuously or repeatedly during long period of time by extraction spectrophotometry method. The rate of hydrolysis was calculated as  $\Delta[\text{HDBP}]/\Delta t$ .

The effect of  $\text{C}_4\text{H}_9\text{OH}$  and HDBP on the drop coalescence at equilibrium for the two-phase system of TBP- $\text{HNO}_3$  has been studied by method analogous to the method described by Gillespie and Rideal (1956). The investigated parameter was the residence time of the isolated drops with similar radius on the flat interface. The coalescence constants were calculated from the data of the residence time for the distribution of big number of drops. Mass transfer coefficients for Zr and REE were determined using the Lewis cell. The routine methods of analysis were used to determine the concentration of acids, metals, water. The concentration of F in the mixture of HF and  $\text{H}_2\text{SO}_4$  was determined by ion-selective electrode EF-YI.

## RESULTS AND DISCUSSION

The TBP hydrolysis in the presence of HCl,  $\text{HNO}_3$ , HF,  $\text{H}_2\text{SO}_4$  and the mixtures HCl +  $\text{HNO}_3$  and HF +  $\text{H}_2\text{SO}_4$  has been investigated. The rate of TBP hydrolysis in the presence of each of these individual acids at various concentrations is given in Table 1. The concentration of water in TBP containing various amount of acid is also presented in Table 1. From the data obtained, the approximate values of the rate constant (k) were calculated in assuming that the hydrolysis reaction observes first order both for acid and for water. Such assumption is valid if the predominant extractable compound for the investigated acids under the experimental conditions is monosolvate.

The strict calculation obtained previously for TBP hydrolysis in the presence of  $\text{HNO}_3$  for various compositions of the complexes of  $\text{HNO}_3$  with TBP<sub>3</sub> (Sinegribova et al., 1990) gave the value of k equal  $1.3 \cdot 10^{-6} \text{ mole}^{-1} \cdot \text{h}^{-1} \cdot \text{dm}^3$ . The approximate values of k presented in Table 1 may be used to relate the catalytic action of the different acids on TBP hydrolysis. The order of the catalytic effect is the following:



This order indicates that the protonated acid species of HCl in organic phase are the most effective catalyst of the TBP hydrolysis. The hydrolysis of TBP in acid also depends on the strength of the complex. The rate of hydrolysis in the presence of mixtures of acids ( $\text{HNO}_3 + \text{HCl}$ ,  $\text{H}_2\text{SO}_4 + \text{HF}$ ) is given in Table 2.

**TABLE 1**  
Rate of HDBP formation (W) and concentration of water at various  
concentration of mineral acid (HA) in TBP

HCl, $k \sim 1.7 \cdot 10^{-5} \text{ mole}^{-1} \cdot \text{h}^{-1} \cdot \text{dm}^3$								
[HA], mole/dm <sup>3</sup>	0.12	0.20	0.34	0.47	0.62	0.79	1.14	1.34
[H <sub>2</sub> O],mole/ dm <sup>3</sup>	3.95	4.20	4.70	5.30	5.50	6.40	7.44	7.72
W*10 <sup>5</sup> ,mole/ dm <sup>3</sup> .h	1.7	2.10	2.50	4.76	5.16	9.70	10.1	11.5
HNO <sub>3</sub> , $k \sim 1.9 \cdot 10^{-6} \text{ mole}^{-1} \cdot \text{h}^{-1} \cdot \text{dm}^3$								
[HA], mole/ dm <sup>3</sup>	0.80	1.18	1.60	2.10	2.80	3.26	3.80	4.10
[H <sub>2</sub> O],mole/ dm <sup>3</sup>	3.35	3.08	2.60	2.17	1.52	1.22	1.24	1.35
W*10 <sup>6</sup> ,mole/ dm <sup>3</sup> .h	6,6	7.45	9.08	8.90	7.15	5.41	7.60	9.50
HF, $k \sim 4.3 \cdot 10^{-7} \text{ mole}^{-1} \cdot \text{h}^{-1} \cdot \text{dm}^3$								
[HA], mole/ dm <sup>3</sup>	0.94	1.25	1.60	2.14	2.75	2.97	3.40	3.64
[H <sub>2</sub> O],mole/ dm <sup>3</sup>	3.97	4.05	4.17	4.20	4.00	3.84	3.50	3.35
W*10 <sup>6</sup> ,mole/ dm <sup>3</sup> .h	0.7	1.87	2.38	3.16	4.90	6.05	6.55	7.20
H <sub>2</sub> SO <sub>4</sub> , $k \sim 1.1 \cdot 10^{-7} \text{ mole}^{-1} \cdot \text{h}^{-1} \cdot \text{dm}^3$								
[HA], mole/ dm <sup>3</sup>	0.65	1.20	1.55	1.98	2.16	2.42	2.67	2.90
[H <sub>2</sub> O],mole/ dm <sup>3</sup>	5.16	5.50	5.41	5.33	5.25	5.12	4.95	4.70
W*10 <sup>7</sup> ,mole/ dm <sup>3</sup> .h	5.2	7.30	8.80	10.9	13.0	16.1	18.6	20.7

The effect of a mixture of HNO<sub>3</sub> and HCl on the TBP hydrolysis appeared to be additive but a mixture of HF and H<sub>2</sub>SO<sub>4</sub> is more effective than each of the individual acids.

This phenomenon is caused by the change in the activity of the mixed acids solution due to decreasing water content. The enhancement of activity was the most prominent for H<sub>2</sub>SO<sub>4</sub> under present experimental conditions.

**TABLE 2**  
Effect of combination of acids on rate of TBP hydrolysis

Aq. phase, mole/dm <sup>3</sup> initial		Organ. phase, mole/ dm <sup>3</sup> equilibrium			Rate of TBP hydrolysis, mole/ dm <sup>3</sup> ·h
[HNO <sub>3</sub> ]	[HCl]	[HNO <sub>3</sub> ]	[HCl]	[H <sub>2</sub> O]	
1.00	6.00	0.72	0.75	4.20	4.1*10 <sup>-5</sup>
2.00	6.00	1.71	0.14	2.55	3.8*10 <sup>-5</sup>
3.00	5.00	2.14	0.05	1.64	1.0*10 <sup>-5</sup>
1.50	-	0.71	-	3.39	6.2*10 <sup>-5</sup>
-	3.62	-	0.79	6.40	9.7*10 <sup>-5</sup>
3.25	-	1.73	-	2.50	1.0*10 <sup>-5</sup>
-	1.51	-	0.12	3.95	1.7*10 <sup>-5</sup>
5.65	-	2.14	-	2.12	9.3*10 <sup>-5</sup>
-	1.00	-	0.05	3.70	5.0*10 <sup>-5</sup>
[H <sub>2</sub> SO <sub>4</sub> ]	[HF]	[H <sub>2</sub> SO <sub>4</sub> ]	[HF]	[H <sub>2</sub> O]	
8.00	1.00	1.93	0.47	4.32	3.3*10 <sup>-4</sup>
8.00	2.00	1.71	0.91	2.54	2.6*10 <sup>-4</sup>
8.00	3.00	1.44	1.95	1.24	9.8*10 <sup>-5</sup>
8.00	4.00	1.21	2.58	0.66	7.5*10 <sup>-5</sup>
5.70	-	1.20	-	5.50	7.3*10 <sup>-7</sup>
9.95	-	1.98	-	5.33	1.1*10 <sup>-6</sup>
-	1.95	-	0.94	3.95	7.0*10 <sup>-7</sup>
-	5.00	-	1.95	4.25	3.0*10 <sup>-6</sup>
-	8.50	-	2.61	4.01	4.7*10 <sup>-6</sup>

The influence of TBP hydrolysis products on the stability of the organic drops on the flat interface in two-phase equilibrium system of TBP - HNO<sub>3</sub> (3 mole/dm<sup>3</sup>) has been investigated. The data obtained were analyzed on the basis that a film was formed between the drop and the interface and this film drained unevenly. Rupture of the film leading to coalescence is a statistical process. The residence time of ~100 drops was measured. Dependence of ln N/N<sub>0</sub> on t, where N - a number of drops with life time t, N<sub>0</sub> - total number of drops, is shown in Fig.1. From this data t<sub>0</sub>, time without coalescence for all drops, was found. According to (Gillespie and Rideal, 1956), if a film between the drop and the interface drains unevenly:

$$\log N/N_0 = -K \cdot (t - t_0)^{3/2}, \text{ where } K - \text{the coalescence constant.}$$

Dependence of log N/N<sub>0</sub> on the value of (t - t<sub>0</sub>)<sup>3/2</sup> for the investigated systems is given in Fig.2.

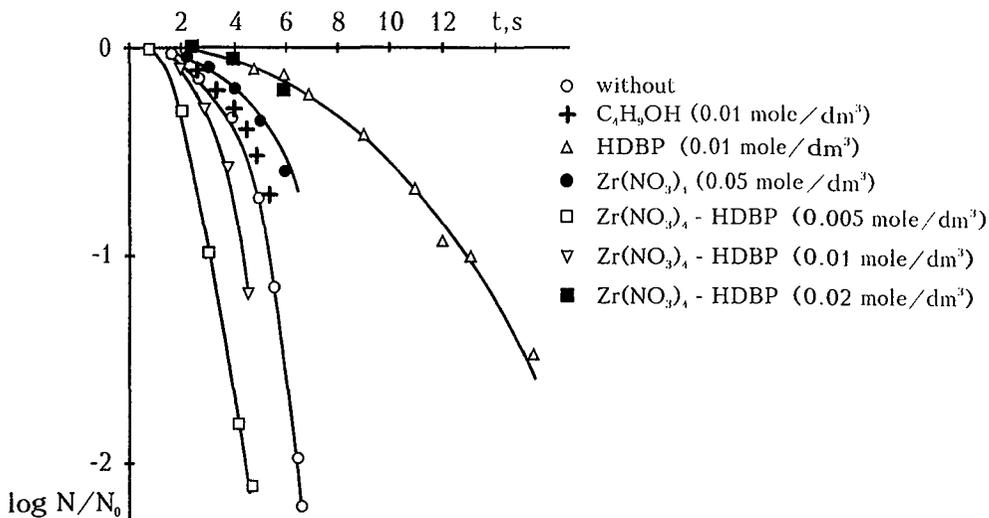


Figure 1. Influence of admixtures on stability of TBP drops at TBP-HNO<sub>3</sub> interface. [HNO<sub>3</sub>]=3 mole/dm<sup>3</sup>; drop radius 2.3x10<sup>-3</sup>m.

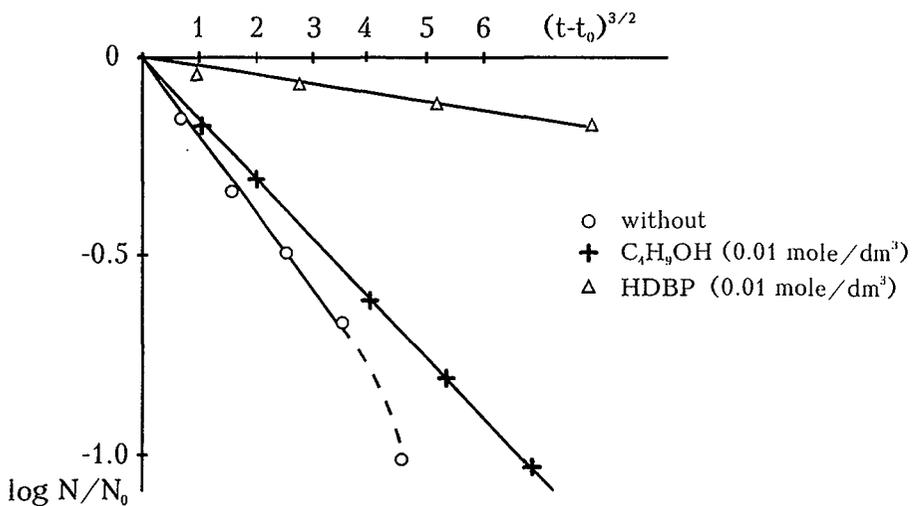


Figure 2. Effect of admixtures on proportionality between  $\log N/N_0$  and  $(t-t_0)^{3/2}$  for TBP drops at TBP-HNO<sub>3</sub> interface. [HNO<sub>3</sub>]=3mole/dm<sup>3</sup>; drop radius 2.3x10<sup>-3</sup>m.

The data of Fig.1 indicate that the addition of  $C_4H_9OH$  and especially HDBP to TBP leads to a decrease of the rate of drop coalescence. The coalescence constants calculated from data of Fig.2 are 0.180 for TBP -  $HNO_3$ , 0.150 - in the presence of butanol and 0.014 in the presence of HDBP. For high values of  $t$ , when the film between a drop and the interface becomes very thin, the plot for the system TBP -  $HNO_3$  ceases to be linear due to the possible electric double-layer repulsion and electroviscous effects. The solvates of  $HNO_3$  with TBP act as a stabilizing agent. It is proposed that these solvates are characterized by some surfactive properties. In the presence of surfactive butanol and HDBP which displaces the  $HNO_3$  \*TBP solvates on the surface, the plot is linear at all intervals of time (Fig.2). The presence of zirconium nitrate in TBP -  $HNO_3$  system delays the drop coalescence but if the also system contains HDBP, the rate of drop coalescence depends on the ratio of HDBP and zirconium nitrate (Fig.1). The reason of the high rate of coalescence at the ratio of HDBP : Zr  $\sim$  2 is probably due to the formation of non surfactive  $Zr(NO_3)_2DBP_2$  (Solovkin et al., 1969). At higher ratio, the concentration of HDBP on the interface increases and the life time of drops at the interface grows.

The low HDBP concentration does not affect practically on the mass transfer of La, Sm, Y, Zr from nitrate solution into TBP in the Lewis cell (Table 3).

**TABLE 3**

Effect of HDBP on the mass transfer coefficient ( $K_y$ )

$[La]_{aq} = 0.8 \text{ mole/dm}^3$ ;  $[Sm]_{aq} = 1.0 \text{ mole/dm}^3$ ;  $[Y]_{aq} = 0.7 \text{ mole/dm}^3$   
 $[Zr]_{aq} \text{ in } HNO_3 (4 \text{ mole/dm}^3) = 0.3 \text{ mole/dm}^3$

[HDBP],mole/dm	Mass transfer coefficient K , m/s			
	Lanthanum	Samarium	Yttrium	Zirconium
0	$7.5 \cdot 10^{-6}$	$9.8 \cdot 10^{-6}$	$7.4 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$
0.005	$8.4 \cdot 10^{-6}$	$1.2 \cdot 10^{-5}$		$1.3 \cdot 10^{-6}$
0.010	$8.8 \cdot 10^{-6}$			
0.015	$8.6 \cdot 10^{-6}$		$8.2 \cdot 10^{-6}$	

It should be noted that in all the experiments with HDBP and metals perfoed in this work, a visible film on the interface was not observed.

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## PREDICTION OF FLUID DYNAMICS AND MASS TRANSFER IN SOLVENT EXTRACTION COLUMNS WITH STRUCTURED PACKINGS BASED ON SINGLE DROP EXPERIMENTS

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### ABSTRACT

Single drop experiments were carried out to investigate the drop motion, break-up and mass transfer in pulsed and nonpulsed extraction columns with structured packings. Drop velocity and break-up parameters as well as the single drop mass transfer coefficient were determined in dependence on the drop size and pulsation energy input. Based on these single drop parameters obtained in a laboratory scale apparatus, the fluid dynamics and mass transfer performance of the extraction columns on a pilot scale may be predicted with a simplified drop population balance model.

### INTRODUCTION

Several advantages of the structured packings have led to an increasing use of this type of column packings in solvent extraction processes. In particular the structure of the packing allows a high phase throughput in addition to a good separation efficiency due to the reduced backmixing. As there is almost no basic information available on the fluid dynamic and mass transfer behaviour of the extraction columns with structured packings, the design of this type of column is still based on extensive and, therefore, expensive pilot tests.

Fundamental investigations in single drop experiments provide a chance to reduce the extent of pilot tests required for the design of extraction processes. The information obtained from simple single drop experiments in laboratory-scale standard apparatus supplies the basic data required for modelling and may be used to predict the behaviour of the extraction columns. The effects of impurities or surfactants etc. on the fluid dynamics and mass transfer may be taken into account by drop experiments carried out with the original substance to be used in the process. As shown by different authors (Haverland (1988), Qi (1992), Hoting, Qi and Vogelpohl (1993)), this scale-up method is suitable for the prediction of the fluid dynamic and mass transfer behaviour of the sieve plate extraction columns. In recent investigations this modelling concept is also used for the description of fluid dynamics in columns with structured packings (Leu and Vogelpohl (1993), Leu (1995)).

To expand the knowledge on fluid dynamics and mass transfer in columns with structured packings, experimental studies were carried out with standard test systems without mass transfer and under mass transfer conditions. In different single drop experiments, the drop velocity and break-up parameters were determined in dependence on drop size and pulsation intensity as well as the single drop mass transfer coefficient in the presence of structured packings. Based on these simple single drop experiments, drop size distribution profiles and hold-up profiles along the column may be predicted by using a drop population balance model. Continuous and dispersed phase concentration profiles are computed also with the drop population model in combination with the axial dispersion model. The computed results are confirmed by experimental data from pilot scale columns.

## SINGLE DROP EXPERIMENTS

The single drop experiments were carried out in a laboratory-scale standard apparatus with the standard test systems butyl acetate(dispersed)/acetone/water and toluene(dispersed)/acetone/water as recommended by Misek, Berger and Schröter (1985). The main part of such a standard apparatus is a characteristic compartment of the type of column to be used in practice. For columns with structured packings a characteristic compartment is given by a single packing element. The single drop studies presented in this paper were carried out with structured packings of the type Montz Pak B1® with a specific surface of 350 m<sup>2</sup>/m<sup>3</sup>, lamella angle of 45 °, an element height of 190 mm and punched with holes with a diameter of 4 mm (M S350/A45/H190/P4). The system used was butyl acetate(dispersed)/acetone/water. The experimental results are shown in Fig. 1.

### Single Drop Velocity

A basic parameter in the modelling of fluid dynamics in the extraction apparatus is the drop velocity in dependence on the drop size. In general, the calculation of the slip velocity is based on the characteristic velocity of the freely rising drop. For the investigated system butylacetate(dispersed)/water the general dependency of the droplet velocity on the drop size is observed, but the results confirm the importance of basic measurements as commonly used correlations may not be suitable to describe the detailed dependency as shown, for example, for the relation given by Hu and Kintner (1955). The drop velocity in the packing is reduced due to the influence of friction and impacts. In the packing the dependency of the drop velocity on the drop size is reduced especially because the motion of large drops is hindered. In comparison to the velocity of freely rising droplets, the maximum of the velocity is shifted to smaller drop diameters. As shown in Fig. 1 for this system, no influence of the pulsation on the drop velocity in the packings was found. For modelling the drop velocity inside the packing a concept developed by Leu (1995) is used. Based on a detailed physical description of the drop movement in packings the drop velocity is calculated in dependence on the packing geometry and the characteristic velocity of the freely rising drop. Required parameters are determined from the experimental single drop data.

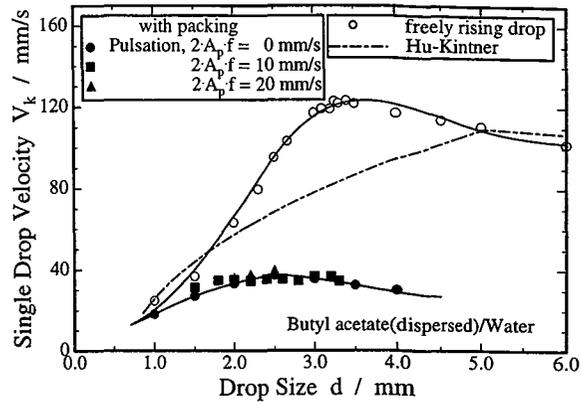
### Break-up Parameters

When passing a characteristic column compartment, in this case a single packing element, different droplet behaviour is observed in dependence on drop size and pulsation energy input. For characterising the break-up behaviour a special diagram is used as shown in Fig. 1. In general two main regions 'no break-up' (region A) and 'total break-up' (region B) as well as an intermediate region 'partial break-up' (region AB) are found. In region A the interfacial forces stabilising the droplet can not be overcome by the forces caused by the impact with the packing structure and, thus, no drop breakage occurs ( $p = 0$ ). In region B the resulting forces cause a droplet break-up in each case ( $p = 1$ ). While the drop behaviour in the main regions A and B is clearly determined, the stochastic behaviour in the intermediate section AB must be described by using a break-up probability  $0 < p < 1$ . The single drop experiments supply the basic parameters required for the modelling of drop breakage. These parameters are the maximum stable drop diameter and the minimum diameter of total break-up characterising the region AB in dependence on the pulsation intensity as well as the break-up probability and the daughter drop size distribution resulting from the droplet breakage. The drop breakage is affected by the mass transfer. In systems with a negative gradient of the interfacial tension  $d\sigma/dx$ , as given for the investigated system, the changed system properties due to the presence of the transferred component as well as interfacial disturbances caused by the mass transfer decrease drop stability. Therefore, the characteristic drop diameters are lowered under mass transfer conditions.

### Single Drop Velocity

Parameter

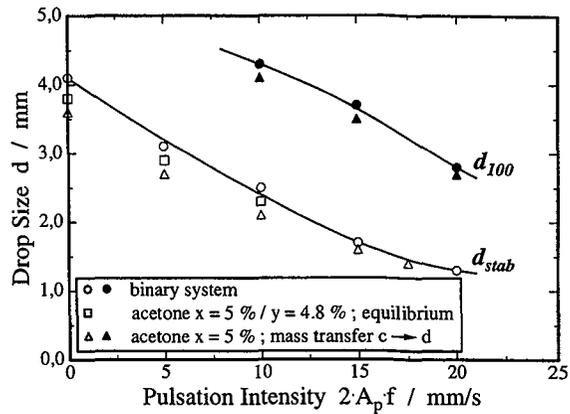
- velocity, freely rising drop  $V_{k,o}(d)$
- velocity with internals  $V_k(d)$



### Single Drop Break-up

Parameter

- max. stable drop diameter  $d_{stab}$
- min. diam., total break-up  $d_{100}$
- break-up probability  $p(d)$
- daughter drop distribution  $q_{dd}(d_{da}, d)$



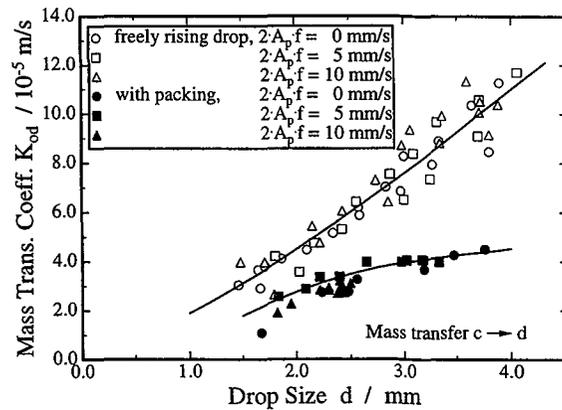
### Single Drop Mass Transfer

Parameter

- mass transfer coefficient  $K_{od}(d)$

as defined by:

$$\dot{w} = K_{od} a_p v_p \rho_d (y^*(x) - y)$$



**System:** Butyl acetate(dispersed)/Acetone/Water

**Packing:** Montz Pak B1® 350 (M S350/A45/H190/P4), nominal diameter 80 mm

**Fig. 1:** Single drop parameters, experimental results

### Single Drop Mass Transfer Coefficient

According to the Maxwell-Stefan-equation, the mass flux of each component in a multi-component system depends in a complex way on the molar concentrations of all other components and their diffusivities. Thus for practical reasons, the Maxwell-Stefan-equation is not suitable for modelling mass transfer in extraction columns. Therefore, the mass transfer is often described in the simplified form using an overall mass transfer coefficient as shown in Fig. 1. In single drop experiments the average mass transfer coefficient for the dispersed phase was determined for a freely rising droplet as well as in the presence of a packing in dependence on drop size and pulsation intensity. In all cases the mass transfer rate increases with increasing drop diameter and no influence of pulsation was found for the investigated system. One reason for lower mass transfer coefficients observed in the presence of the packing is the reduced drop velocity. In addition, the mass transfer is reduced because the formation of the wake in the rear of the droplets is hindered by the way of drop motion gliding along the flanks of the lamella.

### MODELLING

The modelling of the fluid dynamics and the mass transfer behaviour of an extraction column with structured packings is based on a simplified drop population balance model as presented by Haverland (1988). If the influence of coalescence is negligible, the drop size distribution  $q_{3,n}(d)$  above a packing element  $n$  may be calculated from the distribution below this element  $q_{3,n-1}(d)$  using break-up probabilities  $p(d)$  and resulting daughter drop size distributions  $q_{3,dd}(d)$  determined in single drop experiments

$$q_{3,n}(d) = q_{3,n-1} - p(d) \cdot q_{3,n-1}(d) + \int_d^{d_{\max}} p(d^*) \cdot q_{3,n-1}(d^*) \cdot q_{3,dd}(d^*, d) \delta d^* \quad (1)$$

Starting from a measured or calculated inlet distribution, the drop size profile may be determined. Using the relationship between slip velocity, hold-up and phase velocity, as given by eq. (2) for a polydispersed drop size distribution

$$\frac{V_c}{1 - \Phi} + \frac{V_d}{\Phi} = \sum V_{slip,i} \cdot q_3(d_i) \cdot \Delta d \quad (2)$$

and the slip velocity between the drop class  $i$  (class width  $\Delta d$ ) and the continuous phase

$$\frac{V_{d,i}}{\Phi_i} + \frac{V_c}{1 - \Phi} = V_{slip,i} = V_{k,i} (1 + \Phi) \quad \text{with} \quad V_{d,i} = V_d \cdot q_3(d_i) \cdot \Delta d \quad (3)$$

the cross-sectional hold-up  $\Phi$  and the hold-up of each class  $\Phi_i$  may be computed by iteration with the drop swarm velocity derived from the characteristic single drop velocity in the packing. Caused by the restricted mobility in the packing and a drop motion along an exactly defined direction given by the packing geometry, neighbouring drops are rising in groups which are remaining in a stable configuration over a certain period. In opposite to the known results from other types of extraction columns the swarm velocity in structured packings may be enhanced because the drag coefficient of a group of moving drops is reduced compared to the drag coefficient of a single drop. The number of drops rising in a group increases with increasing hold-up, therefore the influence of the swarm on the drop velocity is correlated by the factor  $(1 + \Phi)$ . Computed drop size and hold-up profiles are shown in Fig. 2 in comparison with experimental data from pilot column studies.

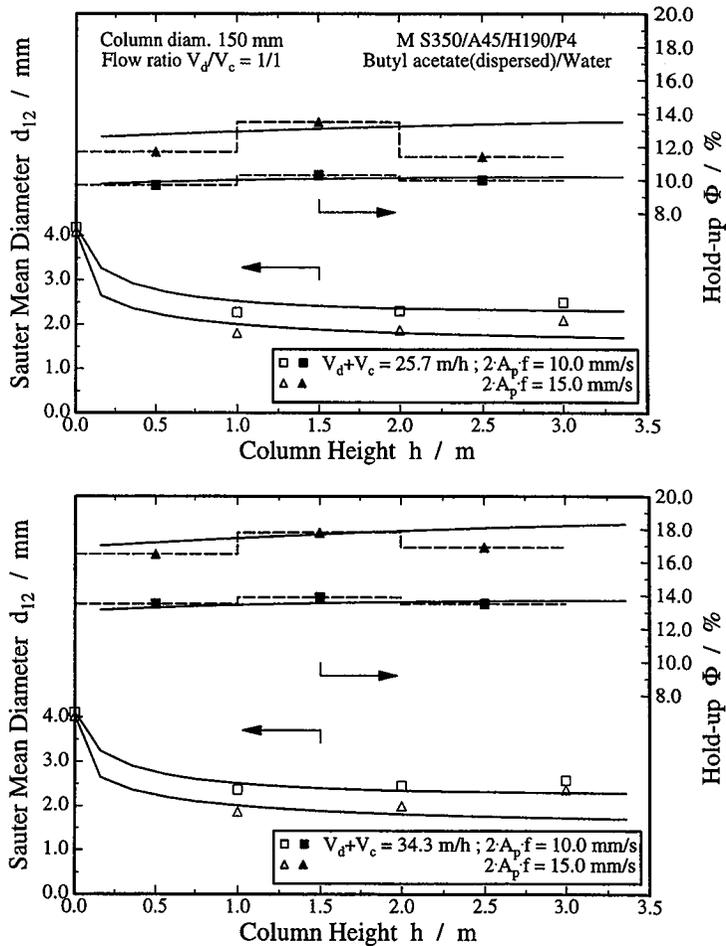


Fig. 2: Computed drop size and hold-up profiles in comparison with experimental data

The calculation of mass transfer performance is based on mass balances for a differential column cross section with the volume  $dv$ , using computed drop size distributions and hold-up profiles as shown above. The mass transfer from the continuous into the dispersed phase is considered for each class of drop sizes with the mass transfer coefficient determined in the single drop experiments

$$\dot{w} = \sum \dot{w}_{d,i} = \sum K_{od,i} \frac{6\Phi_i}{d_i} \rho_d (y^*(x) - y) dv . \quad (4)$$

Using the one dimensional dispersion model the backmixing in the continuous phase is described with an axial dispersion coefficient determined in pilot scale columns. With the resulting system of differential equations the concentration profiles of both phases may be calculated using the Runge-Kutta-procedure e.g.. Further details of the calculation of concentration profiles are presented in

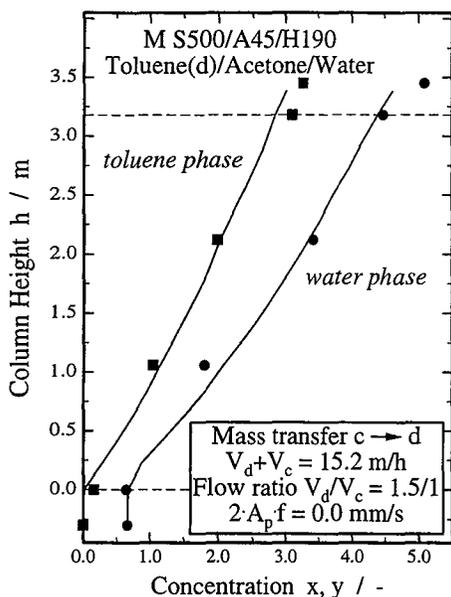


Fig. 3: Comparison of computed concentration profiles with experimental data

packings the scale-up method based on basic information on drop motion, break-up and mass transfer obtained from suitable single drop experiments may be used to predict the fluid dynamics as well as the mass transfer performance of extraction columns.

#### NON-STANDARD NOMENCLATURE

$d_{stab}$	maximum stable drop diameter (m)
$d_{100}$	minimum diameter, total break-up (m)
$\Delta d$	class width (m)
$q_{3,dd}$	daughter drop size volume distribution (1/m)
$q_3$	drop size volume distribution (1/m)
$w$	mass flow rate (kg/s)

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Hoting, Qi and Vogelpohl (1993). Fig. 3 shows computed concentration profiles of the continuous and the dispersed phase based on single drop parameters obtained in this study in comparison with experimental data taken from the literature. The results are shown for a column with structured packings of the type Montz Pak B1® with a specific surface of 500 m<sup>2</sup>/m<sup>3</sup> and the system toluene(dispersed)/acetone/water.

The comparison of computed drop size, hold-up and concentration profiles with experimental results shows that single drop parameters obtained in simple experiments in a laboratory-scale standard apparatus may be used to predict the fluid dynamics and the mass transfer in pulsed extraction columns with structured packings adequately.

#### CONCLUSION

As shown by the presented investigation carried out for columns with structured



## MASS TRANSFER STUDY OF $\text{Er}^{3+}$ IN HEH/EHP-HCl WITH LAMINAR FLOW CELL

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### ABSTRACT

The mass transfer and kinetics of  $\text{Er}^{3+}$  in the 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH/EHP or HL) -kerosene -HCl system have been investigated by using a constant interfacial area cell with laminar flow. The results have been interpreted according to two alternative models: (a) the mass transfer rate is controlled by interfacial film diffusion and (b) the mass transfer is controlled by a slow reversible interfacial reaction. The diffusion of the unsaturated complexes from the interface to the bulk organic phase is the rate controlled step for the conditions: HL concentration  $3 \times 10^{-2} \sim 1 \times 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$ ;  $\text{Er}^{3+}$  concentration  $3 \times 10^{-3} \sim 1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ;  $\text{pH} = 1.7 \sim 2.5$  and temperature  $25^\circ\text{C} \sim 55^\circ\text{C}$ . The diffusion mechanisms suggests that  $(\text{ErL}_2)_n$  is formed in the interfacial layer to retain the mass transfer rate and diffused into the organic phase. A reversible chemical reaction  $[\text{Er}(\text{OH})_n^{m+} \leftrightarrow \text{Er}^{3+} + \text{OH}^-]$  is believed to be the rate controlling step for the same conditions except  $\text{pH} = 2.5 \sim 6$ . The observed activation energy is  $E_a = 42.11 \text{ kJ} \cdot \text{mol}^{-1}$ , and the rate equation is  $R = K[\text{Er}^{3+}]^{0.1920} [\text{HL}]^{0.8412}$

**Key words:** diffusional mass transfer, erbium, HEH/EHP, kinetics, Lewis cell, laminar flow.

### INTRODUCTION

Mass transfer and kinetics are very important factors in solvent extraction chemistry. Research on these topics is helpful for the extraction process. Acidic organophosphorous extractants are commercial extractants with great selectivity for lanthanide separation. The HEH/EHP-kerosene-HCl-RE(III) extraction system is widely employed in the rare earth separation process. In the industrial process, the mixing time in the heavy rare earth extraction stages is long and sometimes, equilibrium has not been reached, which makes the process unsatisfactory. Therefore, it is meaningful to study heavy rare earth extraction kinetics. Some reports on the mass transfer and kinetics in the system were published by using different methods. (Danesi, P. R., Vandegrift, G. F., 1981; Minagawa, Y., Yamaguchi K., 1990; Yue Santang and Li Deqian, 1990) And some other reports on the mass transfer and kinetics in the Co and Ni extraction system were published by using a different modified Lewis cell. (Dreisinger D. B. and Charles Cooper W., 1989) Different results were obtained. In this paper, the mass transfer and kinetics in the  $\text{Er}^{3+}$ -HCl-HEH/EHP-kerosene system have been studied by using a constant interfacial area with laminar flow. (Zheng Zhong and Li Deqian, 1996) The investigation has been aimed at obtaining information on the rate control step. This information provides an understanding of the mechanism of mass transfer in the system.

### EXPERIMENTAL

#### Apparatus

Figure 1 shows a schematic diagram of the apparatus. The cell was cubic in shape. The volume of

each compartment is  $96\text{cm}^3$ . The interfacial area is  $15\text{cm}^2$ . The linear velocity which was determined by tracing technique was employed to judge the mass transfer rate. The interface was quiescent as the result of no flow towards the interface. The operation was carried out under laminar flow. Two stirrers were used whose maximum rotation speed (100~500 rpm) is limited such that the interface remains quiescent. The diffusion theory and hydrodynamics was employed to analyze the system.

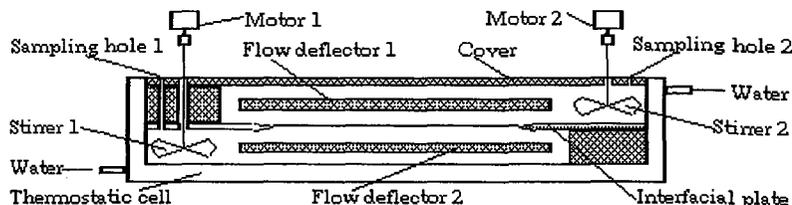


Fig. 1 the schematic diagram of the cell

When the velocity near the interface is the same in each phase, a typical mass transfer equation is derived.

$$N^* = 0.5303D^2(C_1 - C) \cdot D^{\frac{1}{2}} \cdot \left(\frac{V}{L}\right)^{\frac{1}{2}} \quad (1)$$

The equation is the same as that derived by L. E. Scriven and R. L. Pigford, 1969 using liquid-liquid jet reactor (LLJR) equipment except for the constant.

#### Reagent

HEH/EHP was purified as reported earlier (Komatsu Y., Freiser H., 1989).  $\text{Er}_2\text{O}_3$  purity was 99.99%. Kerosene was sulfonated and washed with distilled water to  $\text{pH}=4$  and then the  $170^\circ\text{C}\sim 250^\circ\text{C}$  distillation fraction was collected. Other reagents were analytical grade and purchased from Beijing Chemical Engineering Factory.

#### Procedure

The aqueous phase was added into the cell, mixed and kept at a constant temperature for 30 minutes, then the organic phase which was kept at the same temperature for 30 minutes was added into the cell and the test was started. The samples were taken at 5~10 minute intervals, and the aqueous samples were analyzed by titration using EDTA. 6~10 samples were taken in a run. The data were processed by using regression analysis to calculate the extraction rate (N).

### RESULTS AND DISCUSSION

When the temperature is constant, the extraction rate can be expressed as below.

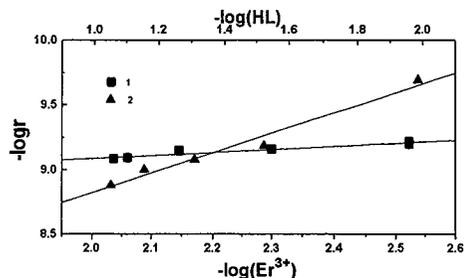
$$r = K[\text{Er}^{3+}]_{(a)}^a \cdot [\text{HA}]_{(o)}^b \cdot [\text{H}^+]_{(a)}^c \quad (2)$$

Keeping [HL],  $[\text{H}^+]$  and T constant, and plotting the  $\lg r - \lg[\text{Er}^{3+}]_{(o)}$  graph, gives  $a=0.1920$ . Keeping  $[\text{H}^+]$ ,  $[\text{Er}^{3+}]$  and T constant, and plotting the  $\lg r - \lg[\text{HL}]$  graph, gives  $b=0.8411$ . Therefore, we can get the equation below for  $\text{pH}=1.78$ .

According to the Arrhenius's equation

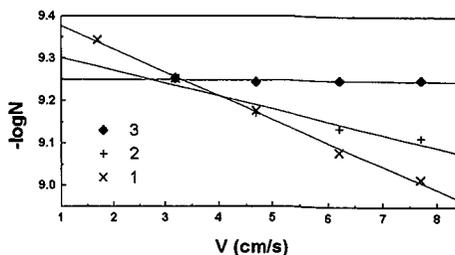
$$\log K = -\frac{Ea}{2.303R} \cdot \frac{1}{T} + C \quad (3)$$

Where C is a constant. Plotting the  $\lg L-T^{-1}$  graph, gives the activation energy  $E_a=42.11 \text{ KJ}\cdot\text{mol}^{-1}$ . Figure 2 shows the effect on the extraction rate of the concentration of the two phases. Line 1 demonstrates the effect of the HL concentration change in the organic phase, and line 2 demonstrates the effect of the  $\text{Er}^{3+}$  concentration change in the aqueous phase. It is known that the effect of the [HL] concentration change on the mass transfer rate is stronger than the effect of the  $\text{Er}^{3+}$  concentration change under the same conditions.



$s=2.5 \times 6 \text{ cm}^2$ ;  $T=30^\circ\text{C}$   
 Aque:  $\text{PH}=1.78$ ;  $V_a=3.2 \text{ cm}\cdot\text{s}^{-1}$   
 org:  $V_o=3.2 \text{ cm}\cdot\text{s}^{-1}$

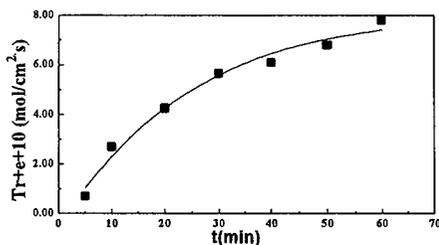
Fig. 2 The effect on the rate of concentration



$s=2.5 \times 6 \text{ cm}^2$ ;  $T=25^\circ\text{C}$   
 Aque:  $\text{PH}=1.78$ ;  $C_a=3.0 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$   
 org:  $C_o=3.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$

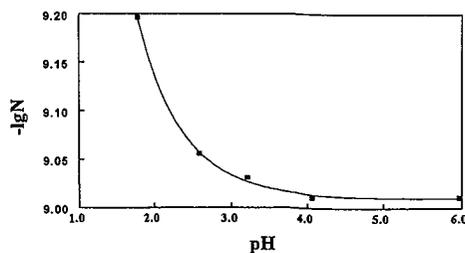
Fig. 3 The effect on the rate of velocity

Figure 3 is the effect on the extraction rate of the flow velocity change. Line 1 demonstrates the effect of a simultaneous flow velocity change of the two phases. It is known that no plateau is found in the flow velocity range. Therefore, it is believed that the extraction rate is controlled by the diffusion step. Line 2 demonstrates the effect of the organic flow velocity change. Line 3 demonstrates the effect of the aqueous flow velocity change. From figure 2 and figure 3, it is known that the effect of HL on the extraction rate is greater than the effect of  $\text{Er}^{3+}$ .



$s=2.5 \times 6 \text{ cm}^2$   $T=30^\circ\text{C}$   
 Aque:  $C_a=3.0 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ;  $\text{PH}=1.78$ ;  $V_a=3.2 \text{ cm}\cdot\text{s}^{-1}$   
 org:  $C_o=3.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ ;  $V_o=3.2 \text{ cm}\cdot\text{s}^{-1}$

Fig. 4 The relationship of time and the quantity of mass transfer



$s=2.5 \times 6 \text{ cm}^2$   $T=30^\circ\text{C}$   
 Aque:  $\text{PH}=1.78$ ;  $C_a=3.0 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ;  $V_a=3.2 \text{ cm}\cdot\text{s}^{-1}$   
 org:  $C_o=3.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ ;  $V_o=3.2 \text{ cm}\cdot\text{s}^{-1}$

Fig. 5 The effect on the rate of pH

Figure 4 is a plot of the relationship between the mass transfer and time. From the graph, we can see that mass transfer rate is high for shorter contacting times, and then became constant. According to the reports, (Hughes M. A., 1978 and Ma Aizheng, 1988 ) the unsaturated HEH/EHP-lanthanide complex compounds could form a sticky, soft and wax like material and its copper compound could exit on the interface between the two phases. During the test, the evidence of interfacially active material could be found at the interface. At the beginning of the test, the interface looked bright under the reflected light, and then it gradually became dim. Therefore, it seems that the unsaturated complex of erbium and HL ( $[\text{ErL}_3]_n$ ,  $[\text{ErL}_3\text{HL}]_n$  or  $[\text{ErL}_3\text{H}_2\text{L}_2]_n$ ) (Sun Jing, 1994) could form a linear polymer and accumulate at the interfacial layer to retard mass transfer. Meanwhile the inorganic linear polymer could dissociate and coordinate with HL from the bulk organic phase and distribute into the organic phase. The curve became constant when the accumulation and dissociation reached a balance.

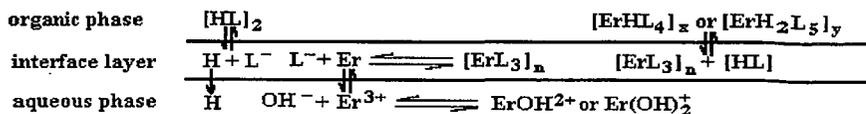


Figure 5 shows the effect on the extraction rate of pH. It is known that the extraction rate increases with an increase in the pH at pH=1.7~2.5. It is known that an increase in the  $\text{OH}^-$  concentration favors dissociation of HL in the interfacial layer and that the equation at the interface goes to the left. When pH=2.5~6, it is known that the extraction rate increases gradually and became constant with the increase of pH, and even decreased. Thus it is demonstrated that  $\text{OH}^-$  and  $\text{L}^-$  compete to coordinate with  $\text{Er}^{3+}$  and prevent the rate from increasing.

Finally, some practical result can be obtained from the above results and discussion. The HEH/EHP- $\text{Er}^{3+}$  extraction system is a diffusion controlled step system when the  $\text{pH} \leq 2.5$ , and the diffusion into the organic phase makes up the main resistance to the mass transfer. When  $\text{pH} = 2.5 \sim 6$ ,  $\text{OH}^-$  and  $\text{L}^-$  compete to form a complex with  $\text{Er}^{3+}$  and begin to affect the extraction rate.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the support provided for this work by National Science Committee on "The Basic Research of Rare Earth Science".

#### NOMENCLATURE

**L:** The interfacial length along the direction of flows (m).

**N:** Mass transfer rate ( $\text{mol/s} \cdot \text{cm}^2$ ).

**V:** Linear velocity of the phase flow.

**r:** Mass transfer speed ( $\text{mol/s} \cdot \text{dm}^3$ ).

#### Subscript

**o:** Organic phase.

**a:** Aqueous phase.

**i:** Interface.

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## SOLVENT EXTRACTION OF Sc(III), Zr(IV), Th(IV), Fe(III) AND Lu(III) WITH CYANEX 302 AND CYANEX 301 FROM SULPHURIC ACID MEDIA

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### ABSTRACT

The solvent extraction of Sc(III), Zr(IV), Th(IV), Fe(III), and Lu(III) with Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid) and Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) in n-hexane from sulphuric acid solutions has been investigated systematically. The effect of the equilibrium aqueous acidity on the extraction with these reagents was studied. The separation of Th(IV), Fe(III), and Lu(III) from Sc(III) with Cyanex 302 can be achieved by controlling the aqueous acidity. However, Cyanex 301 exhibited a poor selectivity for the above metals. The extraction of these metals with Cyanex 272, Cyanex 302, and Cyanex 301 has been compared. The stripping percentages of Sc(III) for Cyanex 302 and Cyanex 301 in a single stage are near 78% and 75% with 3.5 mol/L and 5.8 mol/L sulphuric acid solutions, respectively. The effect of the extractant concentration on the Sc(III) extraction with Cyanex 302 was investigated, the stoichiometry of the extraction was determined. The role of the different components of Cyanex 302 on the Sc(III) extraction is discussed.

### INTRODUCTION

Thiosubstituted organophosphorus compounds have been studied widely for analytical applications and hydrometallurgical processes. The most important previous work concerning the thiosubstituted organophosphorus reagents concentrated on the extraction of soft and borderline metals such as Cd(II), Ag(I), Co(II), Ni(II), etc. However, less work has been conducted on the extraction of hard acid metals such as Sc(III), Zr(IV), etc. Motomizu and Freiser (1985) studied the extraction of lanthanides with di-n-octyldithiophosphoric acid (HDODTP) and di(2-ethylhexyl)dithiophosphoric acid (HDEHDTP), and found that the hard acid metals such as Am(III) or Eu(III) could be extracted fairly well with the extractants HDODTP or HDEHDTP. These interesting results suggest to us that thiosubstituted organophosphorus reagents will possibly show favorable performance in the extraction of hard acid metals such as Sc(III), Zr(IV), etc. More recently, Cyanex 302 and Cyanex 301, which are the respective monothio and dithio analogues of Cyanex 272, have been made commercially available by Cyanamid Canada, Inc. It has been reported that these reagents are significantly more resistant towards decomposition by hydrolysis than their phosphoro analogues (Rickelton, et al., 1990). The extraction of Sc(III), Th(IV), Fe(III) and Lu(III) with Cyanex 272 or purified Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid, here-

after abbreviated as H(BTMPP)) from sulphuric acid has been reported in a earlier work (Wang, et al. , 1994). This paper deals extensively with the solvent extraction of Sc(III), Zr(IV), Th(IV), Fe(III) and Lu(III) with Cyanex 302 and Cyanex 301 on the basis of the previous work, and compares the characteristics of these Cyanex extractants.

## EXPERIMENTAL

### Reagent

Cyanex 272, Cyanex 302 and Cyanex 301 were kindly supplied by Cyanamid Canada, Inc. Cyanex 272 and Cyanex 302 were purified by precipitation of the copper salt (Komatso, et al. , 1989) and cobalt salt (Bart, et al. , 1991), respectively. Cyanex 302 and Cyanex 301 were used as received, except in the study of role of different components of Cyanex 302 in the Sc(III) extraction. Tri-n-octylphosphine (TOPO) was an analytical grade reagent received from Fluka. All extractants were diluted with n-hexane of analytical grade. The preparation of metal stock solutions were described previously (Wang, et al. , 1994). All other reagents were analytical grade.

### Extraction and analytical procedures

The extraction, stripping, and analytical procedures were the same as those in the previous work (Wang, et al. , 1994). In some cases, the metal concentrations of organic phases were also measured following stripping with sulphuric acid solutions. A Shimadzu spectrophotometer, Model UV-365, was used for measuring absorbance. <sup>31</sup>P-NMR spectra of raw Cyanex 302 and purified Cyanex 302 was carried out using a Varian NMR spectrometer, Model Unity-400, with 85% H<sub>3</sub>PO<sub>4</sub> as an external standard.

## RESULTS AND DISCUSSION

### Extraction of metals with Cyanex 302 and Cyanex 301

The effect of the equilibrium aqueous acidity on the extraction of Sc(III), Zr(IV), Th(IV), Fe(III) and Lu(III) with Cyanex 302 and Cyanex 301 from sulphuric acid solutions is shown in Figure 1. It was found that the extractabilities of the metals with Cyanex 302 and Cyanex 301 decrease in the order: Zr(IV) > Sc(III) > Th(IV) > Fe(III) > Lu(III) and Zr(IV) > Sc(III) ~ Fe(III) ~ Th(IV) > Lu(III), respectively. The results indicate that it is possible to separate Th(IV), Fe(III) and Lu(III) from Sc(III) with Cyanex 302 by controlling the aqueous acidity. However, Cyanex 301 exhibits a poor selectivity for the above metals, except for Lu(III). Neither Cyanex 302 nor Cyanex 301 show a good separation result for ion pairs of Sc(III) versus Zr(IV).

### Comparison of the extraction properties of Cyanex extractants

The extraction properties of Cyanex 272, Cyanex 302 and Cyanex 301 are compared with each other under similar experimental conditions. The extraction equilibrium data with

Cyanex 272 were reported previously (Wang, et al., 1994). In contrast to Cyanex 272, the extraction curves of the above metals with Cyanex 302 shift significantly to the more acidic range, except for Lu(III). On the contrary, the extractability of Zr(IV) with Cyanex 302 is greater than that of Sc(III). The distribution ratio (D) of Sc(III) decreases with increasing aqueous acidity, up to 3.0 mol/L H<sub>2</sub>SO<sub>4</sub>, and increases with increasing aqueous acidity at higher acidity than 3.5 mol/L H<sub>2</sub>SO<sub>4</sub>. This means that the extraction of Sc(III) proceeds by a cation exchange reaction in the range of lower aqueous acidity and a solvation reaction in the range of higher aqueous acidity. In the case of Cyanex 302, by substituting the oxygen atom of the P=O group of Cyanex 272 with a sulfur atom, the pK<sub>a</sub> value (5.63) of Cyanex 302 becomes lower than that (6.37) of Cyanex 272 (Sole, et al., 1992). This means that Cyanex 302 would have a higher affinity towards metal ions than Cyanex 272 in the cation exchange reaction, since the P-OH group is considered to have a dominant role in such a reaction.

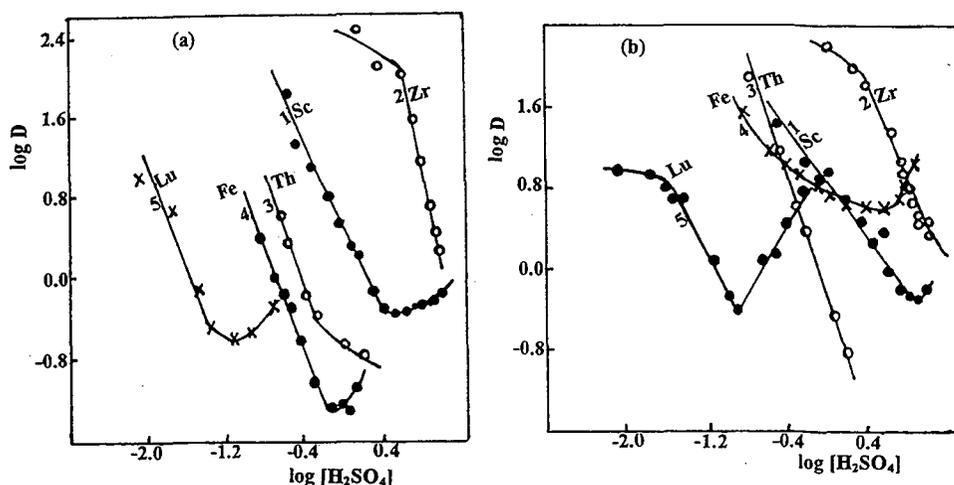


Figure 1. Extraction of metals with Cyanex 302 (a) and Cyanex 301 (b)

$$[\text{Cyanex 302}]_{(o)} = [\text{Cyanex 301}]_{(o)} = 4.82 \times 10^{-2} \text{ mol/L}$$

$$1. [\text{Sc(III)}] = 5.26 \times 10^{-4} \text{ mol/L}, 2. [\text{Zr(IV)}] = 3.81 \times 10^{-4} \text{ mol/L}$$

$$3. [\text{Th(IV)}] = 1.89 \times 10^{-4} \text{ mol/L}, 4. [\text{Fe(III)}] = 6.09 \times 10^{-4} \text{ mol/L}$$

$$5. [\text{Lu(III)}] = 2.54 \times 10^{-4} \text{ mol/L}$$

On the other hand, the extractability of Sc(III) with Cyanex 302 is remarkably smaller than that with Cyanex 272 in the range of higher aqueous acidity. This can be attributed to the fact that the P=S group of Cyanex 302 forms a weaker complex with Sc(III) than the P=O group of Cyanex 272, since the P=O group is thought to be mainly employed in the solvation reaction. The result is in agreement with the principle of Hard-Soft Acid-Bases, which teaches that sulfur is a weaker ligand than oxygen for the 'hard acid' Sc(III). Both oxygen atoms of Cyanex 272 are replaced by sulfur atoms in the case of Cyanex 301. This leads to a pK<sub>a</sub> value (2.61) (Sole, et al., 1992) of Cyanex 301 sharply lower than that of Cyanex 272 and Cyanex 302. Consequently, the extraction curves of Lu(III), Fe(III) and Th(IV) move significantly toward the most acidic range, whereas those of Sc(III) and Zr(IV) move slightly

to that range. Considering the selectivity of these reagents, Cyanex 301 exhibits a poorer separation performance on the metals (except for Lu(III)) than Cyanex 272 or Cyanex 302. Therefore, it can be concluded that in the cation exchange reaction which takes place in less acidic media, the extraction ability of Cyanex extractants towards the above metals increases in the order; Cyanex 272 < Cyanex 302 < Cyanex 301, which is consistent with the order of decreasing pKa. A similar conclusion was reported by Pout et al. (1993), in their recent study of the extraction of thorium(IV) by Cyanex reagents from hydrochloric acid media. From the results obtained from above experiments, it was considered necessary to study the Sc(III) extraction with Cyanex 302 extensively for a comprehensive understanding of the extraction properties of Cyanex 302.

### Stripping of Sc(III) from Cyanex 272, Cyanex 302 and Cyanex 301

The results indicate that Sc(III) can be stripped readily by sulphuric acid solutions of certain concentrations even though the stripping acidity increases gradually according to the order of Cyanex 272, Cyanex 302, and Cyanex 301. The stripping percentages of Sc(III) in a single stage for Cyanex 272, Cyanex 302, and Cyanex 301 are near 82%, 78%, and 75% by 1.5 mol/L, 3.5 mol/L and 5.8 mol/L H<sub>2</sub>SO<sub>4</sub> solutions, respectively. In contrast with the Cyanex extractants, the stripping percentages of Sc(III) for di(2-ethylhexyl) phosphoric acid (HDEHP) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH(EHP)) are only 5% and 20% by 5 mol/L H<sub>2</sub>SO<sub>4</sub> solution, respectively (Li, et al., 1993). Therefore, Cyanex 272 and Cyanex 302 show a better stripping performance with respect to Sc(III) than HDEHP and HEH(EHP).

### Stoichiometry of the Sc(III) extraction with Cyanex 302

It is generally accepted that monobasic organophosphorus acid extractants are dimeric in solvents of low polarity (Cote, et al., 1986). Tait (1993) found that Cyanex 302 is dimeric using the method of the vapour pressure osmometry in his recent work. In the range of lower aqueous acidity, the slope of logD versus log[(HL)<sub>2</sub>]<sub>(o)</sub> is about 2.5. From the experimental data (see Figure 1) it can be calculate that the slope of logD versus log[H<sup>+</sup>] is close to 3 (slope=2.9, correlation coefficient=0.999, the method of data analysis has been described in the previous paper (Wang, et al., 1994)). Therefore, the extraction equilibrium of Sc(III) can be expressed as follow:



where (a) and (o) denote the aqueous and organic phases, respectively, (HL)<sub>2</sub> refers to the dimer of Cyanex 302.

### Role of the different components of Cyanex 302 in the Sc(III) extraction

It has been found that the extraction ability of purified Cyanex 302 (hereafter abbreviated as H(BTMPPTP)) is significantly lower than that of the as-received Cyanex 302. A similar result was reported by Freiser et al. (1985), in the extraction of Eu(III) with purified HDEHDTP and was attributed to a contamination by di(2-ethylhexyl)phosphoric acid(HDEHP). The <sup>31</sup>P-NMR spectra of these reagents were measured and the result indicates that tri-

alkylphosphine oxide impurities were removed from the purified Cyanex 302 product. According to the composition of Cyanex 302 reported by Hiskey, et al. (1992), Cyanex 302 consists of bis(2,4,4-trimethylpentyl) monothiophosphinic acid (78~80%), tris(2,4,4-trimethylpentyl)phosphine oxide (10~12%), bis(2,4,4-trimethylpentyl)phosphinic acid (2~3%), bis(2,4,4-trimethylpentyl)dithiophosphinic acid (~2%) and some unknown components (~8%). It is assumed that trialkylphosphine oxide can be removed by precipitation of the cobalt salt, but dialkylphosphinic acid and dialkyldithiophosphinic acid will remain more or less in purified Cyanex 302. On the basis of the above analysis, a series of experiments was conducted, the results of which are shown in Figure 2. It has been found that the extractability of Sc(III) by H(BTMPP) at a concentration ( $1.50 \times 10^{-3}$  mol/L) corresponding to 3% concentration of raw Cyanex 302 ( $4.83 \times 10^{-2}$  mol/L) is significantly weaker than that by raw Cyanex 302 and close to that by H(BTMPTP) ( $4.83 \times 10^{-2}$  mol/L). The Sc(III) extraction with TOPO proceeds by a solvation reaction, the distribution ratio of Sc(III) increases with increasing aqueous acidity. The extractability of Sc(III) increases when TOPO is added to either of the H(BTMPTP) or H(BTMPP) solutions, but is still considerably lower than that by raw Cyanex 302. This result indicates that there may be a synergistic effect in the extraction when TOPO is present together with H(BTMPTP) or H(BTMPP).

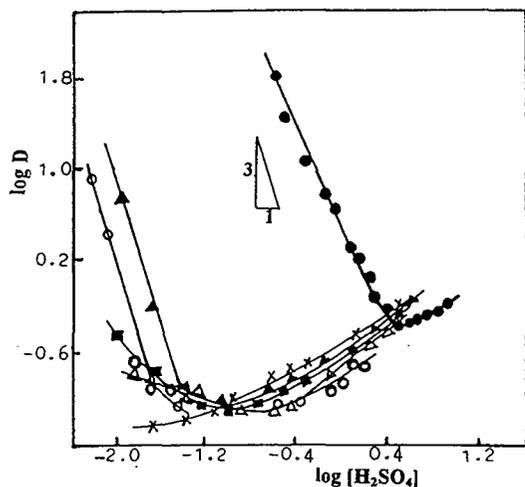


Figure 2. Extraction of Sc(III) with raw Cyanex 302 and purified Cyanex 302 (H(BTMPTP))

[Sc(III)] =  $5.04 \times 10^{-4}$  mol/L

- (●).  $4.83 \times 10^{-2}$  mol/L Cyanex 302
- (○).  $4.83 \times 10^{-2}$  mol/L H(BTMPTP)
- (×).  $4.83 \times 10^{-3}$  mol/L TOPO
- (△).  $1.50 \times 10^{-3}$  mol/L H(BTMPP)
- (▲).  $4.83 \times 10^{-2}$  mol/L H(BTMPTP) +  $4.83 \times 10^{-3}$  mol/L TOPO
- (■).  $1.50 \times 10^{-3}$  mol/L H(BTMPP) +  $4.83 \times 10^{-3}$  mol/L TOPO

In contrast to Cyanex 302, the extractability of Sc(III) by either raw Cyanex 272 or purified Cyanex 272 (H(BTMPP)) is not significantly different and the extractability by Cyanex 272 is slightly greater than that by purified Cyanex 272. This indicates that the presence of the trialkylphosphine oxide impurities in Cyanex 272 can increase the extractability of Sc(III). From the above results, it can be inferred that the extraction ability of H(BTMPTP) ( $4.83 \times 10^{-2}$  mol/L) toward Sc(III) is significantly weaker than that of raw Cyanex 302 ( $4.83 \times 10^{-2}$  mol/L). This is also true of the extracting ability of H(BTMPP) ( $1.50 \times 10^{-3}$  mol/L). The presence of TOPO in the extraction system can increase the extractability of Sc(III). The reason why raw Cyanex 302 can extract Sc(III) more efficiently than purified Cyanex 302 is still not clear, but is not attributed to the presence of H(BTMPP). It is interesting to

study the role of the branched chain trialkylphosphine oxide in the Sc(III) extraction.

### CONCLUSION

The systematic study of the extraction of Sc(III), Zr(IV), Th(IV), Fe(III), and Lu(III) with Cyanex 272, Cyanex 302, and Cyanex 301 led us to the following conclusions:

(1) The separation of Th(IV), Fe(III), and Lu(III) from Sc(III) with Cyanex 302 can be conducted by controlling the aqueous acidity. The stripping of Sc(III) from Cyanex 302 and Cyanex 301 can be easily achieved using sulphuric acid solutions.

(2) Purified Cyanex 302 has a weaker extracting ability for Sc(III) than raw Cyanex 302, and the reason must be clarified in future work.

### ACKNOWLEDGEMENTS

The authors wish to thank Dr. W. A. Rickelton of Cyanamid Canada, Inc., for samples of the Cyanex extractants. This work was supported by the National program "The Basic Research of Rare Earth" of China.

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## CHELATE FORMATION AND ION-ASSOCIATION AT LIQUID-LIQUID INTERFACE

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### ABSTRACT

The role of the liquid/liquid interface in the chelate extraction of Ni(II) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) and the ion-association extraction of acids with 5,10,15,20-tetraphenylporphyrin (TPP) was investigated by means of a high-speed stirring method and *in situ* spectrometry for the interface. In the former system, the formation of the Ni(II)-5-Br-PADAP complex at the heptane/water interface was observed and the kinetic mechanism was discussed from the two processes: rapid Langmuir adsorption of 5-Br-PADAP and slow interfacial chelation. In the latter system, the extraction constants and the adsorption constants of the diprotonated TPP were determined in toluene/acid systems. Furthermore, the fast formation of diprotonated TPP was observed at the dodecane/acid solution interface by the aid of a two-phase stopped-flow method and the results are discussed in terms of the diffusion rate limiting mechanism in the stagnant layer at the interface.

### INTRODUCTION

The mechanism of solvent extraction is primarily due to reactions in bulk phases, while it has been pointed out that interfacial reactions have also a general importance in extraction processes (Watarai, 1993). Previously, the kinetic mechanisms in the chelate extractions of Ni(II) and Zn(II) with *n*-alkyl substituted dithizones (Watarai and Freiser, 1983) and of Ni(II) and Cu(II) with 2-hydroxy oximes (Watarai and Endo, 1991) and the ion-association extraction of Fe(II)-1,10-phenanthroline complexes with anions (Watarai et al., 1990) were interpreted by an interfacial complexation mechanism.

The development of new techniques for the measurement of interfacial reactions continues to be an important subject. We have reported already the high-speed stirring method (Watarai et al., 1982), and recently the optical stirred cell method and the Teflon capillary plate method (Watarai and Chida, 1994).

In the present study, the role of interface in the chelate extraction of Ni(II) with pyridylazo-compound and the ion-association extraction of acids with porphyrin was investigated by means of the high-speed stirring method and a two-phase stopped flow method. The advantage of using highly sensitive colorimetric reagents enables the reliable detection of the interfacially adsorbed species, whose concentrations are at the most in the order of  $10^{-10}$  mol/cm<sup>2</sup>, by means of a conventional spectrophotometer or photodiode array detector.

### EXPERIMENTAL

#### Materials

2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as a typical colorimetric pyridylazo-compound and 5,10,15,20-tetraphenylporphyrin (TPP), Dojindo, were reagent grade and were used as purchased. Heptane, toluene and dodecane, Wako G.R., were purified by fractional distillation.

Trichloroacetic acid (TCA) and other acids and salts were all reagent grade.

#### Measurement of interfacial chelate formation

The interfacial adsorption of 5-Br-PADAP and the formation of the Ni(II)- 5-Br-PADAP complex in the agitated system were measured by means of the high-speed stirring method with photodiode-array detector (Watarai and Satoh, 1994) at  $25 \pm 0.1^\circ\text{C}$ . The interfacial amount was measured from the difference between the organic phase absorbances at stirring rates of 200 rpm and 5000 rpm. The interfacial chelate formation was directly observed by a Teflon capillary method (Watarai, 1993) in which the organic phase was held in capillary holes (0.6 mm diameter) drilled in a Teflon plate (1mm thickness) and immersed in an aqueous solution. Thus, the interfacial absorption spectrum could be observed through the three layers and the two interfaces in the aqueous phase/organic phase/aqueous phase system.

#### Measurement of interfacial ion-association

The ion-association extraction and ion-association adsorption equilibria of TPP in toluene/acid systems were studied by means of the high-speed stirring method. For toluene/sulfuric acid, there was no extraction, but a significant adsorption was observed. For hydrochloric acid, perchloric acid and TCA, both extraction and adsorption were observed, the extent depending on the acid. The interfacial protonation rate of TPP in the two-phase system was measured using a stopped-flow apparatus (Unisoku RSP-601) at  $25 \pm 0.1^\circ\text{C}$ . A dodecane solution of TPP and a TCA aqueous solution were mixed at a 1:1 volume ratio with 1 msec dead time and the absorption spectrum of the dispersed mixture was measured by the photodiode array detector in the range of 346 nm - 554 nm with a 5 msec interval. The mean diameter of the dispersed aqueous droplet was estimated as  $66 \mu\text{m}$  from photographic prints recorded by a video camera. The dispersed phase in a cylindrical optical cell (2mm pass length) was stable for more than 1 sec.

## RESULTS AND DISCUSSION

### Interfacial chelate formation of Ni(II)-5-Br-PADAP complex

When 5-Br-PADAP in heptane and an aqueous phase were vigorously stirred in the stirred cell, the decrease in the organic phase absorbance which was due to the interfacial adsorption of 5-Br-PADAP was observed as shown in Fig. 1. However, there was no interfacial adsorption of 5-Br-PADAP when toluene was used as solvent.

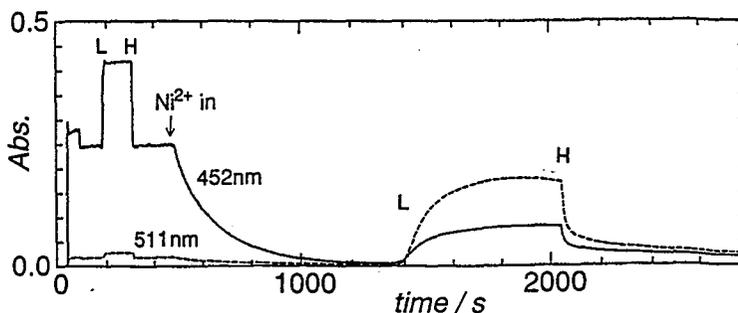
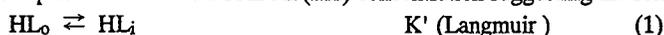


Figure 1. Typical absorbance profile in the heptane phase in the extraction of Ni(II) with 5-Br-PADAP;  $[\text{Ni}^{2+}] = 1.0 \times 10^{-4} \text{ M}$ ,  $[\text{5-Br-PADAP}] = 1.0 \times 10^{-5} \text{ M}$ ,  $\text{pH} = 5.95$ , L and H refer to 200 rpm and 5000 rpm in the stirring rate and 452 nm and 511 nm correspond to the absorption maxima of the ligand and the complex, respectively.

The interfacial adsorption in heptane system under stirring was analysed according to the Langmuir isotherm, and  $aA_i = 1.9 \times 10^{-6}$  mol and  $K'A_i = 4.4 \times 10^{-2}$  L were determined, where  $a$ ,  $K'$  and  $A_i$  stand for the saturated interfacial concentration, the adsorption constant and the total interfacial area. The higher adsorptivities of 5-Br-PADAP and the Ni(II)-complex in the heptane system than in the toluene system should be relevant to the lower distribution constant of 5-Br-PADAP in the former solvent:  $\log K_D(\text{heptane})=3.22$  and  $\log K_D(\text{toluene})=4.78$ . An injection of Ni(II) solution into the stirred system started to consume 5-Br-PADAP in the organic phase through complex formation as shown in Fig.1, but no extraction of the complex was observed, suggesting a complete adsorption of the complex. In the toluene system, slow extraction of the Ni(II) complex was observed accompanied by a significant interfacial adsorption: the Langmuir adsorption parameters of  $aA_i = 2.0 \times 10^{-6}$  mol and  $K'A_i = 3.7 \times 10^{-2}$  L were obtained. The initial formation rates of the Ni(II) complex in the stirred system depended on the 5-Br-PADAP(HL) concentration suggesting the following scheme,



where  $k$  is the formation rate constant of  $\text{NiL}^+_i$ . The value for  $k$  was estimated as  $5.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . This low value may be ascribable to the high  $\text{pK}_a$  value ( $\text{pK}_a = 11.3$ ) for the dissociation of HL (Johnson and Florence, 1975) and a slow ring closure rate as reported in the formation of Ni(II)- $\beta$ -PAN complex (Reeves, 1986).

#### Interfacial ion-association

The neutral TPP did not adsorb at the toluene/water interface, whereas the diprotonated form  $\text{H}_2\text{TPP}^{2+}$  adsorbed significantly. The ion-association extraction and ion-association adsorption reactions can be written as,



and

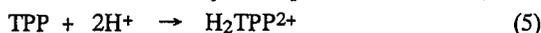


where the subscripts  $o$  and  $i$  refer to the organic phase and the interface and HX to acid. The adsorption constant of  $\text{H}_2\text{TPPX}_2$  can, therefore, be defined by  $K_D' = [\text{H}_2\text{TPPX}_{2,i}]/[\text{H}_2\text{TPPX}_{2,o}] = K'/K_{\text{ex}}$ . In Table 1, the values for  $K_{\text{ex}}$ ,  $K'A_i$  and  $K_D'A_i$  determined in the present study are listed. The order in  $\log K_{\text{ex}}$  ( $\text{H}_2\text{SO}_4 < \text{HCl} < \text{HClO}_4 < \text{TCA}$ ) reflects the decreasing order in the hydration energies of the anions X, and is reversed with respect to the order in  $\log K_D'A_i$  as expected from a general extraction-adsorption free-energy relationship.

TABLE 1  
Ion-association extraction and ion-association adsorption of  $\text{H}_2\text{TPPX}_2$  in highly agitated toluene/acid (HX) systems at 25 °C

Acid	$\log K_{\text{ex}}$	$\log K'A_i$	$\log K_D'A_i$
$\text{H}_2\text{SO}_4$	< -3	0.81	> 4
HCl	-1.37	-1.54	-0.17
$\text{HClO}_4$	2.96	0.79	-2.17
TCA	6.54	3.45	-3.09

The stopped-flow spectrophotometric measurement for the mixture of TPP in dodecane and TCA in aqueous solution showed a decrease in TPP at 416 nm and an increase of the diprotonated form  $H_2TPP^{2+}$  at 438 nm. Both absorbance changes were analysed according to first order kinetics. The apparent first order rate constants  $k(TPP)$  and  $k(H_2TPP^{2+})$  for the decrease of TPP and increase of  $H_2TPP^{2+}$ , respectively, were determined under the conditions of various TPP and TCA concentrations as listed in Table 2. The agreement of the values for  $k(TPP)$  and  $k(H_2TPP^{2+})$  in Table 2 confirms the stoichiometry of the protonation reaction,



which should occur at the interface since  $H_2TPP^{2+}$  is soluble into neither the aqueous nor the organic phase.

**TABLE 2**  
Observed rate constants for the interfacial protonation of TPP

Conditions	$k(TPP) /s^{-1}$	$k(H_2TPP^{2+})/s^{-1}$
$[TPP] = 1.48 \times 10^{-6} M - 3.78 \times 10^{-5} M$ $[TCA] = 0.010 M$	$19 \pm 3$	$17 \pm 3$
$[TPP] = 1.90 \times 10^{-5} M$ $[TCA] = 2.0 \times 10^{-3} M - 0.10 M$	$21 \pm 2$	$20 \pm 3$

Total trichloroacetate ion concentration was maintained at 0.1 M by sodium trichloroacetate.

The observed rate constants did not show any dependency on the TPP and TCA concentrations with an average value of  $19.3 s^{-1}$ . The protonation reaction in homogeneous media was reported to be very fast with a rate constant larger than  $10^6 M^{-1}s^{-1}$  (Hibbert and Hunte, 1977). Therefore, the rate constants observed in the dodecane/acid systems were attributable to the diffusion process rather than an intrinsic reaction rate. The film theory which defines the stagnant layers at both sides of the interface was applied to the present system. Considering  $[TPP] \ll [TCA]$ , the diffusion rate of TPP in the stagnant layer in the dodecane phase is thought of as the rate limiting process. In this situation, the observed rate constant can be written as,

$$k = D A_i / \delta V_o \quad (6)$$

where  $D$ ,  $\delta$ , and  $V_o$  refer to the diffusion coefficient of dodecane, the thickness of the stagnant layer and the volume of dodecane phase. When  $k$  is  $19.3 s^{-1}$ ,  $\delta$  can be calculated as  $4.0 \mu m$  which is reasonable as the thickness under effective stirring.

By the present study, it was concluded that (1) the rate of the chelate formation of Ni(II)-5-Br-PADAP at the heptane/water interface was measured by the high-speed stirring method and the rate constant was attributed to the chemical reaction and not to the diffusion rate, and (2) the interfacial reactions in the ion-association extraction of acids with TPP were elucidated, the protonation rate of TPP in dodecane/acid system was measured by means of the stopped flow method and the kinetic mechanism was interpreted in terms of a diffusion regime rather than a chemical reaction regime.

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## INVESTIGATIONS INTO THE KINETICS OF IRON EXTRACTION FROM HYDROCHLORIC ACID WITH TRIOCTYLAMINE AND TRIBUTYLPHOSPHATE

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### ABSTRACT

In the last years we have developed a new method for the determination of liquid/liquid interfacial mass transfer in solvent extraction systems by use of the Beckman Model E Analytical Ultracentrifuge (AUC). We improved both optical systems of the AUC by use of modern technical equipment like an A/D converter, PC data handling, video recording and digitizing. Software has been developed with respect to the evaluation of kinetic data and a diffusion controlled solvent extraction model was applied for the determination of transfer coefficients. We have investigated the extraction systems  $\text{FeCl}_3\text{-HCl-TBP}$  and  $\text{FeCl}_3\text{-HCl-TOA/xylene}$  at different iron(III)chloride and hydrochloric acid concentrations varied between 0.02 - 0.06 M  $\text{FeCl}_3$  and 1 M - 10 M HCl. With respect to the mathematical modelling of the interfacial transfer, apparent diffusion coefficients of iron have been determined in both phases and distribution ratios have been determined in batch experiments. In order to investigate only the transport of iron through the liquid/liquid interface all systems have been equilibrated with the corresponding hydrochloric acid solution before starting the extraction.

### INTRODUCTION

Solvent extraction has become an important unit operation in technical and analytical separation processes. According to the rapid development of contact equipment there is a growing need for kinetic information. Modern contact equipment like pulsed sieve plate columns, centrifugal extractors or hollow fiber modules are working in a nonequilibrium state and the time of phase contact is a dominant separation parameter. Therefore all information about interfacial phenomena like interfacial transfer kinetics, turbulence, marangoni mass transfer instabilities, release of heat, liquid double layer properties, surface tension effects, interfacial resistance and others are important for the separation quality, for the loading capacity of the extractant, for the total phase flow and for the cost of the whole separation process. All of these facts show the need for more kinetic investigations.

Up to now, several analytical methods for the determination of liquid/liquid extraction kinetics have been developed and tested, but only two general procedures have been established world wide, the stirred cell technique and the single drop column technique. In addition to these two dynamic techniques we have developed a method wherein two unstirred phases are contacted and the interfacial mass transfer can be analysed by use of two different optical systems. We work with a two phase system being formed under particular conditions by use of centrifugal force and we investigate the interfacial kinetics without any external influence on the physical properties of the solvent extraction system, like changing the double layer thickness with rotation speed or changing drop parameters by using capillaries with different sizes for the drop formation.

### ANALYTICAL TECHNIQUE

The investigation of the extraction kinetics can be carried out with the Beckmann Model E Analytical Ultracentrifuge. We use the ultracentrifuge only as an instrument for overlaying two liquids without producing turbulence at the interface during the overlay process. The Beckmann Model E Analytical Ultracentrifuge is equipped with two optical systems, the UV/VIS and the schlieren optical systems. Both systems are able to detect and record the concentration changes in the aqueous and organic phases at different times of phase contact. The core of our experimental technique is the double sector capillary-type synthetic boundary centerpiece which embodies two compartments connected by two capillaries. The centerpiece is covered with windows and placed in a cell housing. Both compartments have small filling holes in the top and can be filled with a syringe. One sector is filled with 0.12 ml of aqueous phase ( i.e.  $\text{FeCl}_3$  in HCl) and the other sector is filled with 0.36 ml of organic phase ( i.e. TBP eq. with HCl). After filling, the sealed cell is aligned precisely in a titanium rotor and the rotor is accelerated inside the evacuated steel chamber of the AUC. From the beginning of acceleration the centrifugal force lasts on both of the liquid columns in the two compartments of the cell. With increasing rotation speed, the centrifugal force lasting on the organic phase, becomes larger than the capillary force, which holds the phase back in the sector. At this point the organic liquid will be pressed slowly through the capillary from the organic sector to the aqueous sector. The phase overlay takes place at 5000 rpm and the solvent extraction process begins. Due to the centrifugal force the surface of the aqueous column is hard and the overstreaming organic extractant do not cause a visible production of turbulence at the interface. The applied centrifugal force at 5,000-10,000 rpm is not high enough to influence the motion of metal ions or small organic metal complexes with respect to

their diffusional motion. Sedimentation of metal ions within the cell dimensions needs nearly 80,000 rpm for several hours. Therefore the mass transfer inside the rotating cell is not influenced or disturbed by the low gravitational field. The extraction process is monitored with the two optical systems of the AUC, the UV/VIS and the schlieren optical systems - Beckman-Instruction-Manual (1966) - .

Using the UV/VIS optical system we get absorption scans of the extraction system. These scans were printed with a differential recorder and simultaneously transferred to a computer using an A/D-converter. Absorption scans can be taken every three minutes and a complete extraction run needs 10 to 20 scans. The absorption scans show the concentration changes in both phases and they do change within time of phase contact according to the metal transferred into the organic phase. The extraction profiles are integrated from the cell bottom to the liquid/liquid interface and from the liquid/liquid interface to the liquid/air interface. This gives the total change of the metal content in the aqueous and the organic phase from the first phase contact up to the time of scan recording. Normalized to an interfacial area of  $1 \text{ cm}^2$  we call this the integral mass flux  $I_t / \text{mol/cm}^2$ . One method for the interpretation of these absorption profiles follows from mathematical modelling of the extraction process. A comparison of experimental results with calculated concentration profiles and integral mass fluxes yielded from a diffusion controlled extraction model allows to decide between a diffusion controlled and a reaction controlled interfacial transfer. The general mass transfer model is described by E.J. Scott, L.H. Tung and H.G. Drickamer (1951) and the application for the AUC technique is described in previous publications by R. Gauglitz (1986, 1989, 1995). In order to detect the transfer velocity of an extraction system,  $I_t$  is calculated with different values for the interfacial resistance and plotted as a function of the time of contact and the resulting curves are compared with experimental  $I_t$  data. In addition to this a direct comparison of calculated profiles with experimental absorption scans can also result in the transfer velocity.

## EXPERIMENTAL

Aqueous solutions were made up from iron(III)chloride nonahydrate dissolved at the required hydrochloric acid level and their concentrations varied from 0.02 - 0.06 M Fe and 1 M to 9 M HCl. The organic phases were pure tributylphosphate (TBP) and a 30 Vol.% (about 0.69 M) trioctylamine (TOA) solution in xylene. Batch loading tests for the determination of the partition ratios were performed at a phase ratio of 1.0 with a contact time of 1 hour. Iron analysis was performed by use of the isotope

Fe-59. The iron concentration was determined by  $\gamma$ -spectroscopy of the aqueous and organic phases at 1099 keV.

## RESULTS AND DISCUSSION

Table 1 shows the effect of hydrochloric acid on iron(III) extraction for an initial iron content of 0.04 mol/l in the aqueous phase and the effect of different initial iron concentrations in 7M hydrochloric acid. The distribution ratios  $K_D$  of iron show a strong increase from 78 to 100,000 with increasing aqueous hydrochloric acid concentrations. The increase of the initial iron content in 7M hydrochloric results in a moderate decrease of the distribution ratios from 122,000 to 86,000 with a maximum at  $c_{Fe}$  0.03 mol/l.

**TABLE 1**  
Distribution Ratios of  $FeCl_3$  between hydrochloric acid and TBP

Experiments with 0.04 M $FeCl_3$ in:	$c_{Fe-aq.}/mol/l$	$K_D$
1M HCl / TBP equi. 1M HCl	$5.06 \cdot 10^{-4}$	$7.8 \cdot 10^1$
2M HCl / TBP equi. 2M HCl	$3.31 \cdot 10^{-4}$	$1.2 \cdot 10^2$
3M HCl / TBP equi. 3M HCl	$1.80 \cdot 10^{-4}$	$2.2 \cdot 10^2$
4M HCl / TBP equi. 4M HCl	$7.89 \cdot 10^{-5}$	$5.0 \cdot 10^2$
5M HCl / TBP equi. 5M HCl	$1.72 \cdot 10^{-5}$	$2.3 \cdot 10^3$
6M HCl / TBP equi. 6M HCl	$2.00 \cdot 10^{-6}$	$2.0 \cdot 10^4$
7M HCl / TBP equi. 7M HCl	$3.00 \cdot 10^{-7}$	$1.14 \cdot 10^5$
8M HCl / TBP equi. 8M HCl	$4.00 \cdot 10^{-7}$	$1.04 \cdot 10^5$
9M HCl / TBP equi. 9M HCl	$4.49 \cdot 10^{-7}$	$9.3 \cdot 10^4$
Experiments in 7 M HCl:	$c_{Fe-aq.}/mol/l$	$K_D$
0.02 M $FeCl_3$ / TBP equi. 7M HCl	$2.00 \cdot 10^{-7}$	$1.03 \cdot 10^5$
0.03 M $FeCl_3$ / TBP equi. 7M HCl	$2.00 \cdot 10^{-7}$	$1.22 \cdot 10^5$
0.04 M $FeCl_3$ / TBP equi. 7M HCl	$3.00 \cdot 10^{-7}$	$1.14 \cdot 10^5$
0.05 M $FeCl_3$ / TBP equi. 7M HCl	$5.41 \cdot 10^{-7}$	$9.25 \cdot 10^4$
0.06 M $FeCl_3$ / TBP equi. 7M HCl	$7.00 \cdot 10^{-7}$	$8.60 \cdot 10^4$

Table 2 shows the apparent diffusion coefficients of iron(III)chloride in hydrochloric acid and of the organic iron complexes, solvates and ion pairs in the organic phase. The iron diffusion in hydrochloric acid is generally faster than iron diffusion in

organic systems. The apparent diffusion coefficients in aqueous systems increase from  $4 \cdot 10^{-6} \text{ cm}^2/\text{s}$  to  $7 \cdot 10^{-6} \text{ cm}^2/\text{s}$  with increasing hydrochloric acid concentration. Compared to that, the influence of a differing iron content from 0.02–0.06 mol/l in a given system is negligible. In organic systems, the apparent diffusion coefficients are found to be smaller. They decrease from  $1.2 \cdot 10^{-6} \text{ cm}^2/\text{s}$  to  $0.5 \cdot 10^{-6} \text{ cm}^2/\text{s}$  with increasing hydrochloric acid content and from  $1.3 \cdot 10^{-6} \text{ cm}^2/\text{s}$  to  $0.75 \cdot 10^{-6} \text{ cm}^2/\text{s}$  with increasing iron content.

**TABLE 2**  
Diffusion coefficients  $\text{FeCl}_3$  in hydrochloric acid / TBP and TOA/xylene

Experiments with 0.04 M $\text{FeCl}_3$ in:	$D_{\text{app.-aq.}}/\text{cm}^2/\text{s}$	$D_{\text{app.-org.}}/\text{cm}^2/\text{s}$
1M HCl / TBP equi. 1M HCl	$4.01 \cdot 10^{-6}$	$1.05 \cdot 10^{-6}$
2M HCl / TBP equi. 2M HCl	$5.05 \cdot 10^{-6}$	$1.22 \cdot 10^{-6}$
3M HCl / TBP equi. 3M HCl	$5.99 \cdot 10^{-6}$	$1.16 \cdot 10^{-6}$
4M HCl / TBP equi. 4M HCl	$6.83 \cdot 10^{-6}$	$1.29 \cdot 10^{-6}$
5M HCl / TBP equi. 5M HCl	$6.06 \cdot 10^{-6}$	$0.52 \cdot 10^{-6}$
6M HCl / TBP equi. 6M HCl	$6.59 \cdot 10^{-6}$	$0.55 \cdot 10^{-6}$
Experiments in 7 M HCl:	$D_{\text{app.-aq.}}/\text{cm}^2/\text{s}$	$D_{\text{app.-org.}}/\text{cm}^2/\text{s}$
0.02 M $\text{FeCl}_3$ / TBP equi. 7M HCl	$5.68 \cdot 10^{-6}$	$1.26 \cdot 10^{-6}$
0.03 M $\text{FeCl}_3$ / TBP equi. 7M HCl	$5.23 \cdot 10^{-6}$	$0.80 \cdot 10^{-6}$
0.04 M $\text{FeCl}_3$ / TBP equi. 7M HCl	$5.85 \cdot 10^{-6}$	$0.84 \cdot 10^{-6}$
0.05 M $\text{FeCl}_3$ / TBP equi. 7M HCl	$5.61 \cdot 10^{-6}$	$0.75 \cdot 10^{-6}$
0.06 M $\text{FeCl}_3$ / TBP equi. 7M HCl	$5.47 \cdot 10^{-6}$	$0.94 \cdot 10^{-6}$
Experiments with 0.04 M $\text{FeCl}_3$ in:	$D_{\text{app.-org.}}/\text{cm}^2/\text{s}$	
1M HCl / TOA/xylene equi. 1M HCl	$0.53 \cdot 10^{-6}$	
5M HCl / TOA/xylene equi. 5M HCl	$1.07 \cdot 10^{-6}$	
Experiments in 3 M and 7 M HCl:	$D_{\text{app.-org.}}/\text{cm}^2/\text{s}$	
0.02 M $\text{FeCl}_3$ / TOA/xylene equi. 3M HCl	$1.35 \cdot 10^{-6}$	
0.04 M $\text{FeCl}_3$ / TOA/xylene equi. 3M HCl	$1.63 \cdot 10^{-6}$	
0.06 M $\text{FeCl}_3$ / TOA/xylene equi. 3M HCl	$0.79 \cdot 10^{-6}$	
0.02 M $\text{FeCl}_3$ / TOA/xylene equi. 7M HCl	$1.23 \cdot 10^{-6}$	
0.04 M $\text{FeCl}_3$ / TOA/xylene equi. 7M HCl	$0.37 \cdot 10^{-6}$	
0.06 M $\text{FeCl}_3$ / TOA/xylene equi. 7M HCl	$0.82 \cdot 10^{-6}$	

**TABLE 3**  
Transfer coefficients and extrapolated flux densities of FeCl<sub>3</sub>  
in hydrochloric acid / TBP and TOA/xylene

Experiments with 0.04 M FeCl <sub>3</sub> in:	$\beta$ / cm/s	$J_{t=0}$ / mol/cm <sup>2</sup> ·s
1M HCl / TBP equi. 1M HCl	$4 \cdot 10^{-4}$	$6.4 \cdot 10^{-9}$
2M HCl / TBP equi. 2M HCl	$1 \cdot 10^{-4}$	$3.4 \cdot 10^{-9}$
6M HCl / TBP equi. 6M HCl	$5 \cdot 10^{-4}$	$4.3 \cdot 10^{-9}$
7M HCl / TBP equi. 7M HCl	$3 \cdot 10^{-4}$	$7.7 \cdot 10^{-9}$
Experiments in 7 M HCl:	$\beta$ / cm/s	$J_{t=0}$ / mol/cm <sup>2</sup> ·s
0.02 M FeCl <sub>3</sub> / TBP equi. 7M HCl	$4 \cdot 10^{-4}$	$3.5 \cdot 10^{-9}$
0.03 M FeCl <sub>3</sub> / TBP equi. 7M HCl	$2 \cdot 10^{-4}$	$2.8 \cdot 10^{-9}$
0.04 M FeCl <sub>3</sub> / TBP equi. 7M HCl	$3 \cdot 10^{-4}$	$7.7 \cdot 10^{-9}$
0.05 M FeCl <sub>3</sub> / TBP equi. 7M HCl	$2 \cdot 10^{-4}$	$6.7 \cdot 10^{-9}$
0.06 M FeCl <sub>3</sub> / TBP equi. 7M HCl	$2 \cdot 10^{-4}$	$5.8 \cdot 10^{-9}$
Experiments in 3 M and 7 M HCl:	$\beta$ / cm/s	
0.02 M FeCl <sub>3</sub> / TOA/xylene equi. 3M HCl	$5 \cdot 10^{-3}$	
0.04 M FeCl <sub>3</sub> / TOA/xylene equi. 3M HCl	$> 5 \cdot 10^{-3}$	
0.06 M FeCl <sub>3</sub> / TOA/xylene equi. 3M HCl	$1 \cdot 10^{-3}$	
0.02 M FeCl <sub>3</sub> / TOA/xylene equi. 7M HCl	$> 5 \cdot 10^{-3}$	
0.04 M FeCl <sub>3</sub> / TOA/xylene equi. 7M HCl	$5 \cdot 10^{-3}$	
0.06 M FeCl <sub>3</sub> / TOA/xylene equi. 7M HCl	$> 5 \cdot 10^{-3}$	

In the FeCl<sub>3</sub>-HCl-TBP system, the detected interfacial transfer coefficients  $\beta$  / cm/s all are ranging between  $1 \cdot 10^{-4}$  cm/s and  $5 \cdot 10^{-4}$  cm/s. These values are significantly smaller, as expected, for a diffusion controlled interfacial transfer. According to the slow diffusion in the organic phase ( $D_{app.org.} = 1 \cdot 10^{-6}$  cm<sup>2</sup>/s), the transfer velocity should reach  $2 \cdot 10^{-3}$  cm/s. The transfer coefficients do not change significantly with hydrochloric acid concentrations between 1-7 mol/l and influence of the initial iron content on the transfer coefficient is also negligible. The velocity of iron extraction in the system FeCl<sub>3</sub>-HCl-TBP is controlled by a chemical reaction at the liquid/liquid interface. In the FeCl<sub>3</sub>-HCl-TOA/xylene system the interfacial transfer coefficients are larger than  $1 \cdot 10^{-3}$  cm/s and the interfacial transfer is faster than expected. We think the velocity of iron extraction in the system FeCl<sub>3</sub>-HCl-TOA/xylene increases due to the release of the heat of extraction at the liquid/liquid interface.

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## HYDRATION AND DIMERIZATION OF DIOCTYL HEXANAMIDE IN DODECANE

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### INTRODUCTION

The monoamide is one of the most hopeful new extractant alternative to tributyl phosphate(TBP) for the separation process of actinides in nuclear fuel cycle. However, the information regarding the chemical properties of such an extractant is only a few. In the present study, the hydration and dimerization of a monoamide, dioctyl hexanamide(DOHA), were examined on the basis of water distribution between aqueous solutions and dodecane containing the monoamide.

### EXPERIMENTAL

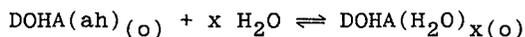
All reagents were of reagent grade. The monoamide, dioctyl hexanamide(DOHA), was originally synthesized by Daihachi Chemicals Co., Japan. The purity was checked by gas chromatography to be 99.6 %. Lithium chloride(purity > 99.0%) and dodecane(purity 99.3%) were used without further purification.

The water distribution experiments were carried out at 298 K. A certain volume of water or an aqueous lithium chloride solution and the same volume of monoamide-dodecane solution were shaken vigorously for 15 min in a stoppered glass tube and centrifuged. The concentration of water extracted into the organic phase was measured by Karl-Fischer titration. The concentration of lithium chloride extracted by the monoamide into the organic phase was also checked in the present study.

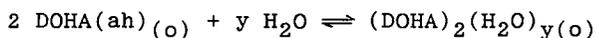
A portion of the organic phase was transferred into another tube and a certain volume of water added. The two phases were shaken for 15 min and lithium chloride in the organic phase was completely back-extracted into water. The concentration of chloride in the aqueous solution was measured by an anion chromatography using a 2.5 m mol dm<sup>-3</sup> aqueous potassium hydrogen phthalate solution as an eluent.

#### THEORETICAL

The hydration of monoamide can be written by the following two equilibria, monomer and dimer hydration:



$$K_{m,x} = \frac{[\text{DOHA}(\text{H}_2\text{O})_x]_o}{[\text{DOHA}(\text{ah})]_o a_w^x}, \quad (1)$$



$$K_{d,y} = \frac{[(\text{DOHA})_2(\text{H}_2\text{O})_y]_o}{[\text{DOHA}(\text{ah})]_o^2 a_w^y}, \quad (2)$$

where the subscript "o" denotes the species in the organic phase, while the lack of subscript denotes those in the aqueous phase. DOHA(ah) is the anhydrous(water-free) amide monomer and  $a_w$  is the water activity in the aqueous phase;  $a_w = 1$  for pure water.

The total concentration of monoamide in the organic phase can be written as:

$$\begin{aligned} [\text{DOHA}]_{o,t} &= [\text{DOHA}(\text{ah})]_o + \Sigma[\text{DOHA}(\text{H}_2\text{O})_x]_o \\ &\quad + 2\Sigma[(\text{DOHA})_2(\text{H}_2\text{O})_y]_o \\ &= (1 + \Sigma K_{m,x} a_w^x)[\text{DOHA}(\text{ah})]_o \\ &\quad + 2 \Sigma K_{d,y} a_w^y [\text{DOHA}(\text{ah})]_o^2. \end{aligned} \quad (3)$$

The number of hydrates which have to be taken into account is not defined in this equation; any number is possible in principle.

The total water concentration in the organic phase can be written as:

$$\begin{aligned}
 [\text{H}_2\text{O}]_{\text{o,t}} &= [\text{H}_2\text{O}(\text{free})]_{\text{o}} + [\text{H}_2\text{O}]_{\text{o,E}} \\
 &= [\text{H}_2\text{O}(\text{free})]_{\text{o}} + \Sigma(x[\text{DOHA}(\text{H}_2\text{O})_x]_{\text{o}}) \\
 &\quad + \Sigma(y[(\text{DOHA})_2(\text{H}_2\text{O})_y]_{\text{o}}) \\
 &= K_{\text{fW}} a_{\text{w}} + \Sigma(x K_{\text{m,x}} a_{\text{w}}^x)[\text{DOHA}(\text{ah})]_{\text{o}} \\
 &\quad + \Sigma(y K_{\text{d,y}} a_{\text{w}}^y)[\text{DOHA}(\text{ah})]_{\text{o}}^2, \tag{4}
 \end{aligned}$$

where  $K_{\text{fW}}$  is the distribution constant of free water between the two phases:

$$K_{\text{fW}} = \frac{[\text{H}_2\text{O}(\text{free})]_{\text{o}}}{a_{\text{w}}} = 0.0027. \tag{5}$$

The value of  $K_{\text{fW}}$  corresponds to the water solubility in dodecane in the molarity unit at  $a_{\text{w}} = 1$ .

## RESULTS AND DISCUSSION

The concentration of water extracted by dioctyl hexanamide (DOHA) into dodecane is shown in Fig.1 as a function of the monoamide concentration in the organic phase at various water activities ( $a_{\text{w}}$ ). The water activities were varied by adding lithium chloride whose distribution ratio to the organic phase is very low. The values of  $a_{\text{w}}$  were determined by water distribution technique using benzene as a solvent. The  $a_{\text{w}}$  values obtained by the water distribution method agreed very well with those obtained using the vapor pressure

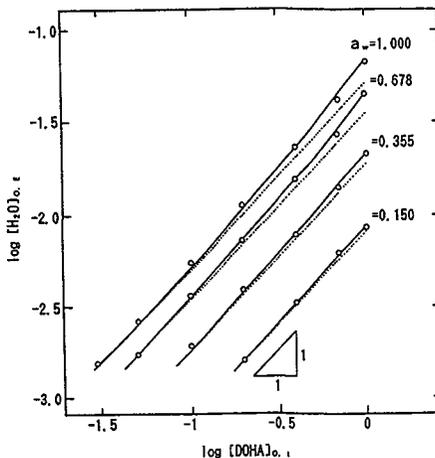


Fig.1  
 $\log [\text{H}_2\text{O}]_{\text{o,E}}$  vs.  $\log [\text{DOHA}]_{\text{o,t}}$

method: above aqueous lithium chloride solutions.

The concentration of water co-extracted with LiCl-Amide complexes was found to be negligible; total water concentration in the organic phase was always in large excess comparing to the concentration of LiCl extracted by DOHA.

When DOHA concentration in the organic phase is sufficiently low, i.e.,  $\leq 0.1 \text{ mol dm}^{-3}$ , the slope of lines in Fig.1 is approximately one at every  $a_w$ . This implies that most DOHA in the organic phase is monomeric in the low DOHA concentration range. The hydration number of the DOHA monomer can be determined by analyzing the distribution data of water as a function of  $a_w$  at the low DOHA concentrations. At  $0.1 \text{ mol dm}^{-3}$  DOHA, for example, the slope of  $\log[\text{H}_2\text{O}]_{\text{O,E}}$  vs.  $\log a_w$  plots is almost one, as is seen in Fig.2. From this, the hydration number of the DOHA monomer is found to be one.

When  $[\text{DOHA}]_{\text{O,t}}$  is higher than  $0.1 \text{ mol dm}^{-3}$ , the slope of lines in Fig.1 increases according to an increase in  $[\text{DOHA}]_{\text{O,t}}$ ; the dotted lines in this figure were calculated by assuming only  $\text{DOHA}\cdot\text{H}_2\text{O}$ . The deviation of the experimental values from the dotted lines is much smaller at low  $a_w$  than at high  $a_w$ . At  $a_w = 0.150$ , for example, the dotted line approximately fits the experimental values, therefore, the value of  $K_{m,1}$  ( $= K_{m,x}$ ) remains constant up to  $[\text{DOHA}]_{\text{O,t}} = 1 \text{ mol dm}^{-3}$ , at this low  $a_w$ . From this, the formation of  $\text{DOHA}\cdot\text{H}_2\text{O}$  occurs stoichiometrically at least up to this high DOHA concentration. Perhaps because even at  $a_w = 1$ , the concentration of water extracted into  $1 \text{ mol dm}^{-3}$  DOHA/dodecane is not so high, i.e.,  $[\text{H}_2\text{O}]_{\text{O,E}} = 0.066 \text{ mol dm}^{-3}$  (about 0.15 wt%) in the dodecane solution and such a small

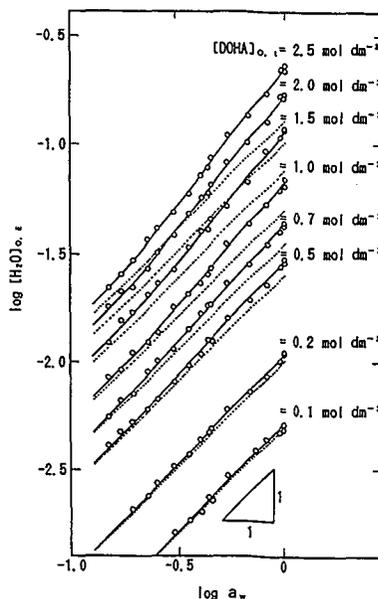


Fig.2

$\log [\text{H}_2\text{O}]_{\text{O,E}}$  vs.  $\log a_w$

amount of water hardly affects the physical properties, such as dielectric constant, in the medium of the organic phase. Therefore, DOHA·H<sub>2</sub>O seems to be formed stoichiometrically while no cluster of free water forms in the organic phase even at the higher water activities. If this is the case, the discrepancies between the experimental values and the dotted lines should be due to other complexation than DOHA·H<sub>2</sub>O formation. The formation of other monomer hydrates is not suitable for the explanation of the discrepancies because the ratio of DOHA(H<sub>2</sub>O)<sub>m</sub> (m ≥ 2) to DOHA·H<sub>2</sub>O is independent of DOHA concentration. Thus, DOHA self-association, such as dimerization, can explain the experimental data in Fig.1. A DOHA dimer hydrate, (DOHA)<sub>2</sub>(H<sub>2</sub>O)<sub>y</sub> (y ≥ 1), was first taken into account in the data analysis. The distribution data of water at a<sub>w</sub> = 1.000, 0.678, 0.355 and 0.150 as a function of [DOHA]<sub>o,t</sub> in Fig.1 were analyzed at the same time on the basis of Eqs.3 and 4. The results are shown in Table 1.

TABLE 1 Hydration and dimerization constants of DOHA in dodecane

Complex	Equilibrium constant
DOHA·H <sub>2</sub> O	$K_{m,1} = 0.052(\pm 0.005)$
(DOHA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	$K_{d,2} = 0.010(\pm 0.001)$

The water distribution was measured also as a function of water activity in the aqueous phase at certain DOHA concentration, and the equilibrium constants were determined for the respective DOHA concentrations. The experimental results where the DOHA concentration is increased up to 2.5 mol dm<sup>-3</sup> (90 vol% DOHA in dodecane) are shown in Fig.2. When the DOHA concentration in dodecane is constant and the extracted water concentration is sufficiently low, the medium of the organic phase can be regarded to be uniform. In such a uniform

medium, stoichiometric equilibrium constants for DOHA hydrates can be determined. Therefore, the stoichiometric equilibrium constants obtained for individual DOHA concentrations can be compared to each other. The equilibrium constants obtained by this method were independent of the DOHA concentrations, as seen in Table 2.

TABLE 2 The dependence of equilibrium constants on DOHA concentration

$[\text{DOHA}]_{\text{o,t}}/\text{mol dm}^{-3}$	$K_{\text{fw}}$	$K_{\text{m},1}$	$K_{\text{d},2}$
0.1	0.0027( $\pm 0.0002$ )	0.052( $\pm 0.004$ )	—
0.2	0.0027( $\pm 0.0002$ )	0.050( $\pm 0.004$ )	—
0.5	0.0028( $\pm 0.0005$ )	0.051( $\pm 0.005$ )	0.010( $\pm 0.004$ )
0.7	0.0029( $\pm 0.0005$ )	0.053( $\pm 0.005$ )	0.011( $\pm 0.003$ )
1.0	0.0028( $\pm 0.0013$ )	0.050( $\pm 0.005$ )	0.010( $\pm 0.001$ )
1.5	—	0.051( $\pm 0.005$ )	0.010( $\pm 0.001$ )
2.0	—	0.052( $\pm 0.004$ )	0.009( $\pm 0.001$ )
2.5	—	0.052( $\pm 0.005$ )	0.011( $\pm 0.001$ )

Activity coefficient of DOHA in the organic phase is known to change from unity at high concentration range. However, without any consideration for the correction in DOHA activity, a set of hydration and dimerization constants shown in Table 1 interprets all of the experimental data up to  $[\text{DOHA}]_{\text{o,t}} = 2.5 \text{ mol dm}^{-3}$  (90 vol% DOHA in dodecane) very well. Thus, it appears that the change in the medium of the organic phase by adding DOHA to dodecane, i.e., physical properties such as dielectric constant, does not alter the stoichiometry of DOHA hydration. Possibly, the change in the activity coefficient of DOHA may be chiefly due to the hydration and dimerization of DOHA in the organic phase, and not due to the medium property change.



## MASS TRANSFER WITH INTERFACIAL CONVECTION AND ADDED SURFACTANTS

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### ABSTRACT

Experiments have been performed with three binary liquid-liquid systems, two of which were interfacially stable whereas the other was interfacially unstable. The mass transfer process has been studied by contacting the phases in a quiescent cell and concentration profiles obtained using a Mach-Zehnder interferometric technique. Results have been obtained for the clean systems and the effects of the addition of three different surfactants have been analysed. Results have also been compared to those obtained by Fick's diffusional theory.

### INTRODUCTION

For the optimum design of liquid-liquid contacting equipment the interfacial behaviour of the system in use should be well understood and the effect of interfacial convection on the mass transfer process should be taken into account. Interfacial convection enhances mass transfer enabling smaller equipment to be employed to achieve the same degree of mass transfer. This is of particular interest in designing equipment for use in confined areas or where compactness is desirable e.g. process intensification and space platforms. It is, therefore, of interest that in the cases of systems where interfacial convection is not present, means to promote it should be sought so that interfacial convection adds value to the liquid-liquid contacting process.

Interfacial convection occurring during mass transfer has been observed by many investigators (e.g. Austin, 1966, Mudge & Heideger, 1970, Mendes-Tatsis and Perez de Ortiz, 1992) and has been the cause of an increase in mass transfer which has been reported by, for example, Maroudas and Sawistowski (1964), Berg (1972) and Perez de Ortiz (1992). Interfacial convection may be caused by interfacial tension gradients at the interface (Marangoni convection) and/or gravitational convection due to unstable density gradients. Sternling and Scriven (1959) developed stability criteria for the prediction of Marangoni instabilities in ternary systems and Perez de Ortiz and Sawistowski (1973) established similar criteria for binary systems. When a surfactant is added to a system a decrease in mass transfer is observed in many cases and it has been explained in terms of a resistance to mass transfer caused by hydrodynamic or barrier effects due to the adsorbed surfactants (Blokker, 1957). However, there have also been reports of increases in mass transfer when surfactants have been present during mass transfer (Nakache *et al*, 1991, Aunins *et al*, 1993). This has happened when the surfactant is in itself a solute and while crossing the interface causes Marangoni interfacial convection, which then enhances mass transfer.

The purpose of the present work has been to study the effect on mass transfer of the addition of surfactants to systems which have stable interfacial behaviour and to systems which show Marangoni interfacial convection.

### **Choice of systems**

The choice of the binary systems studied was based on the knowledge of their interfacial stability and, in addition, each pair of liquids had to be sufficiently optically different to be analysed using the interferometric technique. The systems chosen are: aniline/water, isobutanol/water and n-hexanol/water. Perez de Ortiz and Sawistowski's stability criteria for binary systems predicts the first two systems to be stable and the last one to be Marangoni unstable. These predictions have been confirmed during the present work and similarly by Ying and Sawistowski (1970), who report the system n-hexanol/water as presenting weak instabilities.

To study the effect on mass transfer of the "contamination" of the phases, three different surfactants have been used: Sodium Dodecyl Sulphate (SDS), Softanol 120 and Atlas G1300 supplied by Sigma Chemicals, BP Chemicals and ICI Chemicals, respectively. SDS is an anionic surfactant whilst the other two are non-ionic surfactants.

### **Experimental Set-up and Procedure**

In order that the two separate phases are brought into instantaneous contact with little or no disturbance introduced to the system a quiescent diffusion cell was built. It consists of a cell body with two glass windows separated by a PTFE spacer, held together by an outer aluminium frame, which is mounted onto an optical rail. The internal dimensions of the cell are 75mm x 90mm x 30mm. There is also a sliding partition 3mm thick, which separates the cell internally into an upper and a lower section. Phases are contacted by the removal of this partition. The glass windows of the cell are made hydrophobic by a silanisation process (Angst, 1991) and contact angles of near 90 degrees are achieved.

The organic phases used were of HPLC reagent grade and the water was double distilled. The concentration of the surfactants used were 0.05% for SDS, 1.25% for Atlas G1300 and 1.25% for Softanol 120 and are below the CMC. All percentages are in weight/volume. The organic phase was always pre-saturated with water so that transfer was only from the organic phase to the aqueous phase and experiments were carried out with the three "clean" systems and with the surfactants added to the aqueous phase. In the case of n-hexanol/water, measurements were also made with SDS added to the organic phase.

A Mach Zehnder interferometric set-up (Caldwell, 1956) was used to measure the changes in the refractive index of the phases which correspond to different concentrations of solute at different distances from the interface. Photographs were taken at set times during the run. Contact times for the phases were typically 60-100 minutes. The organic solute was only allowed to penetrate to about 30% of the depth of the aqueous phase (for the validity of the boundary conditions for a semi-infinite medium over the course of a run).

From the measurement of the fringe shifts in the interferograms, values of the experimental concentrations at various times and distances from the interface were obtained, using curves of refractive index vs concentration for the systems investigated.

## THEORY

For diffusional mass transfer at a quiescent planar interface, Fick's law states that

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

The solution of this equation for transient mass transfer in a semi- infinite media, when the following boundary conditions are applied,

$$\begin{aligned} C &= 0, & x &> 0, & t &= 0 \\ C &= 0, & x &= \infty, & t &> 0 \\ C &= C_i, & x &= 0, & t &> 0 \end{aligned}$$

is given by Crank (1975)

$$C = C_i \operatorname{erfc} \left[ \frac{x}{2\sqrt{Dt}} \right] \quad (2)$$

where C is the solute concentration,  $C_i$  is the solute interfacial concentration, D is the diffusivity and x is the distance from the interface.

Equation 2 was used to obtain plots of concentration vs time for the different systems studied and the interfacial concentration,  $C_i$ , was assumed to be the saturation concentration of the solute in the aqueous phase.

## ANALYSIS OF RESULTS

Experiments have been carried out with the systems aniline/water, isobutanol/water and n-hexanol/water, with mass transfer from the organic to the aqueous phase. The first two systems are stable and the last one is Marangoni unstable. The variation of concentrations with time have been measured, close to the interface, for the "clean" systems and when the surfactants, Atlas G1300 and SDS have been added (concentrations used were below the CMC). In the case of Softanol 120, spontaneous emulsification accompanied by interfacial movements, occurred at the interface. This made it impossible to obtain any quantitative measurements with the interferometric technique. The interfacial tension for each of the systems studied has been measured and is presented in Table 1.

Phase A Phase B	Water	Water + SDS	Water + Softanol 120	Water + Atlas G1300
Aniline (Water saturated)	4.0	0.5	4.8	4.7
Isobutanol (Water saturated)	2.3	2.0	1.9	0.5
Hexanol (Water saturated)	6.70	4.50	4.3	1.4

TABLE 1 Interfacial Tension Values at 25°C cPs

Figures 1 and 2 show graphs of concentration vs time for the two stable systems. It can be seen that the mass transfer measured for the "clean" systems is lower than theoretically predicted by Equation 2. Similar results have been reported by other researchers (e.g. Tung and Drickamer, 1952) and in particular for the case of isobutanol (Quinn and Jeanin, 1961), and attributed to an interfacial resistance. In the case of the unstable system, shown in Figure 3, the increase in mass transfer in

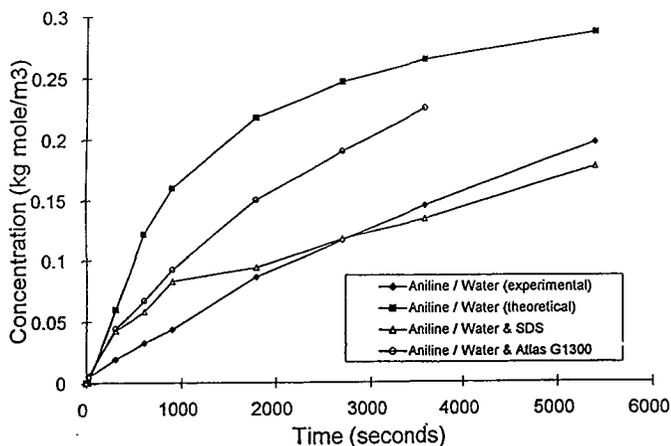


Figure 1 Aniline / Water System at  $x = 1\text{mm}$

comparison with the theory is caused by the interfacial convection present and has also been reported before (Perez, 1992, Berg, 1972). Figures 1, 2 and 3 also show curves for the "contaminated" cases. A comparison of the experimental results for the "clean" aniline/water system (Figure 1) and those obtained when the surfactant Atlas was added shows a large increase in mass transfer.

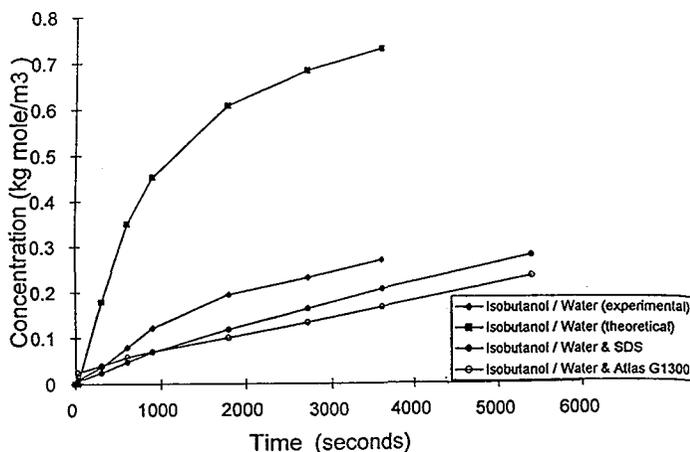


Figure 2 Isobutanol / Water System at  $x = 1\text{mm}$

However, in the case of the two alcohol systems (Figures 2 and 3) when Atlas is present, there is a decrease in mass transfer. The effect of the addition of SDS to the stable systems (Figures 1 and 2)

is to decrease mass transfer while a large increase is observed when SDS is added to the unstable system (Figure 3).

The surfactants Atlas G1300 and SDS, although added to the aqueous phase, are also soluble in the organic phases. Hence, although the “clean” system is binary, when the surfactant is present the system becomes ternary, with the surfactant considered as the solute. To apply Sternling and Scriven’s criteria, to the “contaminated” systems, knowledge of the properties of the phases is necessary, namely, interfacial tension, viscosity and diffusivity of the solutes. As the values for diffusivities were not known at this stage, relative magnitudes were inferred from their solubilities. Hence, when Sternling and Scriven’s stability criteria is applied to the systems studied, it predicts that aniline/water with SDS is stable but that it is unstable with Atlas; that it is stable for isobutanol/water with SDS as well as with Atlas; and that for hexanol/water with SDS it is unstable but it is stable with Atlas. Therefore, in Figure 1 and in Figure 3 the large increases in mass transfer measured in the case of Atlas and SDS respectively, may be explained in terms of the Marangoni

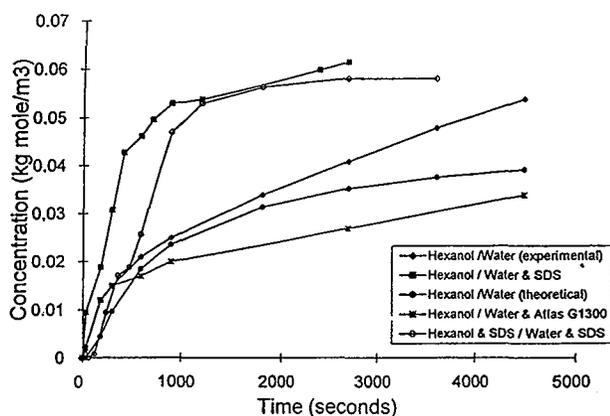


Figure 3 Hexanol / Water System at  $x = 1$  mm

interfacial convection caused by the surfactant transfer into the organic phase and which is predicted by the stability criteria. In the case of Atlas, an emulsion was seen to be formed at the interface which could have been caused by interfacial convection. However, in the case of SDS no interfacial convection was observed during the experiments. Furthermore, when 0.05% weight/volume of SDS was added to the organic phase the effect produced was similar to the one where SDS had only been added to the aqueous phase, indicating therefore that the transfer of SDS from the aqueous to the organic phase might not be the only cause for the measured increase in mass transfer but that there might be another mechanism present. The possibility of the presence of gravitational instabilities has been dismissed from the values measured for the densities of the phases. The observation of interfacial convection in the system heptane/water with SDS has been reported by Aunins *et al* (1993) and a large increase in mass transfer has also been observed by Stuckey (1995) in liquid-liquid extraction experiments when SDS was added to the system used. However, the understanding of what really happens at the interface is still unclear. When Atlas was added to isobutanol/water and hexanol/water, mass transfer was hindered, despite the observation of emulsification at the interface. The stability criteria in this case predict the system to be stable. In this case, the effect of the transfer of the surfactants themselves to the organic phase seems to be one of obstructing the transfer of the organic phase in the opposite direction, and creating an interfacial resistance. The initial increase in mass transfer when SDS was added to aniline/water may have been due to initial disturbances at the

interface caused by the adsorption of SDS, which may be dampened later during the transfer process and an interfacial resistance created. Many hours after the start of the experiment, it was observed that there was a slight cloudiness in the aniline phase. There is also a marked resistance to mass transfer in the case of isobutanol/water, which is predicted to be a stable system even when SDS is present.

There is an obvious need for further investigations to understand what is happening at the interfaces of the "contaminated" systems under study. Consideration should also be given to the type of surfactants used, for example that SDS is an anionic surfactant and that Atlas G1300 (as well as Softanol 120) are non-ionic and also other factors such as the polarity of the phases and the possibility of interfacial reactions. More surfactants should also be tested.

### CONCLUSIONS

The most important finding of this work is that a system which shows interfacial convection may have mass transfer further improved by the addition of a surfactant. Also that mass transfer can also be enhanced in a system which is initially stable by the addition of a surfactant which induces Marangoni convection at the interface. Experimental results have also shown that Fick's diffusional theory overestimates the mass transfer for the stable systems investigated but underestimates it for the unstable system. Further work needs to be carried out to understand fully the effects observed.

### ACKNOWLEDGEMENTS

This work has been supported by the EPSRC, under grant No GR/J52600.

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# GENERAL REGULARITIES IN COORDINATION CHEMISTRY of Acids EXTRACTION by BASIC EXTRACTING AGENTS

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## ABSTRACT

The regular changes in the composition and structure of associates, which form in the extraction of strong, moderate and weak mineral and metal containing (HAn) acids, primarily by tributylphosphate (TBP), have been considered. Using IR spectroscopy we have shown that a distinguishing feature for the extraction of strong acids, formed at  $a_{\text{H}_2\text{O}} \approx 1$  and low  $C_{\text{HAn}}^\circ$ , is the formation of micromicelle-like associates. Their composition and structure were established. The results obtained allow us to suggest the solubilisation mechanism of strong acids extraction by TBP under those conditions.

## INTRODUCTION

Starting in 1960s, the mechanism of acids extraction with such widely used extractants as TBP, ketones, ethers etc. has been extensively studied (Zolotov Yu.A., Ioffa B.Z., Chuchalin L.K. 1973.). It was found that in the extraction of strong acids (e.g.  $\text{HFeCl}_4$ ) their cation part contains a highly-hydrated hydroxonium ion  $\text{H}_5\text{O}_2^+$ . However, it is still unclear why certain of the strong acids  $\text{H}^+(\text{H}_2\text{O})_n\text{An}^-$  where  $\text{An}^- = \text{AuCl}_4^-, \text{FeCl}_4^-, \text{BiCl}_4^-$  etc. with a highly hydrated cation are freely extracted by basic reagents. The progress achieved in recent years towards investigation of the composition of extracted compounds and their structures via vibrational spectroscopy and the interpretation of the IR spectra of the hydrated proton allows a better understanding of the chemistry of acids extraction and systematizes their extraction mechanisms.

This paper presents the results of investigations of the molecular state of strong acids in organic extracts at the water activity  $a_{\text{H}_2\text{O}} \approx 1$ . Comparison between these results and the previously data obtained on the molecular state of the moderate acid  $\text{HNO}_3$  and the weak acid  $\text{HNO}_2$  in extracts allows the systemization of acids extraction with TBP in the series strong-moderate-weak acid.

## EXPERIMENTAL

The water concentration in extracts ( $C_{\text{H}_2\text{O}}^\circ$ ) was determined from the absorption intensity of the band  $\delta(\text{H}_2\text{O}) = 1640 \text{ cm}^{-1}$ . Since the  $\text{H}_5\text{O}_2^+$  cation does not absorb at  $1640 \text{ cm}^{-1}$ ,  $C_{\text{H}_2\text{O}}^\circ$  does not include the two  $\text{H}_2\text{O}$  molecules of the  $\text{H}_5\text{O}_2^+$  cation. The Bi(III) concentration in extracts ( $C_{\text{Bi}}^\circ$ ) was determined from the distribution coefficients found via radiometry using a  $^{210}\text{Bi}$  isotope and the TBP concentration ( $C_{\text{TBP}}^\circ$ ) was found from the changed volume of the organic phase before and after extraction (see Table 1). The hydrated TBP concentration ( $C_{\text{TBP}}^h$ ) in extracts (i.e. that of TBP molecules H-bonded with water molecules) was determined using differential IR spectroscopy with compensation of the hydrated TBP band  $\nu(\text{P}=\text{O}) = 1250 \text{ cm}^{-1}$  intensity (Stoyanov E.S., Lastovka L.V. 1987). To do this, the extract IR differential spectrum was recorded relative to the water-saturated TBP spectrum. The thickness of a reference cell was smoothly varied until the  $\nu(\text{P}=\text{O}) = 1250 \text{ cm}^{-1}$  band was fully compensated (Fig.1) to give the equation

$$C_{\text{TBP}}^h = 0.5 C_{\text{TBP}}^\circ (\Delta D_{\text{CH}}/D_{\text{CH}}),$$

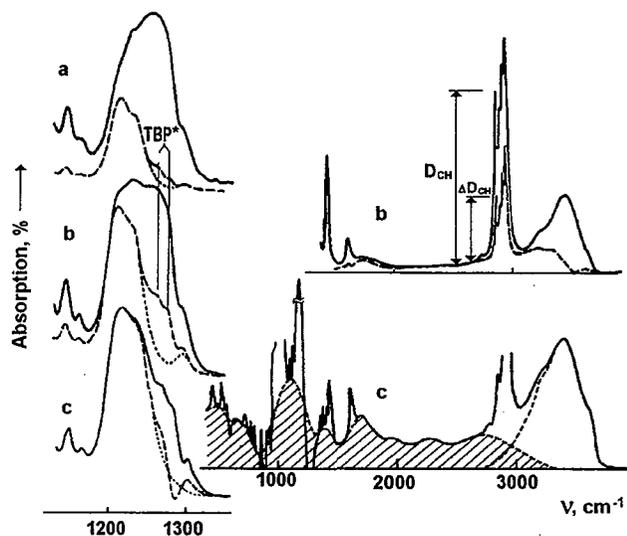


Figure 1. IR spectra of the extracts No 2(a), 3 (b) and 4 (c) without (unbroken lines) and with compensation of unhydrated and hydrated TBP (dotted lines). Absorption of  $H_3O_2^+$  cation is marked by shading.

where  $D_{CH}$  and  $\Delta D_{CH}$  are the optical densities of the  $\nu(CH) = 2870 \text{ cm}^{-1}$  band in the extract IR spectrum and its differential IR spectrum, respectively (Fig.1). IR spectra were recorded on a Specord 75 IR spectrometer in  $CaF_2$  (1100-400  $\text{cm}^{-1}$ ) and silica cells (400-4000  $\text{cm}^{-1}$ )

TABLE 1

The composition of Bi(III) extracts obtained by TBP from 0.25 M  $BiCl_3$  solutions in 1 M HCl

No	$V_o:V_{aq}$	$C_{Bi}^o = C_{H_3O_2^+}^o, M$	$C_{TBP}^o, M$	$C_{H_2O}^o, M$	$C_{TBP}^h, M$	$C_{TBP}^*, M$	$f_A$
	-	0	3.50	3.45	1.75	-	-
1	0.5:1	0.098	3.45	3.45	1.62	0	0
2	1:1	0.237	3.29	3.01	1.40	0.11	0.53
3	1:2	0.438	3.15	2.30	0.98	0.32	0.82
4	1:10	0.927	2.94	1.12	0.10	0.86	1.0

## RESULTS AND DISCUSSION

### Strong acids

The  $H[BiCl_4 \cdot 2TBP]$  acid appears to be suitable for the study of the molecular state of strong acids in TBP extracts. The presence of a large non-hydrated anion  $[BiCl_4 \cdot 2TBP]^-$  makes it easier to study the composition and structure of the acid cation part. According to the Raman spectra data (Zolotov Yu.A., Spivakov B.Ya., et al. 1979), Bi(III) is extracted from 1 M HCl solutions with TBP in the form of  $H[BiCl_4 \cdot 2TBP]$  only (designated as I). IR differential spectroscopy was used to study four Bi(III) extracts from 0.25 M  $BiCl_3$  in 1 M HCl at various volume ratios of the organic and aqueous phases ( $V_o:V_{aq}$ ). The extract compositions are given in Table 1.

After we compensate the  $\nu(P=O) = 1250 \text{ cm}^{-1}$  band of hydrated TBP with that of anhydrous TBP, the differential IR spectra of extracts exhibit the  $\nu(P=O) = 1220 \text{ cm}^{-1}$  band of TBP bonded

with  $\text{Bi}^{3+}$  in the  $[\text{BiCl}_4 \cdot 2\text{TBP}]^-$  anion and a weak doublet band of TBP at 1264 and 1282  $\text{cm}^{-1}$ . The latter frequencies coincide with those of the free TBP  $\nu(\text{P}=\text{O})$  band but differ in the ratio of doublet components intensities (Fig.1). It follows from the spectra that the acid I cation part is not solvated with TBP molecules.

Indeed, the molar absorption coefficient of the  $\nu(\text{P}=\text{O}) = 1220 \text{ cm}^{-1}$  band ( $\epsilon_{1220}$ ) for all 4 spectra is the same and coincides with  $\epsilon_{1220} = 116 \pm 0.6 \text{ l/mol}\cdot\text{cm}$  of a specially synthesized complex  $\text{R}_3\text{CH}_3\text{N}^+[\text{BiCl}_4 \cdot 2\text{TBP}]^-$ . The "free" TBP concentration (hereafter called  $\text{TBP}^*$  and  $C_{\text{TBP}}^*$ , respectively) is easy to determine from the intensity of its band  $\nu(\text{P}=\text{O}) = 1264\text{-}1282 \text{ cm}^{-1}$  (Table 1). So, we obtain the material balance

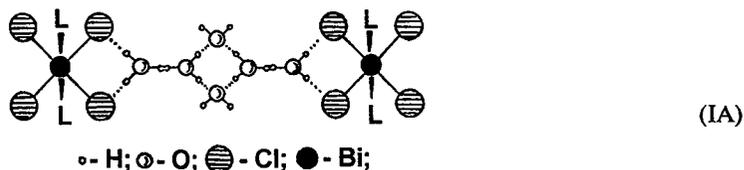
$$C_{\text{TBP}}^{\circ} = 2C_{\text{TBP}}^{\text{h}} + 2C_{\text{Bi}}^{\circ} + C_{\text{TBP}}^* \quad (1)$$

where  $2C_{\text{TBP}}^{\text{h}}$  is the overall concentration of equilibrium hydrated and anhydrous TBP ( $C_{\text{TBP}}^{\text{h}} = C_{\text{TBP}}^{\text{anh}}$ , Stoyanov E.S., Lastovka L.V. 1987) not interacting with I;  $2C_{\text{Bi}}^{\circ}$  equals the TBP concentration in the  $[\text{BiCl}_4 \cdot 2\text{TBP}]^-$  anion.

The data in Table 1 satisfies equation (1). Hence, the acid I cation part does not really interact with TBP what is surprising at first sight.

The IR spectrum of cation part the of  $\text{H}[\text{BiCl}_4 \cdot 2\text{TBP}]$  in all extracts (Fig. 1c), as well as the majority of previously obtained IR spectra of strong acids extracts are assigned to the hydrated cation  $\text{H}_5\text{O}_2^+$  but not to  $\text{H}_3\text{O}^+$  (Stoyanov E.S. 1992.).

Extract 4 is almost deprived of free TBP (see the Table 1) and represents a liquid non-diluted acid  $\text{H}_5\text{O}_2^+[\text{BiCl}_4 \cdot 2\text{TBP}]^-$  (IA). The concentration of water contained in IA ( $C_{\text{H}_2\text{O}}^{\circ} - 2C_{\text{TBP}}^{\text{h}}$ ) is 0.92 M (Table 1), i.e. for each  $\text{H}_5\text{O}_2^+$  cation there is one  $\text{H}_2\text{O}$  molecule. The IR spectrum of extract 4 exhibits the band  $\nu_s(\text{O}\cdots\text{O}) = 450\text{-}500 \text{ cm}^{-1}$  (Fig.1) which is prohibited for the symmetric cation  $\text{H}_5\text{O}_2^+$ . Hence, the surrounding of  $\text{H}_5\text{O}_2^+$  in IA is not symmetric. And finally,  $\text{H}_5\text{O}_2^+$  peripheral OH-groups exhibit two types of frequencies: the band  $\nu(\text{OH}) = 3425 \text{ cm}^{-1}$  coinciding with the  $\nu(\text{OH})$  band of the acid  $\text{H}_5\text{O}_2^+\text{SbCl}_6^-$  in which the protons of  $\text{H}_5\text{O}_2^+$  interact slightly with  $\text{Cl}^-$  ions of  $\text{SbCl}_6^-$  (Ortwein R., Schmidt A. 1976) and the continuous absorption background (CAB, denoted by shading in Fig.1) which is due to peripheral protons of the  $\text{H}_5\text{O}_2^+$  cation, forming a O-H $\cdots$ O fragments with strong H-bonds. Taking into account, that the  $\text{H}_5\text{O}_2^+$  cation should have a filled internal coordination sphere in a non-symmetric surrounding, the above data indicate a dimeric structure of IA whose structure is probably as follows:



On the  $\text{H}_5\text{O}_2^+$  cation hydration, the CAB intensity in the  $\text{H}_5\text{O}_2^+$  IR spectra is known to increase. This increase tends to slow down upon the consequent adding of the 1st, 2nd, 3rd and 4th water molecule to  $\text{H}_5\text{O}_2^+$  and further remains unchanged (Leuchs M., Zundel G. 1978). However, the dependence of the CAB intensity at 2500  $\text{cm}^{-1}$  ( $\epsilon_{2500}$ ) on the  $C_{\text{H}_2\text{O}}^{\circ}/C_{\text{H}_5\text{O}_2^+}^{\circ}$  ratio in the series of extracts 4, 3, 2, 1 grows linearly and attains, at  $C_{\text{H}_2\text{O}}^{\circ}/C_{\text{H}_5\text{O}_2^+}^{\circ} \geq 26$ , the maximum value of 140  $\text{l/mol}\cdot\text{cm}$  which is close to  $\epsilon_{2500} = 160 \text{ l/mol}\cdot\text{cm}$  for  $\text{H}_5\text{O}_2^+$  in  $\text{HCl}$  aqueous solutions (Fig.2). This dependence can be explained as follows. The extracts contain two types of  $\text{H}_5\text{O}_2^+$  cations. The first type enters IA with  $\epsilon_{2500} = 18.8 \text{ l/mol}\cdot\text{cm}$ , while the second one, strongly hydrated  $[\text{H}_5\text{O}_2^+ \cdot 4\text{H}_2\text{O}]_{\text{aq}}$ , enters IB with  $\epsilon_{2500} = 140 \text{ l/mol}\cdot\text{cm}$ . The organic phase is saturated with associates I B as  $C_{\text{Bi}}^{\circ}$  grows from zero up to 0.13 M and at  $C_{\text{Bi}}^{\circ} > 0.13 \text{ M}$ , associates I B begin to transform into I A.

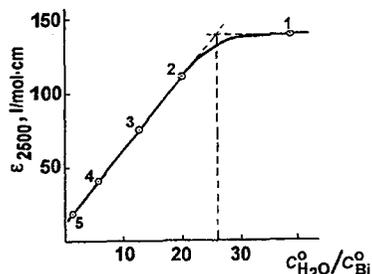


Figure 2. Plot of  $\epsilon_{2500}$  vs  $C_{H_2O}^0/C_{Bi}^0$ .  $C_{Bi}^0$  in extracts is (in M): 0.098 (1), 0.170 (2), 0.237 (3), 0.438 (4) and 0.927 M (5). Extracts were obtained by TBP from Bi(III) solutions in 1 M HCl at different  $V_o/V_{aq}$

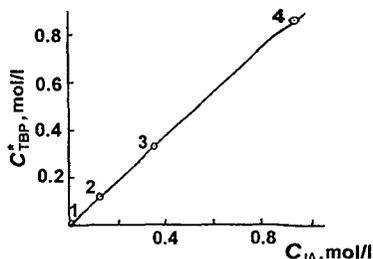


Figure 3. Plot of  $C_{TBP}^*$  vs concentration in the extracts of 1A-associates No 1, 2, 3, 4 (see Table 1)

If so, one can easily find the portion of  $H_3O_2^+$  in IA from the total amount of  $H_3O_2^+$  as follows:

$$f_A = (140 - \epsilon_{2500}) / (140 - 18.8).$$

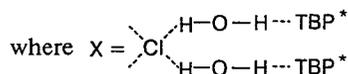
Figure 3 shows the  $C_{TBP}^*$  vs  $f_A$  dependence. The proportional character of this function confirms the validity of the  $f_A$  calculation and shows IA to contain TBP\* at the molar ratio of TBP\* : IA = 1. The coincidence of the TBP\* and the free TBP frequencies  $\nu(P=O)$  indicates the outerspheric dipole-dipole interaction of TBP\* molecules with IA.

The final overall formula of IA is as follows



The composition of associate IB follows from the material balance (data from table 1) and the dependence in Fig. 2: for each  $H_3O_2^+ [BiCl_4 \cdot 2TBP]^-$  ion pair, there are 26-28  $H_2O$  molecules and ~14 TBP molecules. In other words, associate IB represents a micromicelle whose structure is schematically shown in Fig.4. The core consists of 26-28  $H_2O$  molecules and one  $H_3O_2^+$  cation forming a solvate-separated ion pair with the  $[BiCl_4 \cdot 2TBP]^-$  anion. The core is surrounded by ~14 TBP molecules forming a monomolecular hydrophobic layer. Being far from the  $H_3O_2^+$  cation, the TBP molecules are not influenced by its presence and therefore, do not differ from TBP molecules of associates  $(TBP \cdot 2H_2O)_p$  formed in water-saturated TBP.

Studies on extracts 1-4 with low-angle X-ray scattering have shown that they contain 37 A micromicelles. The content of these micelles decreases in the series of extracts 1, 2, 3 and reaches zero in extract 4. Studies on the TBP extracts of another strong acid HCl have shown (Stoyanov E.S. 1993) that in organic phase at  $C_{HCl}^{aq} < 2.3$  M, micelles II form which are similar to IB in composition. The core contains ~26  $H_2O$  molecules surrounded by ~13 TBP molecules (Fig.5). However, unlike  $[BiCl_4 \cdot 2TBP]^-$ , the  $Cl^-$  anion enters the core and two TBP\* molecules bond with the  $Cl^-$  anion through the water molecule (Fig. 5) are not equivalent to the rest of the TBP molecules. In the extract from aqueous solutions at  $2.3 \text{ M} < C_{HCl}^{aq} < 5.6 \text{ M}$ , the micelles decompose to form the dimers  $[H_3O_2^+(H_2O)_2 X^-]_2$  (III)



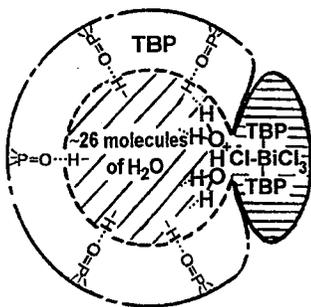


Figure 4. Structure of micelle-like associate I B

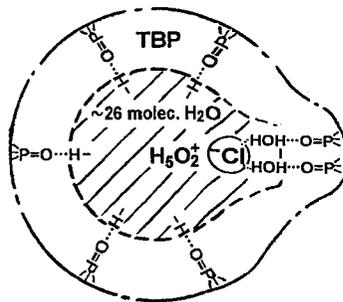


Figure 5. Structure of micelle-like associate II

The IR spectra data of extracts of other strong acids:  $\text{HClO}_4$ ,  $\text{HTiO}_4$ ,  $\text{HFeCl}_4$  obtained at low  $C_{\text{HAN}}^{\text{aq}}$  allow to suggest that they also exhibit the formation of micromicelles of the IB and II types. Since the initial extractant, i.e. water-saturated TBP contains the micromicelles  $(\text{TBP} \cdot 2\text{H}_2\text{O})_p$  (Stoyanov E.S., Lastovka L.V. 1987), the mechanism of strong acids HAN extraction with TBP at  $\alpha_{\text{H}_2\text{O}} \sim 1$  and  $C_{\text{HAN}}^{\text{o}} < 0.13 \text{ M}$  may be considered as HAN solubilization with micromicelles  $(\text{TBP} \cdot 2\text{H}_2\text{O})_p$

#### Weak acids

These acids, such as  $\text{HNO}_3$ , for example, unlike strong ones, are extracted only as a waterless monosolvate of L HAN type (Stoyanov E.S., Chizevskaya S.V., Sharonov A.V., Chekmarev A.M. 1991).

#### Moderate acids

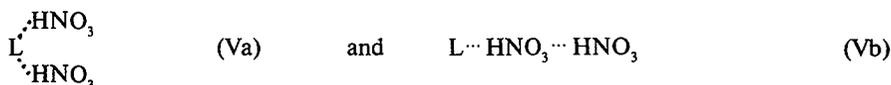
A typical example of such acids is nitric acid. It exhibits the most complicated mechanism of extraction with TBP.

Two tendencies are observed in its associates formation (Stoyanov E.S., Mikhailov V.A., Chekmarev A. M. 1992):

##### 1. Anhydrous monosolvates



form which are typical for the weak acids extracts. With increased  $C_{\text{HNO}_3}^{\text{o}}$ , the second  $\text{HNO}_3$  molecule adds to the monosolvate IV to yield two types of semisolvates

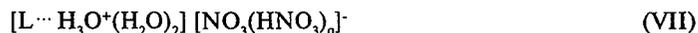


Then the third and so on  $\text{HNO}_3$  molecules add to Va and Vb.

2. Hydrated associates form, which are typical for the strong acids extracts. At low  $C_{\text{HNO}_3}^{\text{aq}}$ , a contact ion pair (IP)



appea with a variable composition of the first coordination sphere of  $\text{H}_5\text{O}_2^+$  ( $n = 3-0$ ,  $m = 0-2$ ). At high  $C_{\text{HNO}_3}^{\text{aq}}$ , nitric acid is partially extracted as a strong «superacid»  $\text{H}[\text{NO}_3(\text{HNO}_3)_q]$  providing type VII associates



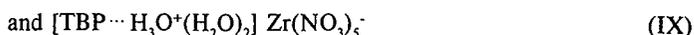
where  $q = 1, 2, 3$ .

When TBP is diluted with the inert solvent  $\text{CCl}_4$ , the portion of associates VI and VII in the

extracts decreases while that of IV increases.

As extractants of various types are used in the series of increasing basicity: ketones-TBP-phosphine oxides, the portion of associates V in the extracts decreases reaching zero with phosphine oxides. Quantitative IR spectroscopy data were used to construct the curves of associates IV-VI formation in TBP extracts and to explain the  $C_{\text{H}_2\text{O}}^{\circ}/C_{\text{HNO}_3}^{\circ}$  dependences (Stoyanov E.S., Mikhailov V.A., Chekmarev A.M. 1992).

The mechanism of metal-containing acids extraction from concentrated (8-12 M)  $\text{HNO}_3$  solutions is of interest. Under such conditions, Zr(IV) is extracted by TBP in the form of two acids (Stoyanov E.S., Chizevskaya S.V., Chekmarev A.M. 1993)



With increasing  $C_{\text{HNO}_3}^{\circ}$  and decreasing  $C_{\text{Zr}}^{\circ}$ , the equilibrium VIII  $\leftrightarrow$  IX shifts towards IX formation. Zr extraction at low  $C_{\text{Zr}}^{\circ}$  may be considered as the replacement of  $\text{NO}_3(\text{HNO}_3)_5^-$  anions of VII ion pairs by  $\text{Zr}(\text{NO}_3)_5^-$  providing the IP IX. As the content of IP IX in the extracts increases, the common cation effect becomes more pronounced and Zr extraction via an anion-exchange mechanism is suppressed. Then, the second extraction mechanism plays an increasingly important part: the strong acid  $\text{HZr}(\text{NO}_3)_5$  displaces the weaker  $\text{HNO}_3$  bounded with TBP in associates IV and Vb to form IP VIII with the transfer to L-basic molecules.

### CONCLUSIONS

Extraction of strong acids HAn with TBP at  $a_{\text{H}_2\text{O}} \approx 1$  and  $C_{\text{HAn}}^{\circ} < 0.13$  M proceeds via the mechanism of HAn solubilization with micromicelles  $(\text{TBP} \cdot 2\text{H}_2\text{O})_p$  and yields micromicelles of IB or II types:  $[\text{H}_3\text{O}_2^+ \cdot 2p\text{H}_2\text{O} \cdot p\text{TBP}] \text{An}^-$  with  $p \approx 13$ . When  $C_{\text{HAn}}^{\circ} > 0.13$  M, micromicelles decompose forming low-hydrated compounds of type IA and III and no intermediates.

For moderate acids,  $\text{An}^-$  shows an increase in proton-donor properties and may incorporate into the  $\text{H}_3\text{O}_2^+$  first coordination sphere. As a result, instead of micromicelles the contact IP of type VI form which are the monomeric analogs of associates IA and III. And finally, the proton-acceptor properties of weak acids anions are so strong that  $\text{H}^+$  is transferred to the anion to form the non-hydrated H-complexes of IV type.

The chemistry of moderate acids extraction is most complicated. At high  $C_{\text{HAn}}^{\circ}$ , strong acids  $\text{H}[\text{An}(\text{HAn})_q]$  may form and change, thus, the extraction mechanism. So, the mechanism of metals extraction from solutions of such acids of various concentration can also change.

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### ACKNOWLEDGEMENT

This research was supported by a grant from the International Science Foundation



## DESIGN OF NOVEL ORGANOPHOSPHORUS EXTRACTANTS HAVING TWO FUNCTIONAL GROUPS FOR THE EXTRACTION OF RARE EARTH METALS

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### ABSTRACT

Novel organophosphorus extractants, which have two functional moieties in the molecular structure, have been developed for the separation of rare earth metals using liquid-liquid extraction. The separation efficiency and extraction ability of the newly synthesized extractants were investigated for nine kinds of rare earth metals. The new extractants have an extremely high extractability to all the rare earth metals compared with those of commercially available phosphorus extractants. Two isomers having an identical chemical formulation can have significantly different behavior in rare earth extractions. This result means that the extraction and separation abilities are highly sensitive to the structure of the spacer connecting two functional phosphorus groups. The results of computer modeling also suggest that the structural effect of extractants is one of the key factors to enhance the selectivity and extractability in rare earth extractions.

### INTRODUCTION

Rare earth metals have been noted as important elements for producing high technology materials such as advanced semiconductors, supermagnets and crystals for lasers. However, their high purification is very difficult and a huge energy is often required to obtain high-purity products of rare earth metals, because their chemical and physical similarities make the mutual separation of adjacent elements among rare earth metals very difficult.

Conventional solvent extraction is well-known as one of the most effective techniques for the separation of rare earth metals on an industrial scale due to the advantage for large-scale operation. In the liquid-liquid extraction of actinides or lanthanides, acidic organophosphorus extractants are considered to be the best extractant for separating them effectively from both extractive and separative points of view (Ceconie (1989), Ohto (1993)). Even with the organophosphorus extractants, however, a large number of stages in a series of mixer-settlers are necessary for separating all the rare earth elements because there are some poor selectivity fields in the series of lanthanides. Thus a new extractant to enhance the separation efficiency and extractability is desirable to simplify the solvent extraction process.

A number of studies have been carried out on the separation and extraction of rare earth metals. In most reports, however, the conventional, commercially available extractants such as D2EHPA (di-2-ethylhexyl phosphoric acid) and PC-88A (2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester), or synthesized di-alkyl organophosphorus extractants have been used in the liquid-liquid operations. In the late 1950s, Peppard et al. reported the extraction of actinides from nuclear wastes using some newly developed organophosphorus extractants (Peppard (1957)) and recently, Yuan (1988) synthesized a series of acidic organophosphorus extractants in order to investigate the structure-extractability relationship, and the steric structure of extractants is elucidated to have a crucial effect to the selectivity of rare earths. However, the development of new types of organophosphorus extractants on the basis of a new concept has not been performed except for the idea of changing the alkyl chain in a mono-acidic organophosphorus extractant.

In this study, we have synthesized new types of organophosphorus extractants having two functional phosphoric groups in the molecular structure. The purpose of this work was to develop new extractants capable of extracting rare earths with a high extractability and selectivity based on the new concept to connect the bi-functional groups with a spacer, and to obtain useful information on the design of appropriate extractants for the solvent extraction of rare earth metals. Using the newly developed extractants, we have investigated the extraction behavior of nine kinds of rare earth metals for comparison with conventional mono-acidic organophosphorus systems. In addition, the structural effect of extractants on the extraction behavior of rare earth metals is discussed from the viewpoint of molecular modeling with molecular mechanics and semi-empirical molecular orbital methods.

## EXPERIMENTAL

### New extractants

Three new extractants having two phosphoric acid groups, tri(ethylene glycol) *o*, *o'*-di-(4-*tert*-octylphenyl phosphoric acid) (abbreviated with EG<sub>3</sub>PA), 1,2-di(2-hydroxyethoxy)benzene *o*, *o'*-di(4-*tert*-octylphenyl phosphoric acid) (abbreviated with *o*-type) and 1,4-di(2-hydroxyethoxy)benzene *o*, *o'*-di(4-*tert*-octylphenyl phosphoric acid) (abbreviated with *p*-type) have been synthesized, and the mono-functional extractant which has the similar structure of the right/left part of the new extractants (abbreviated with MPA) was also prepared and used to compare the extraction behavior. Figure 1 shows the structure and abbreviation of extractants employed in this study. Hereafter, we use the abbreviations to express their extractants. The *o*- and *p*-types have an identical structural formulation, therefore, the two extractants have an isomer relationship.

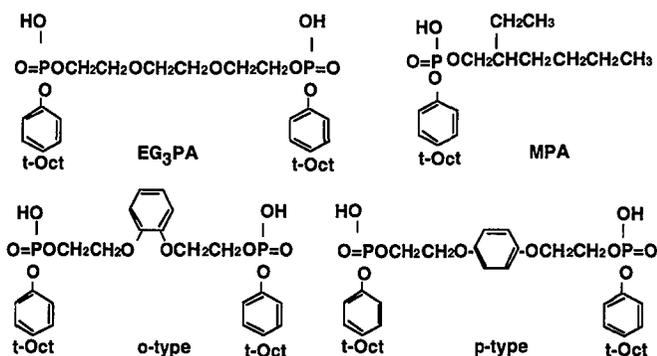


Figure 1 Structure and abbreviation of extractants synthesized in this study

### Experimental procedure

An organic solution was prepared by weighing each extractant into analytical-grade toluene. The aqueous solutions were prepared by dissolving each rare earth chloride into a hydrochloric solution (0.1-2 M). The aqueous solution always contained three kinds of metals, La, Pr, Nd, or Sm, Gd, Dy, or Ho, Y, Er. Equal volumes (5 ml) of aqueous and organic solutions were shaken with a mechanical shaker at 303 K for at least 5 h, which was sufficiently long to reach equilibrium. After phase separation, the equilibrium concentrations of rare earth metals in the aqueous phase were measured by ICP/AES (Seiko SPS1200VR) along with the concentrations before the extractions.

The concentration of each metal ion in the initial aqueous solution was 0.1 mM and the concentration of the extractant was 10 mM except for the investigation of extractant dependency on the rare earth extraction. Extraction species of a complex between a rare earth metal ion and each extractant was determined on the basis of both slope analysis and Job's methods. Measurement of aggregation number and acid dissociation constants were also investigated for all the extractants using vapor-phase osmometer (Corona model-117) and automatic titrator (Kyoto elec., AT-117), respectively.

### Computer modeling of new extractants

Semiempirical PM3 calculations of the extractant molecules were conducted on Sun4/10 UNIX computer using the MOPAC 93 (Stewart (1993)). The precise mode, which sets the convergence criteria for GNORM=0.01 and SCFRT=0.00001, was used. Standard bond distances and angles were employed for the initial conformation. The calculations of molecular mechanics for rare earth complexes were performed on IBM PC computer using the version 3.1 of MOMEC (Comba and Hambley). The optimized structures were calculated under the convergence criteria for RMS=0.001.

## RESULTS AND DISCUSSION

### Aggregation behavior and acid dissociation constants of new extractants

Organophosphorus extractants such as D2EHPA or PC-88A are well-known to dimerize in a nonpolar solvent. In this study, we have investigated the aggregation behavior of the newly synthesized extractants in toluene. On the basis of the osmometry measurement, it was found that EG<sub>3</sub>PA and o-type mainly exist as dimeric species, while the main species of p-type is a trimer in toluene. The results of computer modeling suggest that the p-type has a high possibility to form the trimer compared with EG<sub>3</sub>PA and o-type owing to the low energy difference between the dimer and trimer conformation, and also we could deduce that the trimer of the p-type is a cyclic conformation although we could not predict why only p-type forms the stable trimer. The difference in the aggregation mode of the extractants in toluene clearly influences the extraction behavior of the three new extractants. In the measurement of acid dissociation constants of the extractants, however, there was not much difference in the values of the three extractants, and the values of pK<sub>a1</sub> and pK<sub>a2</sub> in the bi-functional phosphoric acid in the extractants were around 1.6 and 2.1, respectively.

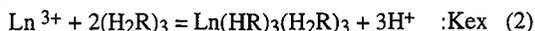
### Distribution equilibria of rare earth metals using the new extractants

Figure 2 shows a typical pH dependence on the distribution ratio ( $D = [\text{Metal}]_{\text{org}}/[\text{Metal}]_{\text{aq}}$ ) in the rare earth extraction using the new extractants of p-type and o-type. All of the plots lie on straight lines with a slope of 3. Another new extractant EG<sub>3</sub>PA showed a similar behavior to o-type. The selectivity for the metal ions appears to be in the order light (Nd) > middle (Gd) > heavy (Ho) rare earth groups, and this order is consistent with those observed for ordinary organophosphorus extractants (Kubota (1993)). However, it is surprising that the two extractants having an identical structure formulation show quite different extraction results for the same metal ions, as the results of computer modeling with the PM3MO method suggest that the two extractants have a similar electric density on the phosphoric acid part in the extractants, the quite different extraction behavior is considered to be caused by a steric effect of the extractants. The dependency on the concentration of each extractant in the rare earth extraction was also investigated (data not shown). Based on the results of the slope analysis and the Job's method in the rare earth extractions, we found that the extraction equilibria of rare earth metals for each extractant could be represented as follows:

For the extractants of EG3PA or o-type,



For the extractant of p-type,



where Ln and H<sub>2</sub>R denote the lanthanide elements and the extractant.

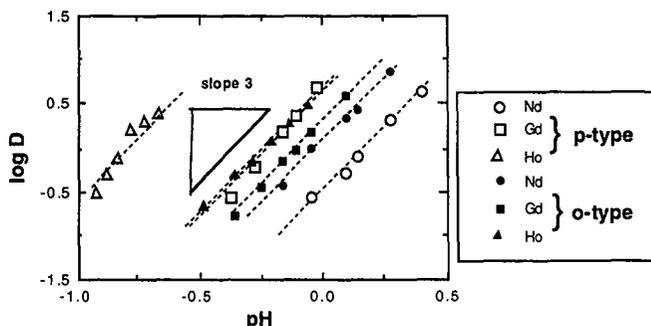


Figure 2 Typical pH dependence on distribution ratio (D) in rare earth extraction using new extractants of p-type and o-type.  
(The extractant and metal concentrations are 10 and 0.1 mM.)

The values of the equilibrium constants ( $K_{\text{ex}}$ ) were evaluated on the basis of equations (1) and (2) by plotting figures similar to those in figure 2, and the obtained values are listed in Table 1. Evidently, the structure of the spacer connecting the bi-functional moieties in the extractant is found to be crucial to the extractability and selectivity of rare earth metals.

TABLE 1

Extraction equilibrium constants ( $K_{\text{ex}}$ ) of the new extractants for rare earth metals

Extractant	$K_{\text{ex}}$								
	La	Pr	Nd	Sm	Gd	Dy	Ho	Y	Er
EG3PA	0.13	0.20	0.24	0.38	0.38	0.48	0.49	0.68	0.77
o-type	0.03	0.06	0.06	0.13	0.13	0.23	0.31	0.47	0.54
p-type	0.01	0.02	0.02	0.23	0.54	2.1	13	26	42

### Extractability of new extractants

Figure 3 shows the comparison of extractability of the yttrium ion on the bi-functional new extractants along with the results of the mono-acidic extractants. The results of D2EHPA were calculated using the  $K_{\text{ex}}$  value in toluene reported previously (Goto (1992)). The concentration of the mono-acidic extractants was adjusted to the twice concentration of the bi-functional extractants to make equal the number of functional groups. Obviously, all of the bi-functional extractants have

higher extractability than the mono-functional extractants. The extractability of p-type is much greater than that of o-type although the difference in the two extractants is only the position of oxygen in the spacer.

On the basis of the difference between MPA and D2EHPA, introducing a phenyl group near the functional part in the molecular structure appears to be effective in enhancing the extractability of rare earth metals (Ohto (1993)). Furthermore, the results indicate that connecting two functional groups is a useful method to increase extractability of an extractant, and this new concept to connect some functional groups with a spacer is clearly a promising technique in order to design a new extractant for the separation of rare earth metals.

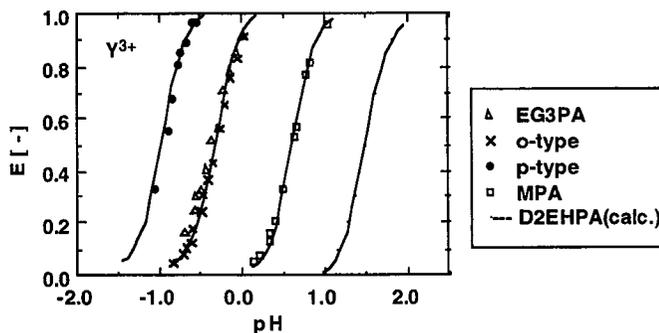


Figure 3 Comparison of extractability of new bi-phosphorus extractants and mono-phosphorus extractant. (The concentrations of EG3PA, o-type and p-type are 10 mM, and those of MPA and D2EHPA are 20 mM.)

### Selectivity of new extractants

As the Kex values of p- and o-types have a different dimension, we cannot compare the results directly to evaluate the extractability and selectivity of the two extractants. Therefore, a 50 % extraction pH was introduced to discuss the extraction behavior of all the rare earth metals using the newly developed extractants. Figure 4 shows the comparison of 50 % extraction pHs of rare earth metals for the three bi-functional extractants. The pH 0.5 in figure 4 means the pH value occurring 50 % extraction for each metal ion. It is found that the structure of the spacer in the extractant molecule strongly affects not only the extractability but also the selectivity in the rare earth extractions. In enhancement of the selectivity, a rigid segment seems to be more effective than a flexible one because the extractant EG3PA which has the most flexible spacer shows the lowest selectivity to the rare earth ions. The new extractant p-type exhibits a high selectivity, in particular, in the region of heavy rare earth metals, the selectivity is extremely high. The separation factor, which is usually defined by the ratio of two Kex values, in the separation of Dy and Ho increased to around 6, which is much larger than the value of 2 in a mono-acidic commercial extractant such as D2EHPA or PC-88A (Kubota (1993)). From a viewpoint of computer modeling, we could not predict why the p-type has high selectivity to all the rare earth metals, the results suggest that the enhancement of the selectivity is based on the steric effect not the electrical effect, because these three extractants are elucidated to have similar electrical properties from the computer modeling. In mono-acidic organophosphorus extractants, extractants that can provide a steric hindrance during the extraction of metals are found to show high selectivity (Ohto (1993;1995)). From the steric hindrance point of view, the steric hindrance of p-type is considered to be higher than that of o-type due to the rigidity of the p-structure compared to the o-structure in the spacer moiety. In the liquid-liquid extraction of rare earth metals in this study, the steric effect of the spacer appears to be a dominant factor to enhance the selectivity. The more detailed analysis of the steric effect using computer modeling is now under way.

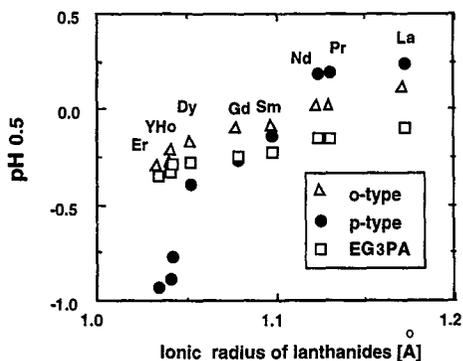


Figure 4 Comparison of 50 % extraction pHs of rare earth metals for new extractants

## CONCLUSION

Three new extractants having two phosphoric groups in the structure have been synthesized for potential use in liquid-liquid extraction of rare earth metals. It is clear that the new types of extractants have a high extractability for rare earth metals compared to ordinary mono-functional extractants. The steric effect of the extractants is considered to be a dominant factor to enhance the extractability and separation efficiency, and, in particular, the structure of the spacer connecting the two-functional groups is a key factor in ensuring a high selectivity to rare earth metals. The results of computer modeling also suggest that the steric effect is more important than the electrical effect to design an effective extractant for the separation of rare earth metals. These results lead to the conclusion that the new concept to connect some functional moieties with a spacer is very useful and is a promising method to develop new extractants for rare earth extraction.

## ACKNOWLEDGMENT

This work was supported by Grants-in-Aid for Scientific Research (Fundamental Research B.; No. 05453103) from the Ministry of Education, Science and Culture of Japan, and by the research fund from the Power Reactor and Nuclear Fuel Development Corporation.

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## RECEPTOR DESIGN FOR THE SELECTIVE SOLVENT EXTRACTION OF ANIONS

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### ABSTRACT

A series of novel tetrahedral polyammonium compounds, lipophilic monotopic and ditopic guanidinium receptors are synthesized and characterized in view of their extraction properties toward inorganic anions and nucleotides. The extraction behaviour of the polyammonium compounds investigated is predominantly determined by the hydration free energy of the anions ( $I^- > Br^- > Cl^-$ ). Thus, strongly hydrated oxoanions as sulfate and hydrogen phosphate show only a weak interaction. In contrast to this, lipophilic bisguanidinium compounds extract both halogenides and oxoanions. Remarkable selectivity of  $SO_4^{2-}$  over  $HPO_4^{2-}$ , and ATP over AMP and ADP extraction are obtained. This result is obviously caused by a perfect receptor-anion complementarity of shape and size superimposed on the general ionic interaction of the guanidinium moieties with the anion.

### INTRODUCTION

The molecular recognition and the selective phase transfer of cations with specific macrocyclic receptors has been an area of extensive research over nearly 30 years (Gokel, 1991). The interest attributes to the biological and technical importance of many cations.

In contrast to this, the selective complex formation and extraction of anions with such compounds were investigated in a considerable minor extent (Schmidtchen, 1988; Dietrich, 1993). The reasons for this situation are related to the typical properties of anions:

- anions have fully occupied orbitals;
- their size is relatively large, but the differences between various types are only small;
- they are often strongly hydrated and exist only in a limited pH range;
- anions possess different geometry.

Therefore the design and construction of tailor-made anion receptors require a high effort. Molecular hosts must be developed that specifically recognize the negatively charged guests by forming supramolecular complexes with well defined molecular properties. In addition, effective and selective transfer of anions from aqueous into organic phase needs a high lipophilicity of the host-guest complex formed.

Our concepts to meet this challenges are based on both the use of preorganized macrotricyclic polyammonium compounds **1 - 4**, and foldable guanidinium hosts **5 - 8**, wherein the selectivity is governed by a combination of electrostatic interactions and receptor-anion complementarity of shape, size and functionality.

The synthesis of the hosts **1 - 8** and binding properties with selected anionic guests in homogeneous protic solution have been communicated (Schmidtchen et al., 1989). The aim of these studies consists in the characterization of extraction properties and in the search for structure-reactivity relationships in aqueous-organic two phase systems.

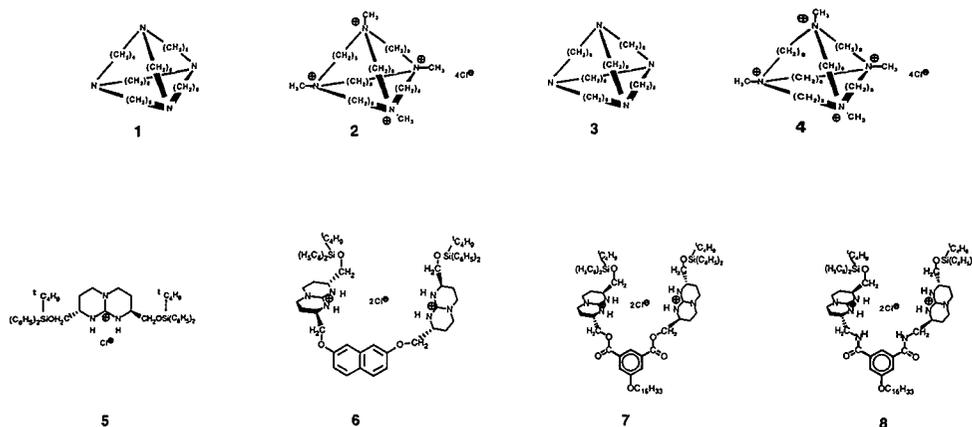
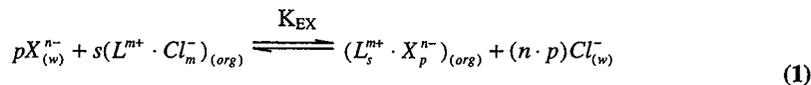


Figure 1. Investigated compounds

## EXPERIMENTAL

Extraction investigations were performed in micro reaction vials ( $2 \text{ cm}^3$ ) at  $25 \pm 1^\circ\text{C}$  by means of mechanical shaking. The phase ratio  $V_{(\text{org})}:V_{(\text{w})}$  was 1:1 ( $0.5 \text{ cm}^3$  of each phase); the shaking time was 30 min. In this time the equilibrium was achieved in all cases. After extraction all samples were centrifuged. The anion concentration in both phases were determined using radiotracer technique. The  $\gamma$ -radiation of  $^{82}\text{Br}$  and  $^{131}\text{I}$  was measured with a NaI(Tl)scintillation counter (Cobra II, Canberra-Packard) and the  $\beta$ -radiation of  $^{14}\text{C}$  (nucleotides),  $^{32}\text{P}$  ( $\text{HPO}_4^{2-}$ ),  $^{35}\text{S}$  ( $\text{SO}_4^{2-}$ ) and  $^{36}\text{Cl}$  with a liquid scintillation counter (Tricarb 2500, Canberra-Packard); isotopes were supplied by Medgenix Diagnostics GmbH.

The liquid-liquid extraction equilibrium of an anion  $X^{n-}$  with an anion exchanging extractant  $L^{m+}Cl_m^-$  is generally described by equation (1):



where  $s \cdot m = n \cdot p$ ; the subscripts (org) and (w) denote the organic and aqueous phase, respectively. Using the distribution ratio  $D_x$  of the anion, which is defined by equation (2), the extraction reaction

$$D_x = \frac{c_{x(\text{org})}}{c_{x(\text{w})}} \quad (2)$$

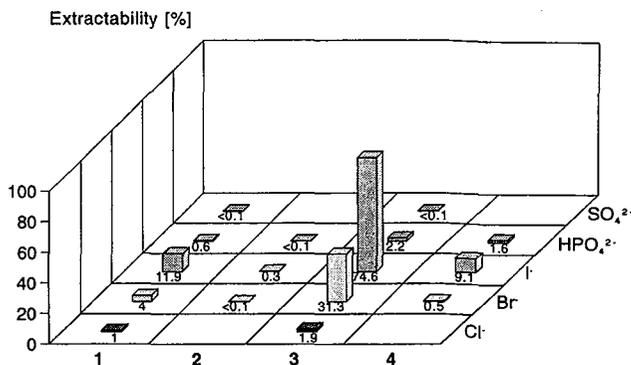
(1) can be analyzed and the composition of the species extracted can be determined from the experimental data by curve fitting of the  $\text{Log } D_X - \text{Log } c_{\text{Receptor}}$  dependence.

Molecular modeling calculations were performed using the molecular modeling software Cerius<sup>2</sup> 1.6 with the Dreiding 2.11 force field (Mayo et al., 1990). The computational studies were done on a DEC Alpha 800. For calculations with the Dreiding 2.11 force field its default parameters and termination criteria were used.

## RESULTS AND DISCUSSION

Macrotricyclic polyammonium compounds have been shown to bind anions in homogeneous solution by incorporation of the guest into their cavities (Schmidtchen et al., 1989) at which a selectivity order of binding constants is characteristic corresponding to the hole size-anion radius relationship. Figure 2 shows the extractabilities of different anions into chloroform with the tetrahedral polyammonium compounds 1 - 4. The highest extraction is achieved for all investigated anions with the most lipophilic compound 3.

The other receptors have only a slight tendency to assist the phase transfer. Especially the quaternary ammonium salts 2 and 4 itself possess furthermore only a limited solubility in organic solvents. Under the selected experimental conditions generally a pronounced graduated selectivity toward  $\text{I}^-$  over  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  is observed. These results obviously correlate with the order of increasing hydration for the anions in aqueous solution, whereas both the tetraeder hole size-anion size relationship and different geometry of the anions do not play any significant role. A striking effect in regard of selectivity is the significant difference between  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  extractability. May be this is a starting point for a specific ligand design. In all cases the formation of 1:1 host guest complexes is observed in the organic phase.



$[\text{Na}_n\text{X}] = 1 \cdot 10^{-4} \text{M}$  (X:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ); pH = 8.7 (TAPS/NaOH-buffer)  
 $[\text{receptor}] = 1 \cdot 10^{-3} \text{M}$  in  $\text{CHCl}_3$  (1 and 3)  
 $[\text{receptor}] = 2.5 \cdot 10^{-4} \text{M}$  in  $\text{CHCl}_3$  (2 and 4)

**Figure 2. Extractability of anions with macrotricyclic polyammonium compounds 1-4**

The idea of ditopic guanidinium receptors is based on the assumption that two chiral bicyclic guanidines connected to each other via an aromatic spacer moiety give a specific foldable structure. The obtained perpendicular fashion of the main planes of both guanidinium units is complementary to the topology of tetrahedral oxoanions. This is illustrated in Figure 3 by molecular modeling of the complexes of 8 with  $\text{SO}_4^{2-}$  and  $\text{HPO}_4^{2-}$  using force field calculations. Especially the complexation of sulfate by 8 should be favourable, because a low energy symmetric arrangement of  $\text{SO}_4^{2-}$  in the

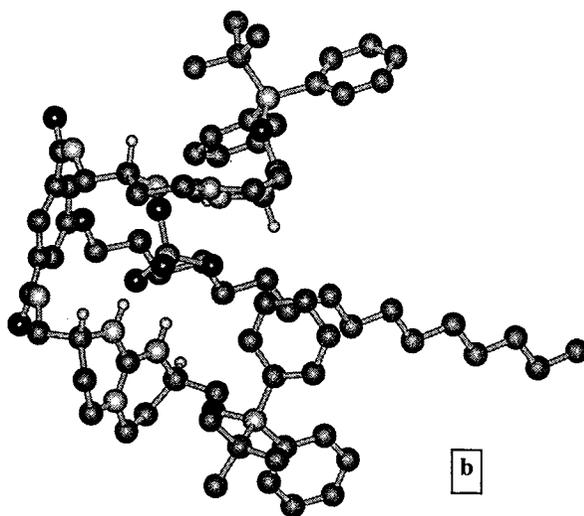
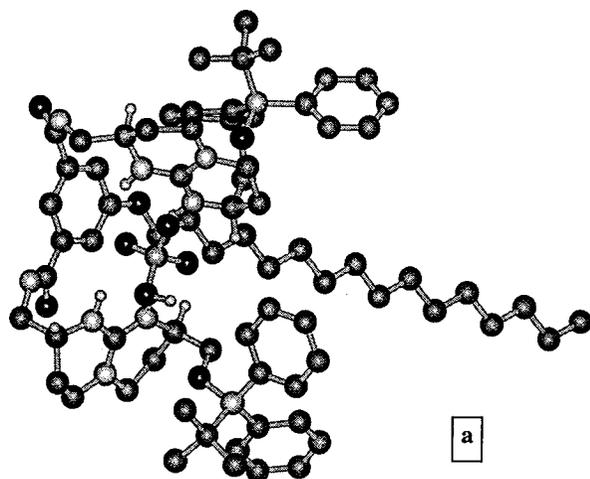


Figure 3. Molecular modeling of complexes for 8 with  $\text{HPO}_4^{2-}$  (a) and  $\text{SO}_4^{2-}$  (b)

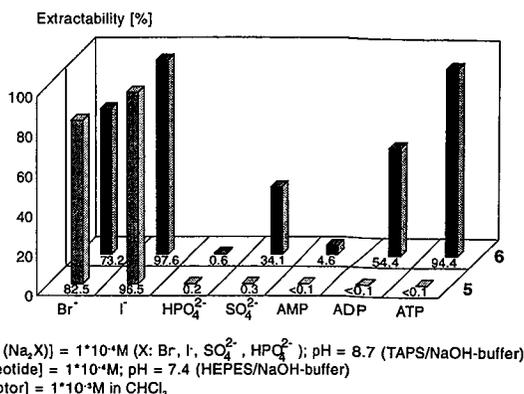
formed cleft of the receptor should be possible; all distances between oxygen and the two guanidinium functions lie between 2 and 2.6 Å. Compared with this the complex structure of **8** with  $\text{HPO}_4^{2-}$ , which has the same tetrahedral geometry and size as  $\text{SO}_4^{2-}$ , is significantly distorted and the distances between oxygen and the guanidinium functions are in a range between 2 and 4 Å.

Figure 4 shows extractabilities of various anions with the ditopic guanidinium host **6**. By way of comparison this figure represents extraction data for the monoguanidinium compound **5**. In both cases the extraction of bromide and iodide is possible with high efficiency. But whereas the monotopic host **5** is only capable of extracting the two hydrophobic anions the bisguanidinium compound **6** extracts the hydrophilic sulfate and nucleotides ATP, ADP and AMP, too.

As expected from the host guest structure calculations the differences between sulfate and hydrogen phosphate are high. In addition to the discussed structure relations furthermore this result could be caused by the higher hydration of the  $\text{HPO}_4^{2-}$  in aqueous solution.

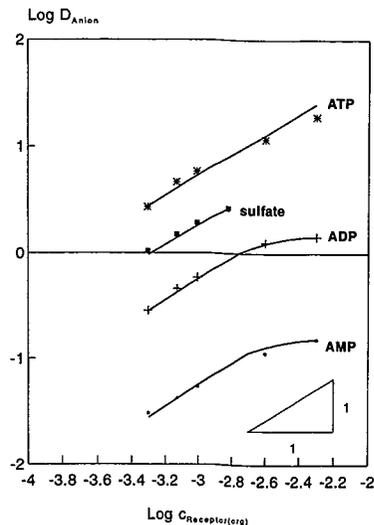
Amazingly, a remarkable graduation of nucleotide extraction was observed, too. Thus, a pronounced selectivity of ATP over ADP and AMP is found correlating with the rising charge of nucleotides. Slope analyses of straight lines obtained in the  $\text{Log } D_X - \text{Log } c_{\text{Receptor}}$  diagram (Figure 5) indicate 1:1 host guest complexes in the organic phase.

As shown in Figure 6 structure variations of the bisguanidinium receptor by changing the spacer or junction elements give an altered extractability. This fact is obviously caused by changing size and rigidity of the receptor and additional interaction possibilities via hydrogen bonding. The replacement of the naphthalene spacer element (**6**) in the molecule by the smaller and more flexible isophthalic acid (**7**) leads to a decrease of the nucleotide extraction. Having an amide group as junction element receptor **8** most strongly



[NaX, (Na<sub>2</sub>X)] = 1\*10<sup>-4</sup>M (X: Br<sup>-</sup>, I<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>); pH = 8.7 (TAPS/NaOH-buffer)  
 (nucleotide) = 1\*10<sup>-4</sup>M; pH = 7.4 (HEPES/NaOH-buffer)  
 [receptor] = 1\*10<sup>-3</sup>M in CHCl<sub>3</sub>

**Figure 4. Extractability of anions with the monotopic and ditopic guanidinium compound 5 and 6**



[Na<sub>2</sub>SO<sub>4</sub>, (nucleotide)] = 1\*10<sup>-4</sup>M; pH = 7.8 (TAPS/NaOH-buffer)  
 [receptor **6**] = 5\*10<sup>-4</sup>...5\*10<sup>-3</sup>M in CHCl<sub>3</sub>

**Figure 5. Extraction of sulfate and nucleotides with guanidinium compound 6**

extracts sulfate and nucleotides. Certainly, the strong binding is connected with a loss of separation selectivity.

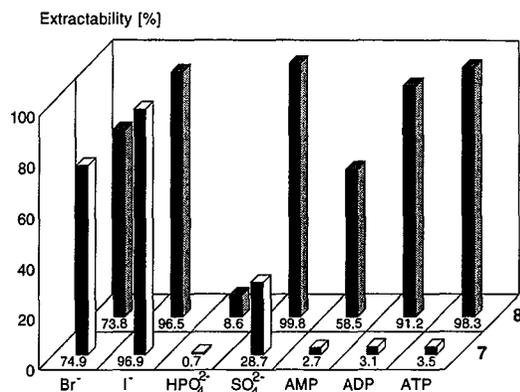


Figure 6. Extractability of anions with ditopic guanidinium compounds 7 and 8 (concentrations are the same as in figure 4)

## CONCLUSIONS

A series of ditopic guanidinium compounds were developed especially for the extraction of tetrahedral oxoanions, wherein the selectivity is governed by a combination of electrostatic interactions and ligand-anion complementarity of shape, size, and functionality.

Remarkable selectivity of sulfate over hydrogen phosphate, and ATP over ADP and AMP extraction is obtained. The complex structure is in all cases well-defined. In contrast to the bisguanidinium receptors the oxoanions investigated are practically not extracted by macrotricyclic polyammonium and simple quaternary ammonium and guanidinium compounds.

The developed anion receptors are opening new possibilities for specific anion recognition and for practical application as sensor material and in the area of environmental cleanup.

## ACKNOWLEDGEMENTS

This work has been supported by the Bundesminister für Forschung und Technologie (Projekt NT 20574).

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## DEVELOPMENT OF A SELECTIVE EXTRACTANT FOR IRON IN HYDROMETALLURGICAL PROCESS SOLUTIONS IN ORDER TO REDUCE THE AMOUNT OF FERRIC SLUDGES

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### INTRODUCTION

#### Hydrometallurgical Zinc Production

In hydrometallurgic zinc processes the basic steps for the production of zinc are the following: roasting, neutral leaching, hot acid leaching, solution purification and finally, electrolysis.

The undissolved solids separated after neutral leaching constitute the zinc plant residue. This residue contains several metals, the most important component being zinc ferrite. Without further treatment, this zinc is lost. Therefore, zinc ferrite must be dissolved through hot acid leaching giving a solution of zinc sulphate together with a high concentration of ferric sulphate, which constitutes a severe impurity and must be removed before electrolysis.

This iron removal from leach solutions is a problem in many hydrometallurgical processes. Several methods have been suggested to remove iron from process solutions by precipitation as hematite or goethite, but in most existing electrolytic zinc plants, the method of iron removal adopted is a controlled hydrolytic precipitation of iron as a basic iron sulphate, called the Jarosite Process. The iron is removed from the hot acid leach liquor as  $(K, Na, NH_4) Fe_3 (SO_4)_2(OH)_6$ , the jarosite precipitate, in the presence of ammonium or alkali metal ions.

However, this precipitation method has economical disadvantages, due to the high cost of deposition of jarosite in controlled tailing ponds. Otherwise such residues contain heavy metals such as Se, In, Ge, Co, As, Te, and sulphur, causing environmental problems. Although insoluble, long-term stability of jarosite is not known.

As a result of these problems, solvent extraction is being investigated as an alternative process for the removal of iron from aqueous solutions, avoiding the generation of iron residues and producing marketable iron products.

#### Solvent Extraction of Iron

The extraction of iron (in the majority of cases in its trivalent state:  $Fe^{3+}$ ) by different extractants, from sulphate or chloride media, has been investigated by many researchers. There exists a review of the numerous papers in this area [Dutrizac J E and Monhemius A J, 1986].

Several processes have been described to remove iron from sulphate media. Primary amines, secondary amines, alkylphosphoric acids and carboxylic acids have been used as extractants for iron removal. However, all these techniques have some drawbacks, such as:

- Leaching with the carboxylic acid will change the usual hydrometallurgical zinc processing;
- High organic losses in the hydrolytic stripping, once the precipitate contains solvent. Washing of the precipitate could be a solution, but high costs would be required;
- Iron precipitation occurs during exchange reaction, which can produce phase disengagement problems and contamination of the solutions;
- High energy consumption.

From chloride leach solutions, there has also been proposed a large number of processes, with TBP and amines as the main extractants.

Many methods have been developed and proposed but difficulties in the stripping of the iron from the organic loaded phase, the poor selectivity and other problems are not yet solved. Furthermore, existing extractants are not able to extract efficiently iron from highly acidic sulphate solutions.

A possible way to avoid these problems is to synthesize new tailor-made solvents for iron extraction, with high capacity and high selectivity for iron, even in highly acidic environments as is proposed in the IRONEX Project reported here.

## EXPERIMENTAL WORK

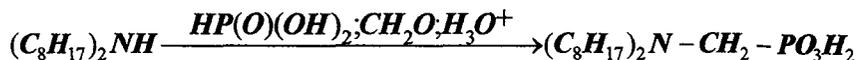
### Synthesis of New Extractants

It is known that water-soluble aminomethylenephosphonic acids are good complexing agents for iron [Kobachnik M I, et al., 1968] These compounds can be seen as phosphorous compounds analogous to amino acids. Therefore the idea from the side of BASF was to synthesize and use oil-soluble derivatives of aminomethylenephosphonic acids as Fe(III) extractants for solvent extraction.

In varying the structural elements there are two different important aspects to be considered. Firstly, the oil solubility and phase behaviour of potential extractants might be influenced by the introduction of lipophilic groups such as alkyl substituents (branched, unbranched, saturated and unsaturated).

Secondly, the capacity for iron in the organic phase might be influenced by the introduction of more or less iron complexing groups such as, for example, the aminomethylenephosphono group. The high density of these substituents should lead to products with high capacities for iron but on the other hand the oil solubility might decrease and solubility in water might increase. Therefore a tradeoff in view of the desired properties has to be made.

Aminomethylenephosphonic acids were synthesized by a "Mannich-Type Reaction" of amines, formaldehyde, and phosphorous acid [Moedritzer K and Irani R R, 1966]. The "Phosphonomethylation Reaction" proceeds according to the equation given below which gives an example for the case of phosphonomethylated di-2-ethylhexylamine:



The hydrogen atom directly bonded to phosphorous in the phosphorous acid is the 'acidic' hydrogen required for the Mannich-type reaction.

The reaction proceeds almost quantitatively, depending on the starting amine, if an excess of formaldehyde and/or phosphorous acid is used. An acid is usually the catalyst. A side reaction takes place which produces methylation products ( $\Rightarrow$  tertiary amines) as by-products. This means that the substituents are methyl instead of aminomethylenephosphono groups.

Phosphonomethylation reactions are one-pot synthesis reactions which were carried out in glass apparatus with mechanical stirring at  $\sim 100^\circ\text{C}$  for about 20 to 70 hours. The organic reaction products were separated from the aqueous phase (directly or by salting out) and purified by washing repeatedly with water. After separation of organic products and washings, residual water was removed under reduced pressure. The products obtained were characterized usually by elementary analysis,  $^1\text{H}$ -,  $^{31}\text{P}$ -NMR spectroscopy, and/or mass spectroscopy. From elementary analysis (P and N values) some information is obtained on the degree of conversion to phosphonomethylated products ( $\Rightarrow$  P/N ratio).

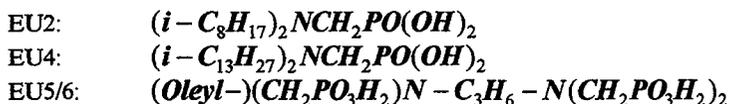
### Test Procedures

The prescreening evaluates the most effective extractants, judging by the following properties:

- ◆ oil solubility in a proper diluent
- ◆ phase behaviour (organic phase/highly acidic aqueous phase)
- ◆ extraction experiments (synthetic binary system Fe/Zn)
- ◆ washing/stripping tests

Extraction, washing and stripping tests are carried out in laboratory scale stirring batch experiments. The prescreening gives information about physical properties, Fe vs. Zn - selectivity, and loading capacity for Fe in the organic phase. Successfully tested chemical samples were selected for further examination.

The most promising candidates out of this prescreening procedure were until now:



The second stage of examination comprised:

- ◆ Comparative extraction and, partly, stripping tests on existing extractants, namely D2EHPA (di-2-ethylhexylphosphoric acid), Versatic 10, Primene JMT, and Amberlite LA2, and the influence of pH and several modifiers on iron extraction.
- ◆ Extraction and stripping tests on the new extractants synthesized by BASF (EU2, EU4, and EU5/6):
  - Influence of diluent (extractant EU2)
  - Influence of modifiers (extractant EU 2)
  - Influence of feed acidity (extractants EU2, EU4, and EU5/6)

The aqueous feed solutions considered in all the work were synthetic solutions similar to typical leach liquors coming from hot acid leaching of zinc ferrites, containing:

80g/l zinc; 25g/l iron; 40g/l free sulphuric acid.

In some tests, acidity was changed and so different quantities of  $H_2SO_4$  were added. The solutions were prepared from the dissolution of the metal sulphates. The extractants used were D2EPHA, EU2, EU4 and EU5/6, together with a modifier and dissolved in the appropriate diluent. The units used were weight/volume percentages (% w/v). The modifiers used were Isodecanol, Tributylphosphate (TBP), EU38 from BASF, and Trioctylphosphine oxide (TOPO). The diluents were D70 (Shell), LP ("Leuchtpetroleum", =EU37) from BASF, and Solvesso 150 (Exxon).

The extraction tests were performed in thermostated mechanically stirred vessels, at  $50^\circ C$ , using an organic/aqueous volume ratio of  $O/A=1/2$  (usually 20 ml organic and 40 ml aqueous). The residence time used was 15 minutes and the stirring speed used was 600 rpm. When necessary, pH control by addition of small amounts of concentrated sodium hydroxide was achieved. After mixing the phases were settled and the separation time was measured. The phases were separated, filtered, and the final volumes were checked to evaluate possible volume changes during the test. For the stripping tests, separatory funnels were used and lower  $O/A$  ratio was considered ( $O/A=1/10$ ). Temperature and time were the same referred for extraction.

Analysis of both metals in initial aqueous and equilibrated aqueous solutions were made by atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES). Zinc organic concentrations were determined after complete stripping with  $2M-H_2SO_4$  and subsequent analysis of the strip liquor containing all the zinc. In the case of iron, organic concentrations were determined by balance using both initial and final aqueous concentrations. When such balance was doubtful, confirmation was made using semiquantitative analysis of organic by X-ray fluorescence or by quantitative stripping of iron with NaOH (in the case of D2EHPA). The extraction or stripping percentages were calculated from metal concentrations taking into account, if necessary, the phase volume variations.

## Results

- ♦ The phase disengagement was in the range of 1 min (EU2) to 4 min (EU5/6), (see figure 1).
- ♦ The tested diluents did not influence significantly the extraction of iron.

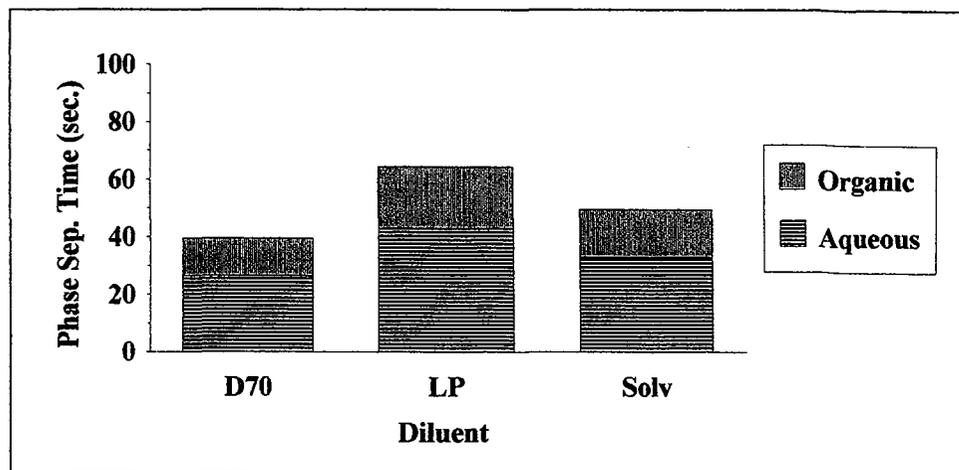


Figure 1. Influence of diluent on phase disengagement for EU2 extractant.

- ◆ Even now, at an early time of the IRONEX project, it can be stated that the loading capacity for iron is, for at least two of the new extractants, markedly higher than that of the reference extractant D2EHPA; these new chemicals exhibiting a more powerful extraction behaviour than known ones (see figure 2).

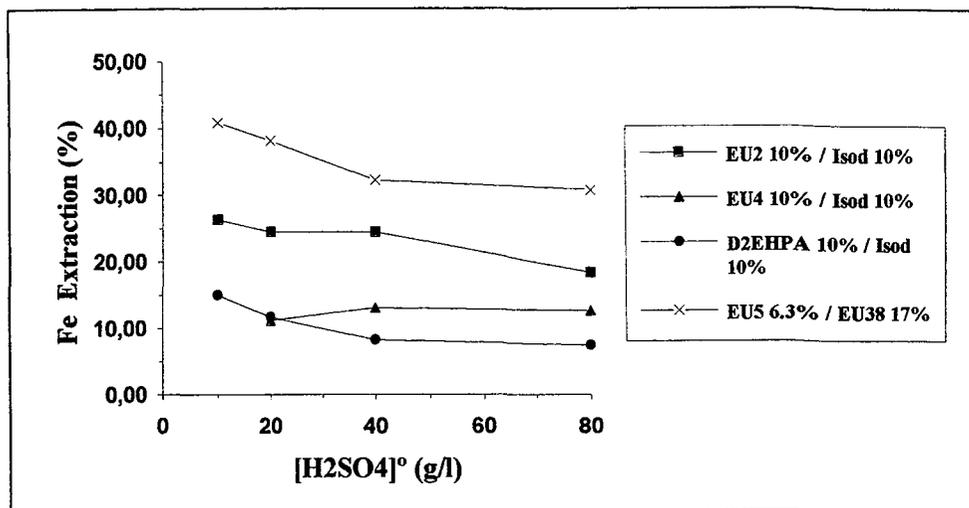


Figure 2. Influence of feed acidity on iron extraction with the new extractants and, for comparison, D2EHPA in LP, from sulphate solutions containing about 25 g/l Fe and 80 g/l Zn.

- ◆ Zinc co-extraction values were in the range of 8 - 20 mg/l (EU2) to 200 - 300 mg/l (EU5/6), (see figure 3).

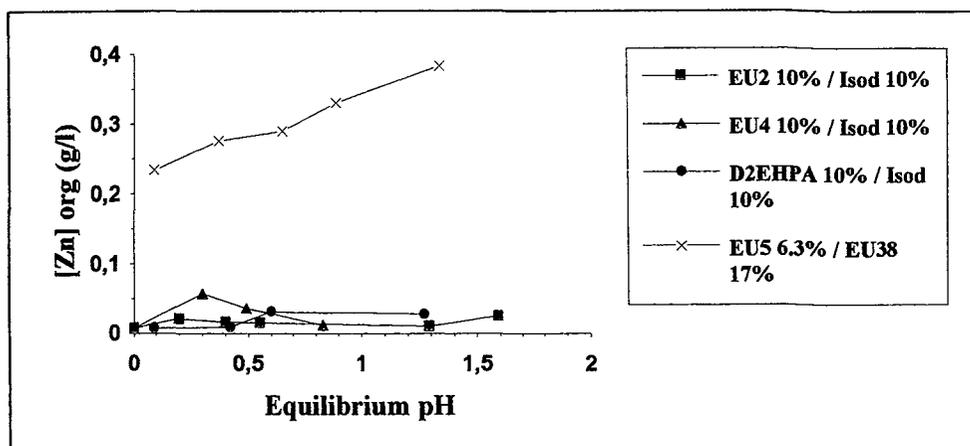


Figure 3. Influence of feed acidity on the co-extraction of zinc with the new extractants and, for comparison, D2EHPA, from sulphate solutions containing 25 g/l Fe and 80 g/l Zn

- ◆ The stripping behaviour for iron depends on the extraction power of the extractant; the lower this extraction power, the easier is the back-stripping of iron. Seemingly, this affects the more powerful extractants if judged by the relative stripping rate (see figure 4). However, if the absolute Fe concentration is considered, the new extractants EU2 and EU5/6 exhibit a higher overall transportation efficiency than D2EHPA.
- ◆ Some of the modifiers tested gave promising results; further investigations are needed.

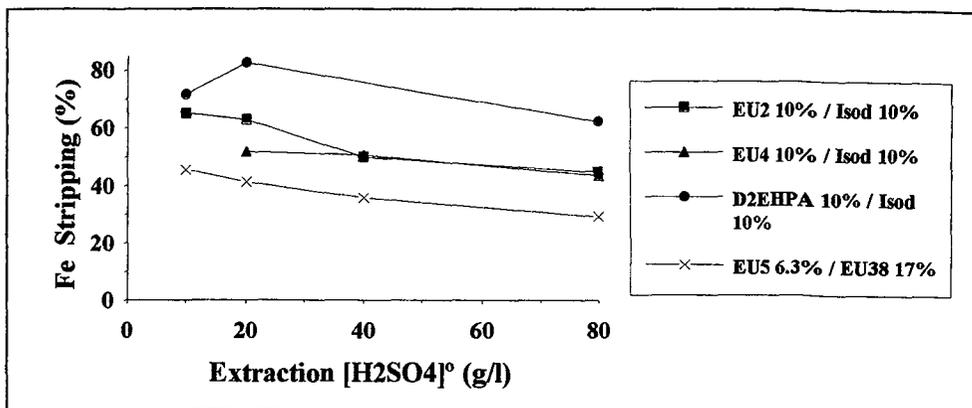


Figure 4. Influence of feed acidity in extraction on further stripping of iron from loaded organics.  $[Fe]_{org} = 9-16$  g/l (EU2);  $5-12$  g/l (EU4);  $15-22$  g/l (EU 5/6);  $4-11$  g/l (D2EHPA).

### CONCLUSIONS

At least two of the newly developed extractants are very promising and quite better than D2EHPA concerning their extraction aptitude for iron, even in highly acidic media. The EU5/6 loading capacity at 80 g/l free acidity is around five times the equilibrium value for D2EHPA at the same conditions which constitutes an unusual good performance. At the same time, the phase disengagement seems sufficiently quick, the co-extraction of zinc is small enough, and the stripping behaviour is good. However, after only one half year of project duration many questions are open still, and a lot of investigations will have to follow.

### ACKNOWLEDGEMENTS

The authors wish to thank all involved colleagues within the IRONEX consortium for their indispensable help. The work is supported in part by the Research and Technical Development Programme of the European Communities, European Commission, DG XII-D1, Brussels, Belgium, specific programme ENVIRONMENT AND CLIMATE. This funding is gratefully acknowledged.

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## SOLVENT EXTRACTION OF TECHNETIUM FROM ALKALINE WASTE MEDIA USING BIS-4,4'(5')[(*tert*-BUTYL)CYCLOHEXANO]-18-CROWN-6

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### ABSTRACT

The crown ether bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 can be utilized in a solvent-extraction process for the removal of technetium (as pertechnetate ion,  $\text{TcO}_4^-$ ) from solutions simulating highly radioactive alkaline defense wastes ("tank wastes") stored at several sites in the United States. The process employs non-halogenated and non-volatile diluents and modifiers and includes an efficient stripping procedure using only water. More than 95% of the pertechnetate present at  $6 \times 10^{-5}$  M in Melton Valley (Oak Ridge, TN) and Hanford (Washington) tank-waste simulants was removed following two cross-current extraction contacts using 0.02 M bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 in 2:1 vol/vol TBP/Isopar<sup>®</sup> M diluent at 25 °C. Similarly, for both simulants, more than 98% of the pertechnetate contained in the solvent was back-extracted following two cross-current stripping contacts using deionized water.

### INTRODUCTION

Technetium-99 is a uranium fission product which decays by pure beta emission with a half-life of  $2.13 \times 10^5$  years. It is present in alkaline nuclear-waste media mainly in the +7 oxidation state as the environmentally mobile oxo-anion, pertechnetate ( $\text{TcO}_4^-$ ). Separation of pertechnetate from alkaline nuclear-waste media is currently being considered as part of waste-cleanup and environmental-restoration efforts, particularly with regard to the approximately  $6 \times 10^7$  gallons of neutralized high-level waste (containing an estimated 1.8 metric tons of technetium) stored in 177 waste tanks at the Hanford, Washington, DOE facility. This waste is also highly concentrated in alkali-metal salts of competitor anions such as nitrate, and the nitrate/pertechnetate ratio typically lies in the range of  $10^4$ - $10^7$  to 1.

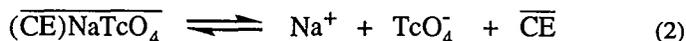
Solvent extraction has been employed as a method for the removal of pertechnetate from both acidic and alkaline solutions (Möbius (1983)). Some reagents that have been employed in the extraction of pertechnetate from alkaline media include cyclohexanone (Schulz (1980)), pyridines (Zaitsev (1964)), tetraphenylarsonium chloride (Tribalat (1953)), tetraalkylammonium iodides (Shanker (1968)), polyethylene glycols (Chaiko (1993)), and crown ethers (Jalhoon (1986); Korpusov (1984)). Whereas adequate extraction of pertechnetate from alkaline media was demonstrated by each method, in every case the method described possessed some characteristic which would make it undesirable for a large-scale process. These characteristics included the use of hazardous chemicals as defined by the Resource Conservation and Recovery Act (RCRA) or difficulty in regenerating the extractant solvent.

We describe here the results of our research efforts aimed at developing an efficient solvent-extraction process that utilizes the crown ether bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 for the direct extraction of pertechnetate from high-nitrate-containing alkaline nuclear-waste media and that seeks to avoid many of the problems of the previous methods. The tank wastes at the Hanford site and other locations (e.g., Oak Ridge) are typically strongly alkaline and contain Tc, actinides, and other

radioactive contaminants. These contaminants may be found in the aqueous supernates under certain conditions, or they may be solubilized from the sludge during washing or leaching operations. Many such waste streams contain high concentrations of salts such as sodium nitrate and thus pose special problems for current extraction technology. We have been investigating crown ethers as potential solvent-extraction reagents for Tc removal (Bonnesen (submitted)) because the high-salt condition actually promotes Tc extraction and because an inexpensive water wash effects stripping of the Tc from the solvent. The mechanism of extraction and stripping can most easily be described by a reversible equilibrium involving complexation of an alkali metal ion by a crown ether. The high alkali metal concentration in the aqueous phase during the extraction portion of the cycle drives the equilibrium toward formation of the crown ether-alkali metal complex. An anion is necessary to conserve charge neutrality, and in this way the pertechnetate anion is also extracted:



Here, CE is the crown ether, and the overbar designates organic-phase species. Stripping is accomplished by simply reversing this equilibrium. The organic solvent containing the crown ether-alkali metal-pertechnetate complex is contacted with deionized water, promoting dissociation of the complex to free alkali metal pertechnetate in the aqueous phase and free crown ether in the organic phase:



As will be discussed further below, the extracted cation need not be  $\text{Na}^+$  but can also advantageously include other cations from the waste. We note that equations 1 and 2 represent at present only a postulated model. Detailed equilibrium studies are in process to test this model as well as to reveal other equilibria that may occur, especially the competing extraction of sodium nitrate.

Experimental efforts are presently focused on evaluating the most effective combination of diluent and modifier with bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 with regard to process economics and development. We specifically desire the best combined extraction and stripping efficiency at the lowest crown ether concentration. Bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 was selected on the basis of its high degree of lipophilicity (and thus low degree of loss to the aqueous phase), its ability to strongly bind both sodium and potassium (which are both present in many tank wastes), and the fact that this crown ether is currently being considered for a process for the removal of strontium from acidic waste media (Horwitz (1991)).

## EXPERIMENTAL SECTION

The compositions of the waste simulants used in these experiments are shown in Table 1. Melton Valley Storage Tank W-29 (MVST W-29) simulant was prepared by the authors based on an analysis obtained at Oak Ridge on the supernatant solution. A simulant which approximates Hanford tank 101-AW Double-Shell Slurry Feed (DSSF-7) was prepared following recommendations obtained from Pacific Northwest Laboratories. Technetium-99 was added to the waste simulants during the last stage of preparation by spiking the simulant with the appropriate amount of  $3.0 \text{ mM NH}_4^{99}\text{TcO}_4$  to give the desired concentration of  $6 \times 10^{-5} \text{ M}$ .

The crown ether bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 (abbreviated di-*t*-BuCH18C6) was used as received from either Parish Chemical or Eichrom Industries, Inc. It should be cautioned that the isomer ratios, and hence performance, for this crown can vary from batch to batch (see Horwitz (1991) for a discussion of this point), and that it is important to use the same batch, or batches of

equivalent performance, when making comparisons. Tributylphosphate (TBP) was from Mobil Chemical Co., Edison, New Jersey and was distilled prior to use. Isopar<sup>®</sup> M (a completely aliphatic isoparaffinic kerosene) was obtained from Exxon Chemical Company, Houston, Texas. Deionized water was used for stripping. All other diluents, modifiers, and reagents were used as received without further purification. All diluent blends were prepared on a volume basis. Beta liquid scintillation counting of <sup>99</sup>Tc was performed using a Packard Tricarb<sup>®</sup> Model 4530 counter and Packard Ultima Gold<sup>™</sup> XR scintillation cocktail.

TABLE 1. Waste Simulants Used in This Study.

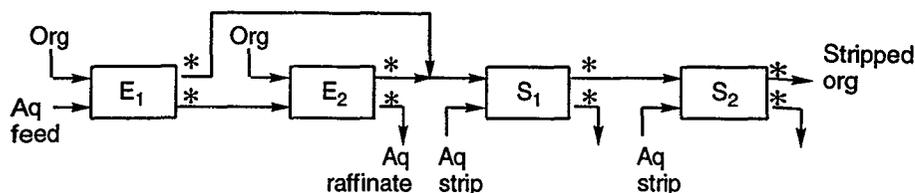
Species	Concentration (M)	
	MVST W-29	DSSF-7 simulant
Na <sup>+</sup>	4.59	7.00
K <sup>+</sup>	2.90 x 10 <sup>-1</sup>	9.45 x 10 <sup>-1</sup>
Cs <sup>+</sup>	4.3 x 10 <sup>-6</sup>	7.0 x 10 <sup>-5</sup>
Ca <sup>2+</sup>	8.7 x 10 <sup>-5</sup>	not present
Sr <sup>2+</sup>	1.1 x 10 <sup>-5</sup>	not present
Al <sup>3+</sup>	1.65 x 10 <sup>-5</sup>	7.21 x 10 <sup>-1</sup>
OH <sup>-</sup> (total)	1.58 x 10 <sup>-1</sup>	4.63
OH <sup>-</sup> (free)	1.58 x 10 <sup>-1</sup>	1.75
Cl <sup>-</sup>	8.5 x 10 <sup>-2</sup>	1.02 x 10 <sup>-1</sup>
Br <sup>-</sup>	6.3 x 10 <sup>-4</sup>	not present
NO <sub>2</sub> <sup>-</sup>	not present	1.51
NO <sub>3</sub> <sup>-</sup>	4.52	3.52
CrO <sub>4</sub> <sup>2-</sup>	4.2 x 10 <sup>-5</sup>	not present
SO <sub>4</sub> <sup>2-</sup>	7.0 x 10 <sup>-3</sup>	8.0 x 10 <sup>-3</sup>
CO <sub>3</sub> <sup>2-</sup>	1.00 x 10 <sup>-1</sup>	1.47 x 10 <sup>-1</sup>
PO <sub>4</sub> <sup>3-</sup>	not present	1.4 x 10 <sup>-1</sup>
<sup>99</sup> TcO <sub>4</sub> <sup>-</sup>	6.0 x 10 <sup>-5</sup>	6.0 x 10 <sup>-5</sup>

<sup>a</sup>MVST W-29 simulant approximates the supernatant liquid in Melton Valley Storage Tank W-29 (Oak Ridge).

<sup>b</sup>DSSF-7 approximates Hanford tank 101-AW Double-Shell Slurry Feed.

Synthetic waste solutions were contacted with equal volumes of solvent for 1 hour at 25 ± 1°C in sealed borosilicate vials by end-over-end rotation at ~40 RPM using a Glass-Col<sup>®</sup> laboratory rotator. This contacting procedure ensures achievement of equilibrium, though kinetic tests show that 95% or more of the Tc is extracted within the first 5 minutes. After the phases were allowed to coalesce, the aqueous and organic phases were subsampled and the <sup>99</sup>Tc activity in each phase determined. An aliquot of the aqueous phase from the first contact was subsequently contacted with an equal volume of fresh extractant solution in the manner described above and the phases subsampled to determine the <sup>99</sup>Tc activity. In the stripping tests, aliquots of the organic phases from the first and second contacts were combined and contacted with an equal volume of deionized water in the manner described above.

After the phases were subsampled, the organic phase from this first stripping operation was contacted with a second equal volume of water, comprising the second strip, and the phases were again subsampled to determine the  $^{99}\text{Tc}$  activity. The entire cross-current two- extraction, two-strip procedure is shown diagrammatically in the scheme below:



**Scheme 1.** Contacting procedure used for tests in this work. The asterisk (\*) denotes when samples were taken for analysis. (Note: This is not meant to represent a process flowsheet).

All tests were run in duplicate, and the technetium extraction ratios ( $[\text{Tc}]_{\text{org}}/[\text{Tc}]_{\text{aq}}$ ) are reported as the average of those obtained in the two stages E<sub>1</sub> and E<sub>2</sub>. In general, the value of E<sub>2</sub> differed insignificantly from E<sub>1</sub>.

## RESULTS AND DISCUSSION

As was shown in Table 1, both waste simulants are extremely concentrated in sodium nitrate, with nitrate/pertechnetate concentration ratios of 75,300 to 1 for the MVST W-29 simulant and 58,700 to 1 for the DSSF-7 simulant. The Tc concentration of  $6.0 \times 10^{-5}$  M was selected as a representative concentration for Tc in most Hanford tanks, though Melton Valley waste probably contains much lower concentrations. In selecting appropriate diluents for the solvent extraction and stripping cycle, we screened for diluents and modified diluents that would provide the best extraction and stripping efficiency, while still being suitable for a process. Requirements that an ideal diluent (or modified diluent) should meet include low volatility with flash point  $\geq 60$  °C (the threshold below which solvents are deemed ignitable and thus RCRA hazardous); low toxicity; low solubility in water; high chemical stability; high radiation stability; good phase-disengagement behavior with low emulsion tendency; and good capability to solvate and extract the desired species. With regard to chemical and radiation stability, the breakdown products should be minimal, should not interfere with the process, and should not impart any hazards. Aliphatic kerosenes such as those comprising the Isopar<sup>®</sup> line (Exxon Chemical) generally meet the above requirements, and are excellent and economical diluents. However, due to their extremely low polarity they are often incapable of solvating the crown ether-alkali metal-pertechnetate complex, let alone the crown ether extractant itself. Addition of a modifier possessing some degree of polarity improves extraction power and promotes solubility without imparting undesirable properties to the system. There is literature precedent for using TBP (Boyd (1960)) and pyridines (Zaitsev (1964)) as extractants for pertechnetate, and this formed a starting point for the selection of candidate modifiers to the base aliphatic kerosene diluent. In addition, TBP is a modifier in the TRUEX process (Horwitz (1985)) and is generally a well-known modifier in the field of solvent extraction.

Extraction and stripping results for both DSSF-7 and MVST W-29 waste simulants are shown in Table 2. Excellent coalescence on both extraction and stripping was observed for all systems, but particularly for the TBP/Isopar<sup>®</sup> M systems, which at crown ether concentrations of 0.02 M and above

also gave the best combined extraction and stripping performance. Excellent extraction efficiency is attainable at 0.01 M [CE] using the pyridines 4-(1-butylpentyl)pyridine as a pure diluent, or 4-(3-phenylpropyl)pyridine diluted with diisopropylbenzene; however, the stripping efficiency is not quite as good as that obtained using the TBP/Isopar<sup>®</sup> M blends. Extraction of Tc from the DSSF simulant exceeds that from the MVST simulant due likely to the higher sodium and potassium content (leading to higher alkali metal loading of the crown ether) and the lower nitrate content (leading to less competition for pertechnetate). It can be seen that essentially the same level of extraction and stripping performance can be obtained using di-t-BuCH18C6 at either 0.04 M in 1:1 TBP/Isopar<sup>®</sup> M or at 0.02 M in 2:1 TBP / Isopar<sup>®</sup> M. Due to the high cost of the crown ether, the latter system is more favorable economically. How to finally dispose of the technetium in the strip solution is an issue, and post-processing options and waste forms for technetium are presently under investigation.

**TABLE 2** Extraction of Pertechnetate from DSSF-7 and MVST W-29 Waste Simulants by di-t-BuCH18C6 in Selected Diluents. Stripping by Back-Extraction with Water.<sup>a</sup>

[CE], M	Simulant	Diluent	$E_{Tc}^b$	% Extr <sup>c</sup>	% Strip <sup>c</sup>
0.02	DSSF-7	2:1 TBP / Isopar <sup>®</sup> M	8.67 ± 0.27	98.93	99.08
0.02	MVST W-29	2:1 TBP / Isopar <sup>®</sup> M	3.90 ± 0.06	95.84	98.60
0.04	DSSF-7	1:1 TBP / Isopar <sup>®</sup> M	8.46 ± 0.21	98.88	99.60
0.02	DSSF-7	1:1 TBP / Isopar <sup>®</sup> M	4.77 ± 0.01	97.00	99.79
0.01	DSSF-7	1:1 TBP / Isopar <sup>®</sup> M	2.55 ± 0.01	92.06	99.26
0.02	DSSF-7	4-(1-butylpentyl)pyridine	11.61 ± 0.79	99.37	90.99
0.01	DSSF-7	4-(1-butylpentyl)pyridine	6.56 ± 0.20	98.25	91.73
0.01	DSSF-7	4-(3-phenylpropyl)pyridine / diisopropylbenzene	4.77 ± 0.03	96.95	95.75

<sup>a</sup>25 °C, 1:1 phase ratio, 1 h contacts. <sup>b</sup> $E_{Tc}$  is the average of the technetium extraction ratios ( $[Tc]_{org}/[Tc]_{aq}$ ) obtained in the two stages  $E_1$  and  $E_2$ . <sup>c</sup>Total % extracted, and total % stripped, respectively, after two extraction steps and two stripping steps.

The extraction of sodium and potassium from DSSF-7 waste simulant using 1:1 TBP / Isopar<sup>®</sup> both with and without di-t-BuCH18C6 was also measured. Table 3 summarizes the organic phase concentrations of Tc, Na, and K following a single extraction contact. The diluent blend alone extracts nearly 42% of the Tc originally present in the aqueous feed, but only small amounts of the sodium and potassium. When the crown ether is added, the amount of Tc extracted increases to 83%, and while the amount of sodium extracted does not increase very much, the amount of potassium extracted increases 30-fold. After correcting for the Na and K extracted by the diluent alone, the crown ether is 17.5% loaded with potassium and 7.7% loaded with sodium, indicating that although the aqueous feed is 7.4 times more concentrated in sodium than potassium, it is the potassium concentration here that is more important in determining the overall concentration of the active extractant: the cationic crown ether-alkali metal complex. This is not surprising, as di-t-BuCH18C6 is known to bind potassium more strongly than sodium (Izatt (1985)). The ratio of  $([Na]_{org}+[K]_{org})/[Tc]_{org}$  provides an indication of how much more of the other anions present in the waste simulant are co-extracted with pertechnetate. The ratio of the most prevalent extractable anions, namely nitrate, hydroxide, nitrite, and chloride, to pertechnetate in the DSSF-7 waste simulant is nearly 115,000 to 1; in the organic phase following extraction using the crown ether it is 246 to 1, demonstrating the high selectivity the solvent has for pertechnetate over other anions in the waste simulant.

**TABLE 3** Extraction of Sodium and Potassium from DSSF-7 Waste Simulant by 1:1 TBP / Isopar<sup>®</sup> M Diluent with and without di-t-BuCH18C6. Comparison to Technetium Extraction.

[CE], M	Simulant	[Tc] <sub>org</sub> <sup>a</sup>	[Na] <sub>org</sub> <sup>a,b</sup>	[K] <sub>org</sub> <sup>a,b</sup>	([Na] <sub>org</sub> + [K] <sub>org</sub> ) <sup>c</sup> /[Tc] <sub>org</sub>
none	DSSF-7	2.50 x 10 <sup>-5</sup>	6.68 x 10 <sup>-3</sup>	1.18 x 10 <sup>-4</sup>	271
0.02	DSSF-7	4.96 x 10 <sup>-5</sup>	8.66 x 10 <sup>-3</sup>	3.61 x 10 <sup>-3</sup>	246

<sup>a</sup>Organic phase concentrations in mole/liter following a single 1 hr contact at 25 °C (1:1 phase ratio).

<sup>b</sup>Concentrations for sodium and potassium were determined by ICP emission spectroscopy.

<sup>c</sup>Corrected for Na and K accompanying the Tc.

### CONCLUSIONS

An efficient solvent extraction and stripping cycle for pertechnetate from realistic alkaline waste simulants can be obtained using di-t-BuCH18C6 dissolved in TBP modified Isopar<sup>®</sup> M aliphatic kerosene, allowing for more than 95% of the Tc contained in the waste simulants to be removed upon two cross-current contacts, and more than 98% of the Tc to be stripped from the solvent upon two cross-current stripping contacts using only water. The selectivity of pertechnetate over other anions present in the waste simulant is high.

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### ACKNOWLEDGMENTS

We thank Jack L. Collins (Oak Ridge) for providing us with an analysis of the supernatant liquid from Melton Valley Storage Tank W-29 and Gregg J. Lumetta and coworkers (Pacific Northwest Laboratories) for information regarding the composition of the DSSF-7 waste simulant. Tamara J. Haverlock is acknowledged for assistance with the ICP experiments. This research was sponsored by the Efficient Separations and Processing Integrated Program of the Office of Environmental Restoration and Waste Management's Office of Technology Development of the U. S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.



## EXTRACTION OF OLEFIN BY USE OF COMPLEX FORMATION WITH CUPROUS ION

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### ABSTRACT

Extraction of liquid olefins using  $\pi$ -complex formation with cuprous ion was studied experimentally to make clear the favorable properties of copper: low price and high capacity.

### INTRODUCTION

A major part of the capital cost for a world-class light olefin unit is olefin/paraffin separations train. Table 1 shows traditional and nontraditional olefin/paraffin separation technologies. The shift from conventional low-temperature distillation to chemical complexation using silver and copper ions is obvious from the Table.

**TABLE 1**  
Separation technologies for olefin/paraffin mixtures

Conventional technologies:	low-temperature distillation
	extractive distillation
	physical adsorption
Nontraditional technologies:	chemical adsorption using supported Cu(I)
	chemical absorption with Ag(I) and Cu(I)
	physical absorption
	facilitated membrane transport with Ag(I)

Studies on olefin separation using  $\pi$ -complex formation with cuprous ion are summarized in Table 2. They are classified in three categories: use of cuprous salt such as CuCl, oxidation of copper and reduction of cupric ion. They have been proved to be useful for the separation of C<sub>4</sub>-C<sub>6</sub> olefins if they are incorporated into absorption although each has faults as shown in Table 2. The reduction of Cu(II) by the contact with copper powder is quite interesting because the controlling of reactants, Cu(II) and Cu(0), is easy in spite of its intrinsic fault: heterogeneous reaction system. The separation performance of this method was excellent when applied to the absorption of C<sub>4</sub> distillates, but its application to liquid olefin has been limited to styrene ethylbenzene separation where a low-polarity solvent was used (Ishii (1982)). The purpose of the present study is to examine that the Cu(II) reduction by Cu(0) for liquid olefin/paraffin separation with aqueous solvents is useful. The effect of Cu(I) on olefin separation was compared with that of Ag(I) which forms  $\pi$ -complexes with unsaturated

hydrocarbons.

**TABLE 2**  
Separation technologies for olefin using cuprous ion

Method	Fault	Ref.
1. Use of cuprous salt:		
(1) CuCl	low solubility, heterogeneity	Gilliland (1941)
(2) Solubilization by NH <sub>3</sub> and Cl <sup>-</sup>	low capacity by the preferential coordination of added ligand	
(3) Use of cuprous salt of trifluoromethyl sulfonic acid	Instable	Ogura(1976)
(4) Use of CuAlX <sub>4</sub> (X: halogen)	Instable	Long(1973)
2. Oxidation of copper:		
(1) Use of aq. perchloric acid soln.	formation of explosive acetylene	
3. Reduction of cupric ion as $C(O) + Cu(II) \rightleftharpoons 2Cu(I)$	heterogeneous system	Ogura(1975)

## EXPERIMENTS

### Apparatus

A 70 mm I.D. stirring vessel with a baffle and a six-flat blades turbine-type impeller was used. Experiments were conducted at a constant temperature, 293 K, with a water bath.

### Methods

Aqueous cupric solution (100 ml) and liquid hydrocarbon mixture (50 ml) were placed in the vessel. The first three components of the feed stock in Table 3 were used as olefins and the last one was as a paraffin. After the establishment of uniform temperature distribution, copper powder was supplied and stirring was initiated. After a given time period the hydrocarbon phase was sampled and analyzed by gas chromatography to determine the amount extracted. Table 3 shows reference experimental conditions.

**TABLE 3**  
Experimental condition selected as a reference

Solvent:	water
Extractants:	1M-Cu(NO <sub>3</sub> ) <sub>2</sub>
copper powder	(1M in aqueous soln.)
Feed stock:	liquid hydrocarbon mixture; 1,5-Hexadiene(10wt%) + 1-hexene (15wt%) + cyclohexene (20wt%) + toluene (15wt%) + n-hexane (40wt%)
Stirring	speed: 6.6 s <sup>-1</sup> , number of baffle: 1
Temperature:	293 K

## RESULTS AND DISCUSSION

### Observed Results

Most of the copper powder was adsorbed at the oil-water interface before agitation. The dispersion type during agitation was oil-in-water type as determined from the observation of the moving direction of coalescing interface. During agitation copper powder seems to have distributed in the aqueous phase because the aqueous phase included copper powder after the completion of coalescence. Solution color changed from blue, Cu(II) color, to slight green, Cu(I) color, in particular at the impeller-tip sweeping region. These results imply the formation of Cu(I)-Olefin complex in the aqueous phase as shown in Figure 1: the Cu(I) ion formed temporarily by the contact of Cu(II) and Cu powder is fixed as  $\pi$ -complex by the olefin dissolved in the aqueous phase.

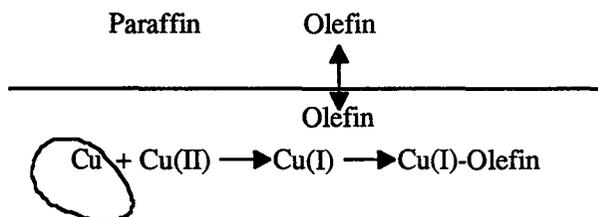


Figure 1 Distribution and  $\pi$ -complex formation near interface

### Comparison between Ag-Complex and Cu-Complex

Figure 2 shows extraction rates of 1,5-hexadiene and 1-hexene for 1M-Cu(NO<sub>3</sub>)<sub>2</sub>/1M-Cu and 1M-AgNO<sub>3</sub> systems. Extraction was fast in the homogeneous reaction system: aqueous AgNO<sub>3</sub> system. Heterogeneity may be the reason for the slow extraction in the Cu(II)/Cu(O)

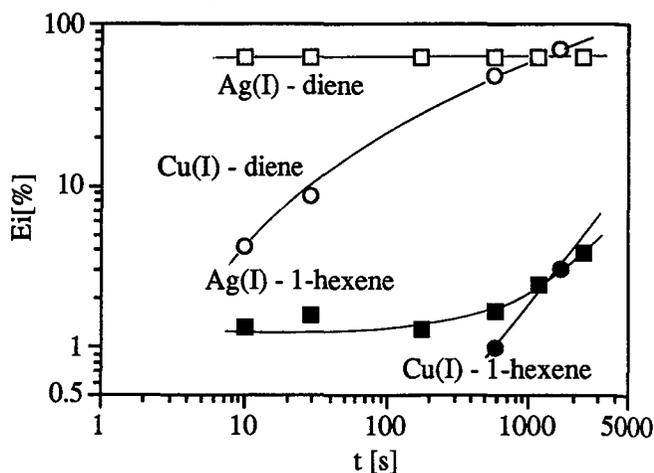


Figure 2 Comparison of extraction rate between silver and cuprous complexes

system.

However, the amount extracted was higher for Cu-complex at near equilibrium than for Ag-complex, which may reflect the higher stability constant of Cu-complex (Hartley (1983)). Particularly high stability constant of 1,5-hexadiene in complexation with Ag(I) was ascribed to chelate formation (Hartley (1983)). Similarly, Cu(I) may form chelate complex with 1,5-hexadiene because the extraction ratios,  $E_i$ , of 1,5-hexadiene were much higher than those of 1-hexene which were higher than  $E_i$  of cyclohexene.

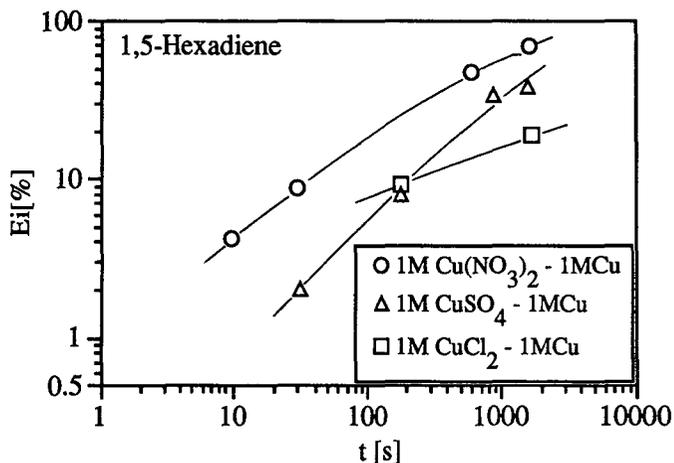


Figure 3 Effects of counter ions on extraction ratios of 1,5-hexadiene

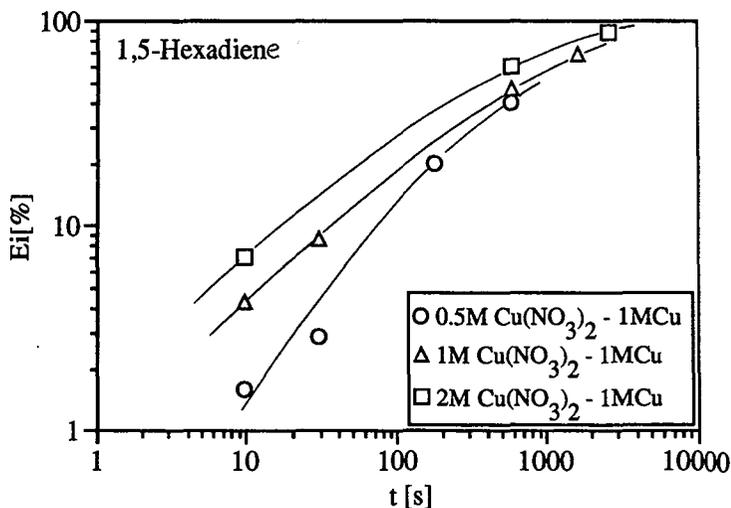


Figure 4 Effects of cupric salt on extraction ratios

### Effects of Counter Ion on Ei

Figure 3 shows the effects of counter ions on extraction ratios of 1,5-hexadiene. Ei with  $\text{NO}_3^-$  was highest as was the case in the absorption of  $\text{C}_4$  distillates (Ishii (1982)). As shown in Figure 4, extraction ratios of 1,5-hexadiene increased with increasing amount of  $\text{Cu}(\text{NO}_3)_2$ .

### Effects of Characteristics of Copper Powder

Figure 5 shows the effects of copper powder on extraction ratios of 1,5-hexadiene. When the amount of copper is higher than 1 M in aq. soln., extraction ratios at near equilibrium were almost independent of copper concentration. Fine powder facilitated extraction as was the case in the absorption of  $\text{C}_4$  distillates (Ishii (1982)). The low extraction rates at  $t < 20\text{s}$  for 2M-Cu powder may be ascribed to copper oxide because the color of copper surface was red in this case.

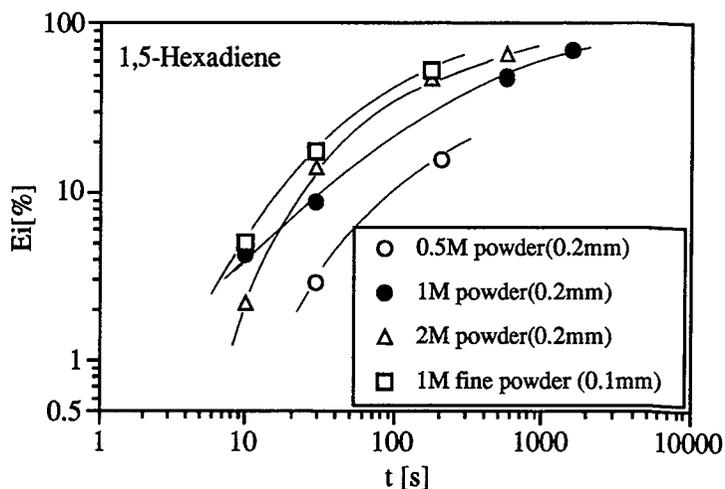


Figure. 5 Effects of amount of copper powder on extraction ratios

### Effects of Agitation Strength

As shown in Figure 6, agitation effect was so strong that Ei at  $t=200\text{s}$  increased twenty times as agitation speed increased four times.

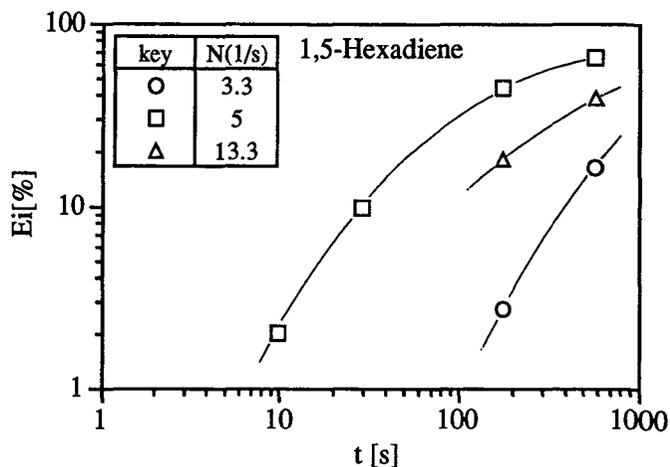


Figure. 6 Effects of agitation strength on extraction ratios

### CONCLUSION

It has been made clear that  $\pi$ -complex formation with cuprous ion in Cu(II)/Cu(0) contact systems has high potential as an extraction technology for liquid olefin/paraffin separation. Extraction is slow owing to the control by heterogenous reaction, and agitation strength has an important role. Counter ions and the characteristics of copper have strong effects on extraction ratios.

### NOMENCLATURE

E<sub>i</sub> Extraction ratio of olefin i  
 N Stirring speed  
 t Extraction time

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## LIX® 79 - A NEW LIQUID ION EXCHANGE REAGENT FOR GOLD AND SILVER

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### INTRODUCTION

The recovery of gold and silver from typical alkaline cyanide leach liquors by solvent extraction requires a reagent having a basicity intermediate between the commonly available amines; such as, Alamine®336\*, and the strong base quaternary amines; such as, Aliquat®336\*. The use of amines, modified amines and quaternary amines has been previously described (Alguacil, Hernandez, and Luis, 1990; Caravaca and Alguacil, 1992; Schweltnus and Green, 1990; Mooiman and Miller, 1986; Wan and Miller, 1990; Riveros, 1990).

Henkel has developed a new solvent extraction reagent, LIX®79\*, for the recovery of gold and silver from alkaline cyanide leach liquors (Kordosky, Sierakoski, Virnig and Mattison, 1992; Kordosky, Kotze, Mackenzie and Virnig, 1993). This paper will examine some of the properties of LIX 79 as well as describe the application of LIX 79 to the recovery of gold and silver. It will also describe the results of pilot plant trials to evaluate the application of LIX 79 to the detoxification of spent cyanide heap leach pads.

### EXPERIMENTAL

**Reagents:** Synthetic aqueous feed solutions were prepared from reagent grade chemicals. In the case of silver, copper, mercury, and zinc, additional sodium cyanide was added to give the following assumed species in solution:  $\text{Ag}(\text{CN})_3^{-2}$ ,  $\text{Cu}(\text{CN})_3^{-2}$ ,  $\text{Hg}(\text{CN})_3^{-1}$ , and  $\text{Zn}(\text{CN})_4^{-2}$ . Actual feed solutions generated from the leaching of ore were employed in circuit studies. The organic phase was prepared by diluting LIX 79 in either Exxon Aromatic®150 (Exxon Corporation), Escaid®110 (Exxon Corporation) or ORFOM SX-1® Solvent (Phillips Petroleum Corporation). Exxal®13, an isomeric mixture of branched chain tridecyl alcohols (tridecanol), available from Exxon Corporation was used as a solubility modifier. No pre-treatment of the organic phase was required prior to use.

**Extraction Procedures:** The determination of extraction isotherms and pH isotherms was carried out by placing the appropriate amounts of organic and aqueous phase into a separatory funnel and then shaking on a mechanical shaker for 30 minutes to an hour. The phases were then allowed to separate, filtered and submitted for analysis. In the case of the pH isotherms, the pH of the aqueous phase was adjusted to the desired point by addition of either concentrated sulfuric acid or sodium hydroxide. The kinetic tests were carried out in the same fashion as described for Henkel's standard LIX reagents for copper with the exception that the plexiglass mixing chamber was replaced by a 600 ml glass beaker with stainless steel baffles.

Analytical Procedures: Metal concentrations in the organic and aqueous phases were determined by either Atomic Absorption Spectrometry (AAS) or Inductively Coupled Plasma Spectrometry (ICP) using either purchased standards or standards prepared in Henkel laboratories.

## RESULTS AND DISCUSSION

### Extraction Chemistry

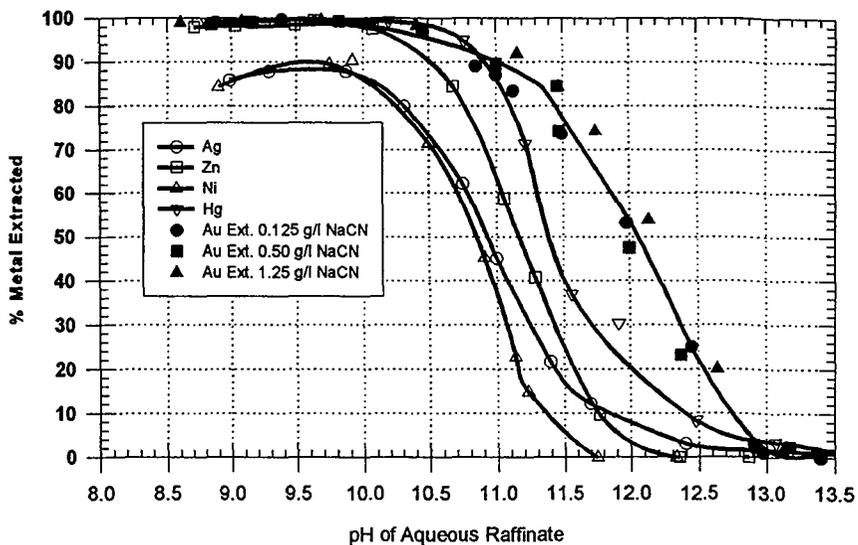


Figure 1 pH Isotherms

The active component in LIX 79 is a trialkyl guanidine. As can be seen from the pH isotherms for gold extraction by LIX 79 shown in Figure 1, LIX 79 is a strong extractant for aurocyanide up to a pH of 11.5 and can be stripped by contact with aqueous solutions having a pH above 13.5. This is consistent with the strongly basic nature of the guanidine functionality as illustrated by the fact that the pKa values for protonated alkyl guanidines typically lie in the range of 12-13. LIX 79 extracts by an ion pair extraction mechanism as previously described (Kordosky, Kotze, Mackenzie, and Virnig, 1993).

Table 1. Extraction Kinetics<sup>1</sup>

Time (min)	Au % Extraction	Ag % Extraction	Zn % Extraction	Cu % Extraction
1	70.7	16.2	47.6	2.3
2	70.0	17.0	47.6	1.5
5	70.7	16.6	48.5	1.5

<sup>1</sup> Organic phase: 8% (v/v) LIX 79 in Escaid 110 containing 50 g/l tridecanol. Aqueous phase: 15 mg/l Au; 50 mg/l of Ag, Zn, and Cu as cyanide complexes; 100 mg/l free cyanide; pH 10.5.

As expected for an ion pair type extraction, the kinetics of extraction are extremely fast. The results of a kinetic test with a mixed metal feed are summarized in Table 1. For all cases, complete equilibrium is achieved within 60 seconds. In a separate experiment with only aurocyanide present, 98% of equilibrium was achieved within 30 seconds.

LIX 79 will extract other anionic metal cyanide complexes. The extraction pH isotherms for silver, zinc, mercury and nickel are also summarized in Figure 1. As would be expected based on the pH isotherms and competitive extraction experiments, the order of extraction is: Au > Hg ~ Zn > Ag > Ni >> Cu. This order is somewhat different from that for the modified amines where Ag is extracted in preference over Zn as reported by Mooiman and Miller (1986).

Alkaline cyanide leach liquors typically contain a number of other anions which may also compete in extraction with the metal cyanide complexes. The effects of varying levels of sodium cyanide on the extraction of aurocyanide are shown in Figure 1. To broaden the study, a series of shakeout experiments were carried out by contacting aqueous solutions containing approximately 10 mg/l of each metal cyanide species and differing levels of sodium cyanide, sodium chloride, sodium thiocyanate or sodium carbonate with an organic phase at two different pH's, 9.5 and 11.0. The results are summarized in Table 2.

Table 2. Effect of Various Anions on Metal Extraction by LIX® 79<sup>1</sup>

pH	Au		Ag		Zn		Hg		Ni	
	9.5	11.0	9.5	11.0	9.5	11.0	9.5	11.0	9.5	11.0
NaCl										
100	98	88	96	49	98	94	85	88	98	64
200	98	88	96	49	98	94	90	94	98	66
500	98	90	93	43	98	96	89	91	98	64
1,000	98	88	89	38	98	92	94	94	98	54
NaSCN										
100	98	86	90	35	98	92	94	93	98	55
200	96	83	70	30	98	88	95	92	96	38
500	88	78	37	26	92	76	92	80	52	26
1,000	77	71	17	19	72	62	94	83	25	22
NaCN										
125	99	85	94	31	99	93	90	90	99	48
500	98	85	91	30	99	93	90	90	98	48
1,250	98	83	87	26	99	88	90	90	97	40
2,500	98	85	85	32	99	91	90	90	96	44
Na <sub>2</sub> CO <sub>3</sub>										
100	98	88	96	39	98	96	93	92	98	63
200	98	88	96	39	98	96	92	91	98	61
500	98	90	93	46	98	98	92	90	98	70
1,000	98	88	93	45	98	96	94	93	98	63

<sup>1</sup> Values are reported as % metal extracted and salt concentrations in mg/l.

Varying levels of sodium cyanide or sodium carbonate did not have an appreciable effect on extraction of any of the metals tested. Higher levels of sodium chloride resulted in a decrease in extraction of silver and nickel. Increasing the level of sodium thiocyanate resulted in significant reduction in extraction of silver, zinc, and nickel cyanide species. Interestingly, mercury and gold extraction were affected only at high levels of thiocyanate.

### Gold Extraction

Continuous circuit runs were performed at two different operating gold mines in the western United States. Both mines were operating Merrill-Crowe systems for the recovery of gold. The results are summarized in Table 3. A circuit configuration using 3 stages of extraction and 2 stages of stripping was employed in both cases. The primary goal of both studies was to test the performance of LIX 79 with regard to phase separation and crud formation. The circuit configuration was chosen to insure maximum gold recovery. Mine I, Run 1 was initially started up with an organic phase containing 10 g/l of tridecanol. After a short period of time, a yellow, very viscous third phase was observed forming on the overflow weirs in extraction and gold recovery dropped as a function of time. The third phase was analyzed and shown to contain very high levels of gold. Increasing the tridecanol concentration to 50 g/l eliminated the formation of this third phase. In both cases, very high recoveries of gold were obtained. The data shows the expected order of selectivity: Au > Zn > Ag > Ni > Cu > Fe. A minimum NaOH level of 28-30 g/l was required in the strip solution to maintain acceptable stripping performance.

Table 3. Summary of Continuous Circuit Testing with Gold Mine Feeds

Met.	Mine Test I <sup>1</sup>						Mine Test II <sup>2</sup>		
	Run 1			Run 2			Feed Aq. (mg/l)	Extr. Raff. Aq. (mg/l)	% Re- cove- ry
	Feed Aq. (mg/l)	Extr. Raff. Aq. (mg/l)	% Re- cove- ry	Feed Aq. (mg/l)	Extr. Raff. Aq. (mg/l)	% Re- cove- ry			
Au	1.30	<0.01	>99	1.38	0.14	90	0.65	<0.01	99
Ag	1.10	0.78	32	1.15	0.96	17	1.44	0.12	92
Zn	14.4	2.15	85	26.6	3.7	86	4.13	<0.01	100
Ni	4.23	3.49	17	N.D.	N.D.	N.D.	1.33	<0.01	99
Cu	1.00	0.96	4	N.D.	N.D.	N.D.	2.89	1.49	48
Fe	0.72	0.77	0	N.D.	N.D.	N.D.	N.D.	N.D.	---
Se	N.D.	N.D.	---	N.D.	N.D.	N.D.	11.0	0.07	99
pH	10.9	11.3	---	11.0	11.3	---	9.3	10.7	---
CN	80.8	N.D.	---	2185	2130	---	N.D.	N.D.	---

<sup>1</sup> Organic: 15% (v/v) LIX 79 in Aromatic 150 containing 50 g/l tridecanol. Strip solution: 40 g/l NaOH, 5 g/l NaCN. Organic/aqueous flows: extraction = 1/1, strip = variable.

<sup>2</sup> Organic = 30% (v/v) LIX 79 in Aromatic 150 containing 50 g/l tridecanol. Other conditions are the same.

Increasing the cyanide concentration from 80 mg/l to 2185 mg/l by addition of sodium cyanide to the aqueous feed resulted in lower gold and silver recoveries (Mine 1, Run 1 vs 2) suggesting that at very high levels of free cyanide, cyanide will compete for reagent with aurocyanide. In the case of Mine 2, the AAS analytical results were confirmed by fire assay. Due to the lower pH of the incoming feed, more copper and nickel was extracted than in the case of Mine 1. Note that the pH increases in going from feed to raffinate in all cases which is consistent with the proposed extraction mechanism. No problems were noted with either phase separation or crud formation over the course of the runs, approximately 30 hours each. A small amount of a light tan solid collected at the interface in the E<sub>1</sub> settler over time. It is believed to be the result of a solid being carried into the circuit by the incoming aqueous feed solution.

### Silver Extraction

Similar tests were carried out at a silver mine in southern Nevada. The results are summarized in Table 4. The pH of the leach liquor was adjusted to pH 9.40 with 28% hydrochloric acid prior to use. Typical silver recoveries averaged 90%. The average composition of the strip liquor during the course of the run was 8.0 g/l NaOH and 5 g/l NaCN with a silver content of 2.93 g/l. Due to the low caustic concentration in stripping, the overall silver stripping efficiency was only 82% resulting in a stripped organic containing 8.7 mg/l of silver. Use of higher caustic levels in stripping would have resulted in lower stripped organic values and improved overall silver recoveries.

Table 4. Summary of Continuous Circuit Testing with Silver Mine Feed <sup>1,2</sup>

Metal	Feed Aqueous (mg/l)	Aq. Raffinate (mg/l)	Recovery (%)
Ag	48.6	4.9	90
Zn	6.1	<0.05	99
pH	9.40	9.66	---

<sup>1</sup> Organic phase: 10% (v/v) LIX 79 in ORFOM SX-1 containing 75 g/l of tridecanol.

<sup>2</sup> Circuit: 3 stages of extraction, 1 stage of stripping. Organic/aqueous flows extraction = 1/1, strip variable.

### Detoxification

Environmental regulations in the western United States require that the spent heap leach pad along with the leached materials and process solutions must be treated to reduce the concentration of the residual cyanide, base metal cyanide complexes, and other anionic metal species to a level where they are judged to no longer represent a hazard. To test the potential for LIX 79 in this application, a pilot plant test was carried out. The results are summarized in Table 5. The circuit consisted of 3 stages of extraction (7.6 l per minute total flow, O/A = 1, 3 minute mixer retention) and 3 stages of stripping. Three strip stages were employed simply because of pilot plant design. The circuit was operated so that no stripping occurred in S<sub>3</sub>. S<sub>1</sub> was operated at essentially 100% recycle to build a pregnant solution with 1 M sodium hydroxide as stripping agent. As in the case of the work with the gold circuits described previously, a minimum of approximately 28 g/l sodium hydroxide in the strip solution was required to guarantee 100% stripping in S<sub>1</sub>. To mimic the conditions that would be encountered

during an actual decommissioning operation where the raffinate would be used to repetitively rinse the ore, a portion of the raffinate (E<sub>3</sub> aqueous) was collected, acidified with carbon dioxide to pH 9.0, and used as feed for a second pass through the pilot plant. Essentially complete removal of the various metals of interest was achieved. The final weak acid dissociable cyanide (WAD CN) level of <0.04 mg/l was well within the typical limits of <0.2 mg/l set by the regulatory authorities.

**Table 5. Summary of Detoxification Pilot Plant Trial <sup>1</sup>**

	Feed Aqueous (mg/l)	Pass 1 Extraction Raffinate Aq. (mg/l)	Pass 2 <sup>2</sup> Extraction Raffinate Aq. (mg/l)	Overall Recovery (%)
Au	0.46	0.03	Non. Det.	100
Ag	2.0	0.03	Non. Det.	100
Hg	2.5	0.004	0.005	99.8
Cu	1.9	0.20	<0.05	>97.4
Zn	1.5	<0.10	<0.01	>99.3
Se	1.7	0.30	0.036	97.9
pH	9.0	10.5	9.6	---
WAD CN	7.5	2.4	<0.04	---

<sup>1</sup> Organic: 15% (v/v) LIX 79 in Aromatic 150 containing 75 g/l tridecanol. Strip solution: 40 g/l NaOH. Organic/aqueous flows: extraction = 1/1, strip = variable.

<sup>2</sup> Pass 1 raffinate was acidified to pH 9.0 with CO<sub>2</sub> and used as feed for Pass 2.

\* LIX, ALAMINE, and ALIQUAT are trademarks of Henkel Corporation.

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## MOLECULAR MODELLING AND DESIGN OF PHOSPHORIC ACID ESTERS HAVING BULKY SUBSTITUENTS FOR EXTRACTION OF RARE EARTH ELEMENTS

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### ABSTRACT

Phosphoric acid esters having bis(4-ethylcyclohexyl) (D4EHPA) and bis(4-cyclohexylcyclohexyl) (D4DCHPA) groups as the bulky substituents were synthesized to investigate their extractabilities, selectivities and loading capacity in the extraction of rare earth elements from acidic aqueous nitrate media with these extractants in toluene. From the concentration dependencies of reactant species on the distribution ratio of rare earth elements, it was concluded that the rare earth elements ( $M^{3+}$ ) were extracted with these extractants as  $M(HR_2)_3$  in organic phase and the extraction equilibrium constants ( $K_{ex}$ ) were evaluated. The  $K_{ex}$  value of each rare earth element become greater in the order, D4DCHPA > D4EHPA > bis(2-ethylhexyl)phosphoric acid (D2EHPA). It was very noticeable that the separation factor between La(III) and Pr(III) ( $\beta(La/Pr)$ ) and  $\beta(Gd/Ho)$  with D4EHPA, and  $\beta(La/Ce)$  and  $\beta(Gd/Eu)$  with D4DCHPA are significantly greater than those with D2EHPA. The loading capacity of Nd(III) with these extractants is excellent compared with that of D2EHPA due to preventing the gelation of organic phase. The discussion of structural effect of the bulky substituents of D4EHPA and D4DCHPA on the extraction behavior of rare earth elements is provided from a molecular modelling computational viewpoint.

### INTRODUCTION

The extractants for the commercial scale separation of rare earth elements should satisfy the following at least three requirements: (1) high loading capacity without any gel formation at high loading, (2) ease of stripping, in addition to, (3) high selectivity among adjacent rare earth elements. The majority of commercial separation and refining of rare earth elements have been carried out by means of the solvent extraction with dialkylphosphoric acids, especially bis(2-ethylhexyl)phosphoric acid (henceforth D2EHPA), and many fundamental studies on the extraction of rare earth elements have been conducted (Pierce (1963); Danesi (1982)). Although these extractants provide fairly good separation factors between adjacent rare earth elements, the extracted metal complexes are apt to polymerize to give rise to a gel insoluble in organic diluents at approximately 50 % saturation, which greatly limits the effective use of the extractants. One approach to the design of the extractant molecules with no gel formation at high loading may be the introduction of bulky substituents, which may impede the mutual approach of metal complexes for polymerization. Recently, Ishida (1993) reported the structural effect of phosphoric acid esters having cyclohexyl groups on the equilibrium extraction of rare earth elements. They synthesized six kinds of bisalkylphosphoric acids containing cyclohexyl groups and/or aliphatic alkyl groups, and measured the extraction of rare earth elements. It was found that the position of the ring substituents in the phosphoric acid esters is closely related to the extractabilities and selectivities of rare earth elements.

In the present study, bis(4-ethylcyclohexyl)phosphoric acid (abbreviated as D4EHPA, henceforth, and expressed as HR for monomeric species, and  $H_2R_2$  for dimeric species) and bis(4-cyclohexylcyclohexyl)phosphoric acid (henceforth abbreviated as D4DCHPA) as shown in figure 1 were synthesized. The extraction equilibria of rare earth elements from acidic aqueous nitrate media with these extractants in toluene were carried out at 303 K. From the concentration dependencies of hydrogen ion and extractant on the distribution ratios of these rare earth elements, the extraction equilibrium constants were evaluated, to elucidate the extractabilities and selectivities of rare earth elements. The loading capacities of Nd(III) with these extractants were carried out to compare with that of D2EHPA from the view point mentioned above. Furthermore, the structural effect of bisalkylphosphoric acid on the extractabilities and selectivities of rare earth elements were discussed from the view point of molecular modelling with molecular mechanics and molecular orbital methods to find out the important factors for dominating the extractabilities and selectivities of rare earth elements as well as the prevention of gel formation at high loading.

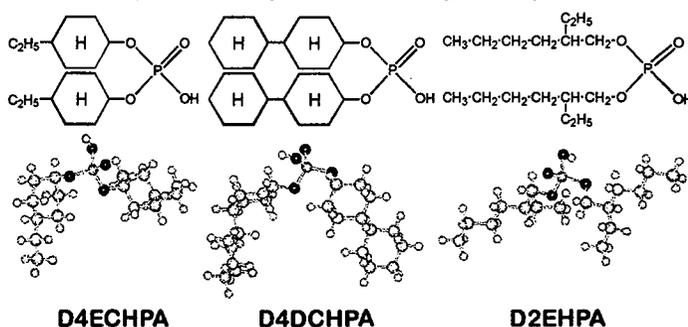


Figure 1. Chemical structures of D4EHPA, D4DCHPA and D2EHPA.

## EXPERIMENTAL

### Reagents

D4EHPA and D4DCHPA were synthesized by the same procedures described in a previous paper (Yoshizuka (1993)). The products were identified by infrared and  $^1H$ -n.m.r. spectroscopies as well as the elemental analysis.

The organic solution was prepared by dissolving the extractants in reagent grade toluene to a required concentration gravimetrically. The aqueous solutions were prepared by dissolving oxides of the corresponding rare earth elements in the aqueous mixtures of  $1000 \text{ mol}\cdot\text{m}^{-3}$  nitric acid and  $1000 \text{ mol}\cdot\text{m}^{-3}$  sodium nitrate. The purity of oxides of rare earth elements is greater than 99.9%.

### Extraction equilibria

The measurement of extraction equilibria of rare earth elements was carried out batchwise in the conventional method. The two phases were shaken for 24 h in a water bath incubator maintained at 303 K to attain equilibrium. The concentration of rare earth element was measured by using a Shimadzu model ICP-1000III inductively coupled plasma atomic emission spectrometer. The amount of rare earth elements extracted was calculated from the difference of the concentration in the aqueous phase before and after equilibration. The experimental conditions are as follows: initial

concentration of rare earth elements =  $0.5 \text{ mol}\cdot\text{m}^{-3}$ , initial concentration of extractant =  $3 - 100 \text{ mol}\cdot\text{m}^{-3}$ , initial pH of aqueous phase =  $0.5 - 6.5$ .

### Loading test of a rare earth element

In order to examine the loading capacity of the extractants for rare earth elements, the loading tests were carried out for Nd(III) as a rare earth element. The experimental procedures are the same as that mentioned above. The loaded organic phase was separated from aqueous phase, and then fresh aqueous solution was added for further extraction. The extraction was repeated until Nd(III) concentration in aqueous phase was not changed before and after the extraction. The experimental conditions are as follows: initial concentration of Nd(III) =  $5 \text{ mol}\cdot\text{m}^{-3}$ , initial concentration of extractant =  $50 \text{ mol}\cdot\text{m}^{-3}$ , initial pH of aqueous phase =  $3.0$ .

### Molecular modelling computation

Molecular modelling computations for the extractants and their rare earth complexes were carried out by using the molecular modelling software, HyperChem™ Release 4 (Hypercube, Inc., Canada). The molecular mechanics, MOMECC (Comba (1994)), was used to obtain the optimal structures and heat of formation. The convergence criterion for the MOMECC computation was set at an RMS gradient of 0.001. Semiempirical PM3 calculations of extractant molecules were carried out on Sun 4/10 unix computer using the MOPAC93 (Stewart (1993)). The precise mode was used which sets the convergence criteria for GNORM = 0.01 and SCFRT=0.00001

## RESULTS AND DISCUSSION

### Extraction equilibria

Figure 2(a) and (b) show the effects of pH on the distribution ratios of rare earth elements,  $D$ , in the cases of D4EHPA and D4DCHPA, respectively. The plots lie on a straight line with the slope of 3 for all rare earth elements as observed in the extraction of trivalent rare earth elements with other acidic organophosphorus extractants such as D2EHPA. This suggests that the extraction of rare earth elements with these extractants have inversely third order dependency on the hydrogen ion activity based on the cation-exchange extraction reaction.

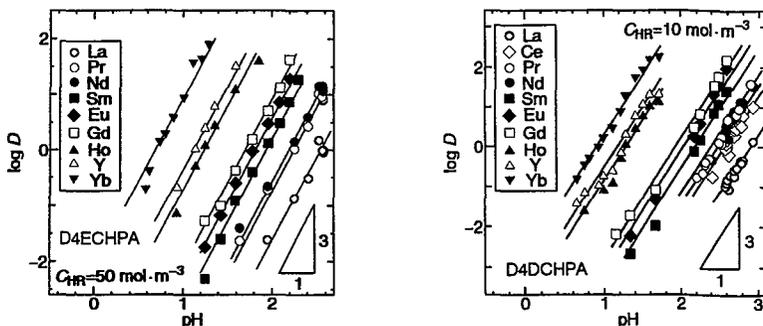


Figure 2. Effect of pH on distribution ratios of rare earth elements,  $D$ , in the cases of D4EHPA (a, left), and in the cases of D4DCHPA (b, right).

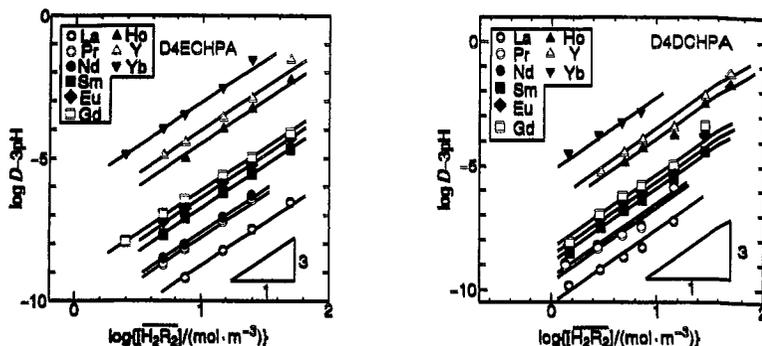
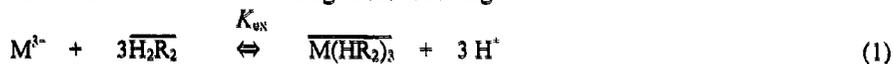


Figure 3. Effect of concentration of dimeric species of the extractant in organic phase,  $[\overline{H_2R_2}]$ , on the distribution ratio of rare earth elements,  $D$ , in the case of D4EHPA (a, left), and in the cases of D4DCHPA (b, right).

Figure 3(a) and (b) show the effects of concentration of the dimeric species of the extractant in organic phase,  $[\overline{H_2R_2}]$ , on the distribution ratio of rare earth elements,  $D$ , in the case of D4EHPA and D4DCHPA, respectively. From the measurement of the apparent molecular weight of D4EHPA and D4DCHPA by vapor-phase osmometry as described in the previous paper (Yoshizuka (1993)), it was already elucidated that these extractants exist as dimeric species in toluene. The concentration of the dimeric species of D4DCHPA was calculated by using the dimerization constant,  $K_d$  ( $= 15.4 \text{ m}^3 \cdot \text{mol}^{-1}$ ), while that of D4EHPA was half of the analytical concentration of the extractant,  $C_{HR}$ . The plots lie on a straight line with the slope of 3 for all rare earth elements. This suggests that the extraction reactions of rare earth elements show third order dependencies on  $[\overline{H_2R_2}]$ .

From the results described above, it can be considered that all the rare earth elements are extracted with D4EHPA and D4DCHPA according to the following extraction reaction:



The extraction equilibrium constant,  $K_{ex}$ , is expressed by:

$$K_{ex} = \frac{[\overline{M(HR_2)_3}] a_H^3}{[M^{3+}] [\overline{H_2R_2}]^3} = D (a_H / [\overline{H_2R_2}])^3 \quad (2)$$

Equation (2) can be rearranged as follows:

$$\log D = 3 \text{pH} + 3 \log [\overline{H_2R_2}] + \log K_{ex} \quad (3)$$

Equation (3) is satisfactory to all the experimental results shown in figures 2 and 3 as expected. From all the experimental results, the extraction equilibrium constants of rare earth elements with D4EHPA and D4DCHPA,  $K_{ex}$ , are obtained.

Figure 4 shows the relation between the logarithm of the extraction equilibrium constant evaluated and the order of atomic number of rare earth elements in the case of D4EHPA and D4DCHPA, together with the literature data of the extraction with D2EHPA in toluene from the perchlorate media (Pierce (1963)). The extraction equilibrium constant of each rare earth element becomes greater in the order, D4DCHPA > D4EHPA > D2EHPA and tend to increase with increasing of atomic number of rare earth elements for each extractant. This series is roughly divided into four groups such as La - Nd, Sm - Eu, Gd - Ho and Y - Yb groups. This phenomenon is called "tetrad

effect" related to lanthanoid contraction and stabilized energy of repulsion between *f*-electrons (Peppard (1970)), which have been observed in many extraction systems for rare earth elements. In comparison with each separation factor, it was especially remarkable that  $\beta(\text{La}/\text{Pr})$  and  $\beta(\text{Gd}/\text{Ho})$  with D4EHPA, and  $\beta(\text{La}/\text{Ce})$  and  $\beta(\text{Gd}/\text{Eu})$  with D4DCHPA are significantly greater than that with D2EHPA.

### Loading test of a rare earth element

The loading test of Nd(III) in the organic phase was carried out to compare the loading capacities of D4EHPA and D4DCHPA with that of D2EHPA. The maximal loading capacities ( $C_1/C_{HR}$ ) with D4EHPA and D4DCHPA were 40 % and 35 %, respectively. Furthermore, the gelation of organic phase was not observed until the maximal loading conditions, while using D2EHPA, the highly viscous gel was formed at 25 % loading. This suggests that the steric hindrance of bulky ring groups of D4EHPA and D4DCHPA can prevent the gelation of organic phase caused by the formation of polynuclear complex of rare earth elements.

### Molecular modelling computation

Figure 5 shows the proposed structures of Sm(III) complexes with D2EHPA, D4DCHPA and D4EHPA *in vacuo* optimized with the molecular mechanics method, MOMECC. For these calculations, we used the parameters for ionic radius of Sm(III) as 0.0958 nm (Shannon (1976)). It was elucidated that all the complexes are existing in similar globular structures, and Sm(III) ion is fully covered with the extractant molecules. The total energies of Sm(III) complexes are calculated as 4690, 7080 and 2310 kJ·mol<sup>-1</sup> for D4EHPA, D4DCHPA and D2EHPA, respectively. It is found that the total energies of Sm(III) complexes with D4EHPA and D4DCHPA are three times and

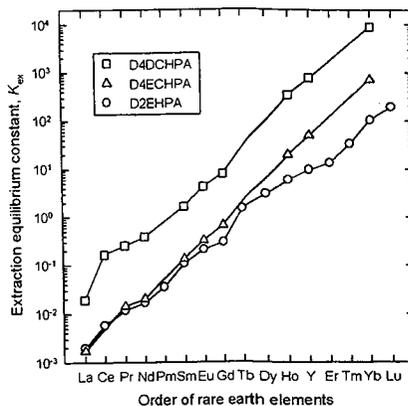


Figure 4. Relation between the extraction equilibrium constant and order of atomic number of rare earth elements.

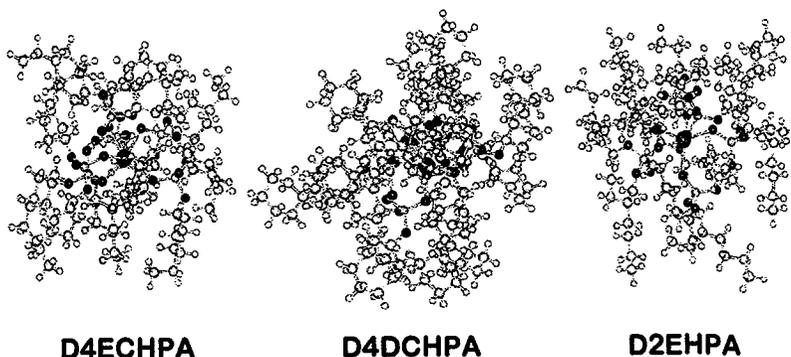


Figure 5. Proposed structures of Sm(III) complexes with D2EHPA, D4DCHPA and D4EHPA calculated by molecular mechanics method, MOMECC.

twice greater than that with D2EHPA. This is due to the bulkiness of 4-ethylcyclohexyl and 4-cyclohexylcyclohexyl substituents of the extractants compared to 2-ethylhexyl groups of D2EHPA. The molecular volumes of these complexes are calculated as 4.40, 5.84 and 4.84 nm<sup>3</sup> for D4EHPA, D4DCHPA and D2EHPA, respectively.

## CONCLUSION

Studies on the extraction equilibria of rare earth elements with bis(2-ethylcyclohexyl)phosphoric acid (D4EHPA) and bis(4-cyclohexylcyclohexyl)phosphoric acid (D4DCHPA) in toluene were conducted at 303 K from the acidic nitrate media. The followings can be concluded:

1. The extracted species of rare earth elements with D4EHPA and D4DCHPA are  $M(HR_2)_3$  and the extraction equilibrium constants for rare earth elements were evaluated.
2. The separation factors,  $\beta(La/Pr)$  and  $\beta(Gd/Ho)$  with D4EHPA, and  $\beta(La/Ce)$  and  $\beta(Gd/Eu)$  with D4DCHPA are significantly greater than that with D2EHPA.
3. The loading capacities of Nd(III) with D4EHPA and D4DCHPA in the organic phase are excellent compared with that of D2EHPA due to the steric hindrance of the bulky ring substituents.
4. The structural effect of the extractant on the complex formation was discussed from the view point of molecular modelling with molecular mechanics and molecular orbital methods.

## NOMENCLATURE

$a_H$	=	activity of hydrogen ion	[mol·m <sup>-3</sup> ]
$C_{HR}$	=	analytical concentration of extractant	[mol·m <sup>-3</sup> ]
$C_t$	=	total concentration of complex of rare earth element in organic phase	[mol·m <sup>-3</sup> ]
$D$	=	distribution ratio of rare earth element	[ - ]
$K_d$	=	dimerization constant of extractant	[m <sup>3</sup> ·mol <sup>-1</sup> ]
$K_{ex}$	=	extraction equilibrium constant	[ - ]
$\beta$	=	separation factor between adjacent rare earth elements derived from $K_{ex}$	[ - ]
[j]	=	concentration of species j (= M <sup>3+</sup> , HR, H <sub>2</sub> R <sub>2</sub> , M(HR <sub>2</sub> ) <sub>3</sub> )	[mol·m <sup>-3</sup> ]
<Superscript>			
—	=	organic phase	

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## RECOVERY OF RARE EARTH METALS WITH A NEW ORGANOPHOSPHORUS EXTRACTANT

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### ABSTRACT

This work studies a new organophosphorus extractant DS5834 developed by Zeneca Specialties, which has been shown to be efficient at removing impurity metal ion. The new reagent is a formulation of a type similar to M2EHPA - monoester, di-acid phosphate extractant but with a lower reported water solubility.

A preliminary study was undertaken to determine if the new reagent, DS5834, is effective for the recovery of gallium, indium and germanium from acid solutions by solvent extraction.

The results showed that DS5834 is a strong extractant for all of the metals studied except germanium. Germanium was not extracted by this reagent. Iron is also extracted by this reagent but with a lower distribution factor.

### INTRODUCTION

Gallium and germanium are assuming an increasingly important role in industry owing to their technological and strategic applications. The demand for these metals is expected to increase significantly over the next 10 years.

More than 95% of the gallium consumed in the United States is used in GaAs devices which have extensive electronics applications such as light emitting diodes, laser diodes, fiber optics and semiconductors. Gallium arsenide semiconductors are potentially 25 times faster than conventional silicon devices, Harbuck (1989).

The major uses for germanium are in infrared optics, fiber optics systems, optical detectors and semiconductor devices including transistors, diodes and rectifiers.

Presently, gallium and germanium are produced almost exclusively as by-products of the aluminium and zinc industry. Gallium, although relatively abundant, is rarely found in a concentrated form in the earth's crust. Gallium is often found as a substituent for aluminium in bauxite and it is recovered from the spent caustic solution in the Bayer process where it gets concentrated up to 200 ppm, Bautista (1989). Waste residue from hydrometallurgical zinc processing operations also contains a substantial amount of these metals, Harbuck (1989).

Indium is an important raw material for electronic devices such as InP semiconductors. Indium usage in the near future is expected to increase significantly because of its use in many new technologies.

Indium is contained in trace amounts in various kinds of zinc ores and is being recovered from the slags or residues produced in zinc and lead refining. It is extracted from sulfuric acid leach liquors of these slags or residues by chelating ion exchange or solvent extraction with acidic organophosphorus extractants or carboxylic acids. Several processes for recovery of indium from zinc refinery residues have been developed recently in Japan and China, and some of these processes have now been implemented in commercial operations, Inoue (1988).

According to Hoffman (1991), many improvements in extractive metallurgy in the last 30 years have been the result of advances in solvent extraction which has led to frequent application of this technology in commercial applications. Solvent extraction has moved from being largely confined to the analytical laboratory to becoming a well established unit operation in many hydrometallurgical plants.

Solvent extraction is now employed in a variety of process such as recovery of metals like gallium, germanium, and indium, separation of rare earths, purification and concentration of copper values in dump and heap leach liquors, etc.

The recovery processes of these metals often use solvent extraction with organic phosphoric or phosphonic acids or a mixture thereof, followed by stripping with aqueous chloride media.

Sato (1975) conducted an investigation of indium extraction from sulfuric acid with di(2-ethylhexyl) phosphoric acid-D2EHPA in kerosene at 293 K. Inoue (1988) conducted an investigation on the extraction of indium from nitric acid with three kinds of acidic organophosphorus compounds; D2EHPA, EHEHPA and di (2, 4, 4-trimethylpentyl) phosphinic acid-DTMPPA.

Sato (1989) investigated the extraction of gallium (III), and indium (III) from hydrochloric acid solutions using D2EHPA and EHEHPA and found that the D2EHPA extraction efficiency was higher than EHEHPA, except for gallium (III) in which its order reverses at higher aqueous acidity.

A new extractant DS5834 (MW=348.5 g/mole), developed by Zeneca Specialties is similar to M2EHPA, a monoester, di-acid phosphate extractant with an iso-C<sub>18</sub>H<sub>37</sub> as the substituted functional group. According Cupertino (1994), in a study for the removal of antimony and bismuth from copper tankhouse electrolytes, the extractant was reported to be completely selective over copper, nickel, arsenic and iron (II). It is reported to have fast extraction kinetics, rapid phase separation characteristics and excellent stability in contact with fresh, hot electrolyte solution.

## EXPERIMENTAL PROCEDURE

Studies were conducted with the extractant, DS5834, for the recovery of gallium, indium, and germanium, from chloride solutions. The experimental work was done using pure solutions of each element. The parameters investigated were the effect of DS5834 concentration and acidity of the aqueous solution on metal extraction and extraction kinetics. Equilibrium isotherms were constructed.

## Material and Methods

The aqueous solutions were prepared by dissolving the metal oxides in hydrochloric acid and the concentration was adjusted by diluting with deionized water. High purity gallium, indium, and germanium, oxides were obtained from the Aldrich Chemical Co. Initial concentrations of indium, gallium and germanium were 414, 372 and 347 ppm respectively. The acidity range was 0,1M to 0,5M HCl. The extractant, DS5834, was obtained from Zeneca Specialties. The diluent used in these experiments was EXXSOL-D80. All materials were reagent grade and used as received.

The batch tests were carried out in 120 ml separatory funnels at a temperature of  $25 \pm 1^\circ\text{C}$ . The aqueous and organic phases were contacted for fifteen minutes in a mechanical shaker at an A/O = 1. The phases were separated and the metal concentrations were determined in the aqueous phase.

## Chemical Analysis

The concentration of metals in the aqueous solutions was determined by EDTA titrations using xylenol orange as an indicator, Pribil (1982). The stability of EDTA complexes is influenced by a number of factors such as temperature, ionic strength, acidity of the solution, presence of other complex forming anions, etc. These factors should be considered before applying this analytical methodology.

### Titration methods for indium, gallium, germanium, samarium and gadolinium

The high stability of the In-EDTA complex makes direct titrations in an acid medium preferable.

A solution containing up to 50 mg of indium is heated to  $50 - 60^\circ\text{C}$  and titrated with 0.05M EDTA using xylenol orange as an indicator from a red to clear yellow at pH 2-4.

Gallium and germanium can be determined by direct titration with EDTA at a pH close to 3. However the back titration method is recommended for the analyses of Ga and Ge. In this type of a titration, a small excess of 0.05M EDTA is added to the acid solutions and the pH is adjusted to 5-5.5 with hexamine. Several drops of xylenol orange indicator are added and the metal is titrated with a 0.05M zinc solution from yellow to an intense red, Pribil (1982). A zinc sulfate solution in the presence of xylenol orange in an acid medium gives good results as a titrant for the excess EDTA. To improve the complexometric reaction of EDTA with Ga, the solution was heated to  $70^\circ\text{C}$  before titration. For germanium, more drastic conditions were required to assure complete complexometric reaction with EDTA so the solution was boiled for 15-30 minutes prior to titration.

A TTT 80 Radiometer automatic titrator provided manual control and high precision to control the titrant dispensing rate. For the determination of indium, in concentrations higher than 20 ppm, the direct titration method less than a 1% error.

The indirect titration of gallium and germanium solutions showed an error close to 1% when the metal concentrations were higher than 50 ppm. For lower concentrations, between 20 and 50 ppm, the error did not exceed 5%.

## RESULTS AND DISCUSSION

### Influence of the DS5834 concentration on indium and gallium extraction

Figure 1 shows the effect of the extractant concentration on the extraction of indium and gallium. The DS5834 is a strong extractant for both elements but is more selective for indium. The recovery of indium and gallium using 0.06 M DS5834 is 99% and 89% respectively. The amount of indium extracted is influenced by the acid concentration. This is further discussed below.

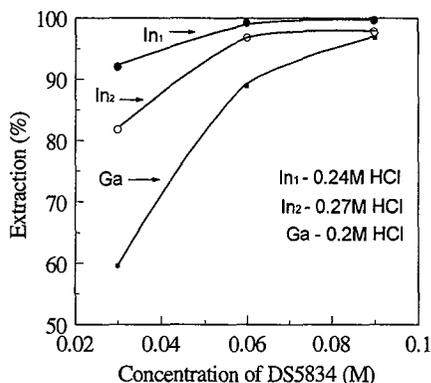


Figure 1 : Influence of extractant concentration on In and Ga extraction.

### Influence of acidity on the extraction of indium and gallium

The curves in figure 2 show that the behavior of indium and gallium extraction is affected by the acid concentration. The recovery of these metals, using the DS5834 extractant, decreases significantly with increasing acidity. Indium is preferentially extracted across the range of acidity levels tested.

### Kinetics of indium and gallium extraction

The kinetics of indium and gallium extraction using DS5834 are shown in figure 3. The indium is extracted very quickly, requiring less than 5 minutes to reach equilibrium whereas the kinetics of gallium extraction are much slower and about fifteen minutes is required to reach equilibrium. The use of differential extraction levels and kinetics can both be used to achieve effective separation of these elements.

### Germanium extraction with DS5834

Preliminary tests for germanium showed very little extraction using DS5834. More drastic conditions were used in further tests to elucidate the behavior of germanium extraction. The extractant concentration was raised to 0.15 M and acidity was lowered to 0.1 M however the

extraction under these conditions never exceeded 5%. No further tests were done due to these results.

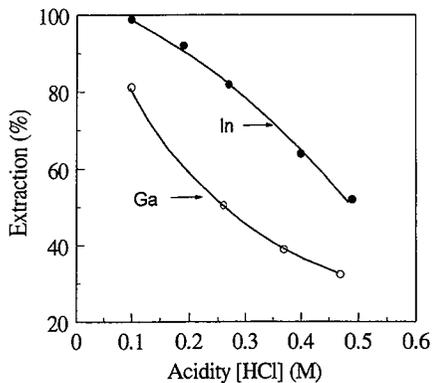


Figure 2 : Influence of acidity on In and Ga extraction.

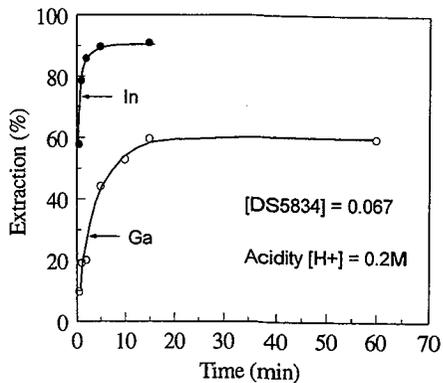


Figure 3 : Kinetics of In and Ga extraction.

### Iron Interference on Indium and Gallium Extraction

Figure 4 shows the extraction isotherms generated from separated tests for indium, gallium and iron using DS5834. The distribution profile for each element was generated from solutions containing only one metal at a time. The initial concentrations of In, Ga e Fe were 414,372 and 1136 ppm respectively. The acidity was maintained 0.2M. The iron extraction occurs simultaneously with indium and gallium but on lower proportions at low concentrations of these metals. Although some selectivity for indium over iron can be achieved, it would be better to remove the iron prior to indium recovery in a real process.

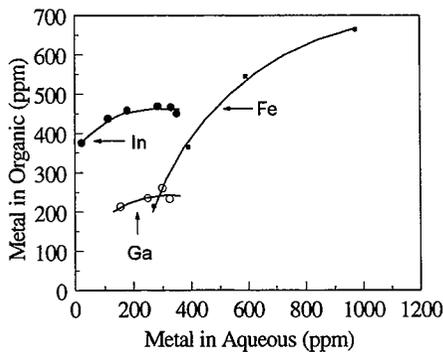


Figure 4 : Distribution of In, Ga and Fe using DS5834 0.03 M.

## CONCLUSIONS AND RECOMMENDATIONS

DS5834 is a strong extractant for indium and gallium. It is possible to reach high extraction of these elements from hydrochloric solutions.

Germanium was not extracted by DS5834 under the conditions studied.

The batch tests shown that indium extraction was higher than gallium extraction using DS5834. The extractions kinetics for indium were also faster than gallium under the same conditions.

Iron (III) is expected to compete for the loading of DS5834. It is extracted by DS5834 with a lower distribution factor than Indium.

This work should be complemented with stripping tests for gallium and indium from the organic solutions. Further studies should be undertaken on multi-element solutions to develop a method for the separation of these elements from iron.

And finally, experimental work should be carried out on extraction and stripping of gallium and indium from solutions produced in industrial process streams.

## ACKNOWLEDGMENTS

The authors are grateful to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for the financial support and the University of British Columbia for the opportunity in developing this work.

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## PROGRESS IN STRUCTURE-REACTIVITY STUDIES OF LIGANDS IN METAL EXTRACTION

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Some new experimental results illustrating the structure-reactivity studies of acidic phosphorus-based ligand in rare earth extraction were reported.  $\gamma$ -Effect is an empirical approach which is helpful for the design of new powerful extractants for rare earth. MNDO and MM2 (85) calculations were first introduced for structure-reactivity studies of extractants.

### INTRODUCTION

The important role of organic solvent extractants in technological and economic aspects of an extraction process is well established. We demonstrated that the reactivity of coordination atom and grouping, steric effect as well as lipophilicity of extracted species are the three most important factors determining the effectiveness of solvent extractants. Yuan(1980,1983, 1986,1988). On the other hand, the configuration of complexes formed during the extraction reaction showed remarkable effect on the contribution of steric influence of the ligands. It is extremely important for the design and selection of powerful reagent for the separation of such metals which form complexes with different configurations.

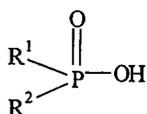
The present paper describes the experimental results in structure-reactivity studies of extractants in our laboratory during the last five years.

### $\gamma$ -EFFECT OF LIGAND IN RARE EARTH SEPARATION

An empirical approach was introduced based on the observation that most of the ligands providing high separation factors in rare earth separation, possess a branch chain in the  $\beta$ -position of the ester oxygen atom or  $\gamma$ -position from phosphorus.

Extraction data of these ligands namely, HEHEP, MANPP, MBOPP and MBOMPP show that the same type of compounds possess similar pKa values but with huge difference in separation factors for rare earths depending on the structure of alkyl groups. Consequently the  $\gamma$ -effect was suggested for the contribution of such structure variation. In order to confirm such effect 12 new phosphorus-based extractants were designed and synthesized. Yuan(1994).

These new phosphorus-based acidic compounds were purified and the purity was carefully checked by  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR, elemental analysis in addition to pKa measurements. Extraction experiments were performed by standard method. The aliquot, consisting of various concentrations of Neodymium, Samarium, Yttrium or Ytterbium as representative



No.	R <sup>1</sup>	R <sup>2</sup>
1	AmCHMeCH <sub>2</sub> CH <sub>2</sub> O	AmCHMeCH <sub>2</sub> CH <sub>2</sub> O
2	AmCHMeCH <sub>2</sub> CH <sub>2</sub>	Me <sub>3</sub> CCH <sub>2</sub> O
3	AmCHMeCH <sub>2</sub> CH <sub>2</sub>	BuCHEtCH <sub>2</sub> O
4	AmCHMeCH <sub>2</sub> CH <sub>2</sub>	HexCHMeO
5	AmCHMeCH <sub>2</sub> CH <sub>2</sub>	AmCHMeCH <sub>2</sub> CH <sub>2</sub> O
6	i-Pr	Me <sub>3</sub> CCH <sub>2</sub> O
7	i-Pr	AmCHMeCH <sub>2</sub> CH <sub>2</sub> O
8	BuCHEtCH <sub>2</sub>	Me <sub>3</sub> CCH <sub>2</sub> O
9	BuCHEtCH <sub>2</sub>	AmCHMeCH <sub>2</sub> CH <sub>2</sub> O
10	HexCHMe	Me <sub>3</sub> CCH <sub>2</sub> O
11	HexCHMe	AmCHMeCH <sub>2</sub> CH <sub>2</sub> O
12	AmCHMeCH <sub>2</sub> CH <sub>2</sub>	AmCHMeCH <sub>2</sub> CH <sub>2</sub>

of light, medium and heavy rare earths in HCl solution with ionic strength  $\mu=1$  by addition of NaCl, was mixed with equal volume of organic solution composed of 0.2M extractant in n-dodecane. From the distribution value(D) in extraction under various conditions, equilibrium constant ( $K_{ex}$ ) was deduced based upon the cation exchange mechanism. The separation factor ( $\beta$ ) was estimated as the ratio of equilibrium constants between rare earths.

TABLE 1  
Extraction of Rare Earths

Entry	R <sup>1</sup>	R <sup>2</sup>	pKa	lgK <sub>ex</sub>				$\beta_{Sm/Nd}$	$\beta_{Yb/Y}$
				Nd	Sm	Y	Yb		
1	i-C <sub>9</sub> H <sub>19</sub> O	i-C <sub>9</sub> H <sub>19</sub> O	3.25	1.56	2.23	4.36	5.23	4.68	7.41
2	i-C <sub>9</sub> H <sub>19</sub>	neo-C <sub>5</sub> H <sub>11</sub> O	4.15	-0.55	0.61	2.86	3.75	14.45	7.76
3	i-C <sub>9</sub> H <sub>19</sub>	i-C <sub>8</sub> H <sub>17</sub> O	4.21	-0.99	0.12	2.55	3.61	12.88	11.48
4	i-C <sub>9</sub> H <sub>19</sub>	s-C <sub>8</sub> H <sub>17</sub> O	4.37	-1.46	-0.51	1.89	2.94	8.91	11.22
5	i-C <sub>9</sub> H <sub>19</sub>	i-C <sub>9</sub> H <sub>19</sub> O	4.08	-0.81	0.34	2.75	3.99	14.13	17.38
6	i-C <sub>3</sub> H <sub>7</sub>	neo-C <sub>5</sub> H <sub>11</sub> O	4.37	-0.80	0.86	2.76	3.24	45.71	3.02
7	i-C <sub>3</sub> H <sub>7</sub>	i-C <sub>9</sub> H <sub>19</sub> O	4.36	-0.56	0.61	2.59	3.72	4.79	13.49
8	i-C <sub>8</sub> H <sub>17</sub>	neo-C <sub>5</sub> H <sub>11</sub> O	4.39	-1.19	-0.14	2.21	3.14	11.22	8.51
9	i-C <sub>8</sub> H <sub>17</sub>	i-C <sub>9</sub> H <sub>19</sub> O	4.42	-1.45	-0.40	1.88	2.91	11.48	10.72
10	s-C <sub>8</sub> H <sub>17</sub>	neo-C <sub>5</sub> H <sub>11</sub> O	4.51	-1.24	0.11	2.22	2.71	22.39	3.09
11	s-C <sub>8</sub> H <sub>17</sub>	i-C <sub>9</sub> H <sub>19</sub> O	4.37	-0.92	-0.06	2.30	3.31	7.20	10.23
12	i-C <sub>9</sub> H <sub>19</sub>	i-C <sub>9</sub> H <sub>19</sub>	5.12	-2.20	-1.27	0.93	2.06	8.51	13.49
MANPP	i-C <sub>8</sub> H <sub>17</sub>	i-C <sub>14</sub> H <sub>29</sub> O	4.48	-1.11	0.13	2.29	3.20	17.30	8.20
P507	i-C <sub>8</sub> H <sub>17</sub>	i-C <sub>8</sub> H <sub>17</sub> O	4.50	-1.83	-0.75	1.48	2.58	12.02	12.59

Data in Table 1 show that:

(1) Among mono-alkyl alkylphosphonates studied (Compounds 2-11), they have similar pKa values between 4.08-4.50 but huge differences in Kex value depending on the location of the branched chain. Taking Compounds 4,6,7,8,9,11 as examples the closer the branch chain is, the higher the Kex for Nd. This is consistent with our prediction based on MM calculation.

(2) Introduction of  $\gamma$ -effect on P-C alkyl group increases the  $\beta$  value significantly for heavy rare earths. Compounds 3,4,5 and 12 provide larger  $\beta_{Yb/Y}$  ( $>11$ ) than that of MANPP and P507.

(3) Introduction of  $\gamma$ -effect on ester alkyl group increases the  $\beta$  value markedly for light rare earths. Compounds 2,6 and 10 possess higher  $\beta_{Sm/Nd}$  ( $>14$ ) than that of MANPP and P507.

### MNDO AND MM2(85) CALCULATION METHODS IN STRUCTURE-REACTIVITY STUDIES

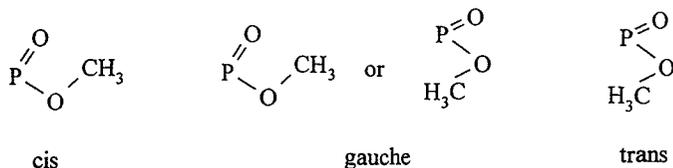
Recently, Rozen(1986) investigated the structure-reactivity relationship of some neutral extractants including phosphorus compounds by MNDO method. However, the conformations of phosphorus compounds they used are not the most stable and the approximations they made usually cause significant errors, which creates difficulties in reflecting the intrinsic relations in quantitative structure-reactivity studies. We used molecular mechanics (MM2) and quantum chemical calculations (MNDO) to investigate the conformation and to evaluate the contribution of structure effect on the extraction of metals by acidic organophosphorus esters.

Although the MNDO method has been used to minimize the molecular structure and to provide the heat of formation for comparison of the stability between various conformations, unfortunately, such method is tremendous in calculations and is therefore time consuming. However, the MM2(85) is used to minimize all possible conformations of the molecule and the optimum conformations as input structures are taken for MNDO calculations. Allinger(1977). Because some empirical calculation parameters in MM2 (85) are not critical, a part of the structure parameters of the molecule were minimized by MNDO method. For acidic organophosphorus esters (1), three bonds [P=O, P-O(H), O-H], three angles [O=P-O(H), O=P-R and O=P-R'] and one dihedral angle O=P-O-H were minimized. For the anions of acidic organophosphorus esters (2), the bonds and angle of O=P=O were minimized. In order to simplify the calculations, the methyl or methoxyl group was chosen as model for the substituents R in each kind of compounds. Li(1992).

#### 1. The most stable conformation of mono-basic organophosphorus esters

According to our calculation model, the dimethyl phosphinic acid (1a) has only one conformation, while for methylphosphonic acid mono-methyl ester (1b) and dimethyl phosphoric acid (1c), several possible conformations are available due to the orientation of the methoxyl group. If the orientation of methoxyl group to phosphoryl oxygen was taken as reference, there are three conformations namely, cis(c)-, gauche(g)- and anti(a)-conformations.

All possible conformations were optimized by MM(85) program. For 1b two stable conformations, cis and anti, were obtained, for 1c three energy minima were given for cis-cis(c,c), cis-anti(c,a) and gauche-anti(g,a) conformations. Then the above energy minima



were recalculated by MNDO method via minimizing a part of structure parameters. The results of MM and MNDO calculations are given in Table 2.

**TABLE 2**  
MM and MNDO calculations of acidic organophosphorus esters  $[R^1R^2P(O)OH]^*$

Compound	R	R <sup>1</sup>	Conform**	$-\Delta H$	$\Delta \Delta H$	Es***	$\Delta Es$
<b>1a</b>	CH <sub>3</sub>	CH <sub>3</sub>	-	96.37	-	-3.33	-
<b>1b-1</b>	CH <sub>3</sub>	CH <sub>3</sub> O	c	145.49	0.0	2.77	0.0
<b>1b-2</b>	CH <sub>3</sub>	CH <sub>3</sub> O	g	142.45	2.94	4.82	2.05
<b>1c-1</b>	CH <sub>3</sub> O	CH <sub>3</sub> O	c, c	195.13	0.0	14.02	0.0
<b>1c-2</b>	CH <sub>3</sub> O	CH <sub>3</sub> O	c, a	194.96	0.17	15.57	1.55
<b>1c-3</b>	CH <sub>3</sub> O	CH <sub>3</sub> O	g, a	192.15	3.02	18.16	4.14

\* Energy unit: kcal/mol.

\*\*Conform is a conformation which is defined by the dihedral angle O=P-O-C, a represents anti; c, cis; g, gauche.

The values of the dihedral angle O=P-O-C for each conformation of these compounds: **1b-1**, -28.6; **1b-2**, 173.8; **1c-1**, 21.9, 22.0; **1c-2**, 4.8, 175.0; **1c-3**, -118.3, 175.7 (in degrees).

\*\*\* Es is steric energy calculated by MM2 (85).

The data in Table 2 show that the relative stability of the conformers calculated by these two methods is in the same order, and  $\Delta \Delta H$  is close to  $\Delta Es$ . The most stable conformations for **1b** and **1c** are the cis conformations (**1b-1** and **1c-1**) in which the methoxyl group is cis to phosphoryl oxygen.

## 2. The structural effect on the charge distribution and frontier orbital parameters of mono-basic organophosphorus esters

The charge distribution and the frontier orbital parameters of mono-basic organophosphorus acid are given in Table 3. The data in Table 3 indicate that the positive charge on phosphorus atom ( $q_P$ ) increases with the increase of the number of alkoxy groups, but the charge density of phosphoryl oxygen ( $q_O$ ) and phospho-hydroxyl oxygen ( $q_{O(OH)}$ ) varies with the number and the conformation of the alkoxy group. Moreover, the conformation gives much larger influence on charge distribution of oxygen atoms than the number of the alkoxy groups. For example, the difference of  $q_O$  between **1a** and **1b-2** ( $q_O$ ) is 0.0173, but the  $q_O$  between **1b-1** and **1b-2** is -0.0308, i.e. the  $q_O$  of **1b-1** is much larger than that of **1a**. If the most stable conformation of each compound is selected for comparison, the electron charge density does not decrease but increases with the increase of the electronegativity of the substituents. This is in contradiction to the general electronic effects of organic molecules. This abnormal phenomenon may be rationalized by the intramolecular inductive effect between polar groups.

On the other hand, the  $q_{O(H)}$  and  $q_{H(O)}$  for the most stable conformations do not change very much with the variation of electronegativity of the substituent. Therefore, the pKa value of these compounds is determined by the difference of heat of formation ( $\Delta \Delta H_{aa}$ ) between acid and its anion of the phosphorus species under investigation.

$$\Delta \Delta H_{aa} = \Delta H_{anion} - \Delta H_{acid}$$

the  $\Delta \Delta H_{aa}$  are correlated well with pKa (see Table 3).

TABLE 3

Charge distribution and frontier orbital parameters of mono-basic organophosphorus esters

Compound	$q_p$	$q_o$	$q_{O(H)}$	$q_{H(O)}$	$E_{HOMO}$	$q_{HOMO}$	$\Delta \Delta H_{aa}$	pKa*
1a	0.8599	-0.6645	-0.4536	0.2204	-10.05	0.7572	-5.96	5.32
1b-1	1.1073	-0.6784	-0.4525	0.2240	-10.67	0.7935	-14.11	4.21
1b-2	1.1137	-0.6472	-0.4883	0.2287	-10.52	0.7935	-	-
1c-1	1.3403	-0.6885	-0.4504	0.2293	-11.36	0.8162	-21.34	3.05
1c-2	1.3493	-0.6580	-0.4802	0.2348	-11.21	0.8093	-	-
1c-3	1.3533	-0.6213	-0.5150	0.2401	-11.09	0.8098	-	-

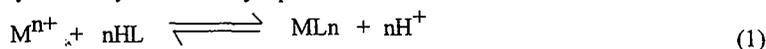
\* pKa values are corresponding to the compound with  $R=C_8H_{17}$ .

\*\*  $\Delta \Delta H_{aa} = \Delta H_{anion} - \Delta H_{acid}$  for the most stable conformation.

In addition, the energy of the HOMO orbital ( $E_{HOMO}$ ) is not influenced by the conformation of alkoxyl groups apparently, but it is dependent on the electronegativity of substituents. Since the orbital coefficient or orbital charge of the HOMO orbital is mainly contributed from the phosphoryl oxygen (Table 3), the pKa values of acidic phosphorus compounds are therefore basically determined by the O-H bond strength, which can be evaluated by  $\Delta \Delta H_{aa}$ . Meanwhile their coordination ability may be governed mainly by orbital properties of phosphoryl oxygen.

### Structural Effect of Organophosphorus Compounds on Metal Extraction

For extraction of metal ions with acidic phosphorus compounds (HL), the extraction equilibrium may be briefly described by equations 1 and 2:



$$K_{ex} = \frac{[ML_n][H^+]^n}{[HL]^n[M^{n+}]} = \frac{K_a^n K_\beta K_{p,ML_n}}{K_{p,HL}^n} \quad (2)$$

where  $K_{ex}$  is the extraction equilibrium constant;  $K_a$ , the dissociation constant;  $K_{p,ML_n}$ , the distribution constant of metal complexes;  $K_{p,HL}$ , the distribution constant of ligand and  $K_\beta$ , the stability constant of complexes.

The  $K_{ex}$  of acidic ligand is, at least, largely influenced by  $K_\beta$  and  $K_a^n$  (or  $npKa$ ). If there is no apparent steric effect, the  $K_{ex}$  decreases with the increase of pKa. However, the increase of pKa, in general, will lead to the increase of HOMO energy ( $E_{HOMO}$ ) which will cause larger

$K_{\beta}$  and therefore favorable to extraction. Subsequently,  $K_{ex}$  or  $\log K_{ex}$  is determined by the relative contribution of  $n pK_a$  and  $K_{\beta}$ . For lanthanides, due to smaller covalent nature and three order dependence of  $K_{ex}$  on  $K_{\beta}$ , the  $K_{ex}$  of lanthanides is mainly governed by  $pK_a$  values of ligands. It has been observed that there exists approximately linear relationship between  $pK_a$  and  $\log K_{ex}$  for lanthanides. The structural effect of acidic ligands on their extraction turns up to be more complicated while steric effect plays a significant role.

**TABLE 4**  
 $\log K_{ex}$  and  $pK_a$  of some acidic phosphorus compounds

Compound*	$pK_a$	$\log K_{ex}, Ce$	$\log K_{ex}, Co^a$	$\log K_{ex}, U$
$(RO)_2P(O)OH$	2.04	0.64	-4.33	3.82
$RP(O)(OR)OH$	2.75	-1.70	-5.55	4.38
$R_2P(O)OH$	3.62	-3.53	-5.85	5.12
$\log K_{ex} / pK_a$	-	-2.54	-0.92	0.81

\* R = n-C<sub>8</sub>H<sub>17</sub>.

a. Yuan, C.-Y., Yuan, S.-G. and Hu, S.-S., Acta Chimica Sinica, 45, 625 (1987).

In the extraction of uranium, the covalent character increases, the contribution of  $K_{\beta}$  to  $K_{ex}$  which is therefore greater than that of  $pK_a$ . Consequently, the  $K_{ex}, U$  increases with increasing  $pK_a$  of the ligands. Some typical examples are given in Table 4.

It can be concluded that for acidic phosphorus compounds without apparent steric effect, the  $K_{ex}$  is mainly determined by  $pK_a$  and  $E_{HOMO}$  of ligands. The relative contribution of  $pK_a$  and  $E_{HOMO}$  is governed chiefly by the nature of the interactions between ligand and metal ions. Then the covalent nature of these interactions is enhanced, the dependence of  $K_{ex}$  on  $pK_a$  is evidently depressed.

#### ACKNOWLEDGEMENT

This project was supported by the State Committee on Science and Technology of China under Programme "Basic Research on Rare Earths".

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## Alkali METALS EXTRACTION by ORGANOANTIMONIC Acid

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### ABSTRACT

P-butyl-phenyl-stibonic (PBPS) acid has been prepared and its chemical properties as a weak acidic extractant of alkali cations have been studied. The PBPS acid shows a high selectivity for lithium, sodium and potassium in the presence of large excess of ammonium hydroxide compared with extracting agents having functional groups of different acidity. Synergistic effects have also been found with 4-nonyl-phenol and a crown ether promising the separation of small amount of alkali metal ions, especially lithium, from a large excess of ammonium salts.

### INTRODUCTION

Antimonic acid as synthetic inorganic ion exchanger exhibits high selectivity for alkali metals, especially sodium ion, compared with other organic cation exchange resins (Abe, 1969; Clearfield, 1982). Its organic derivate the phenyl-stibonic acid is a polymeric substance which depolymerizes in alkali and repolymerizes upon acidification. The phenyl-stibonic acid is insoluble in water, but it dissolves easily in alkali hydroxides and in cold mixture of  $C_2H_5OH/CHCl_3$  and  $C_2H_5OH/C_6H_6$ . For purposes of chemotherapy water-soluble derivates have also been prepared (Gmelin, 1990).

In order to test it as a candidate as a solvent extraction reagent, it is necessary to have a hydrophobic derivate to decrease its solubility. For this reason, p-butyl-phenyl-stibonic (PBPS) acid has been prepared. The chemical properties of the PBPS acid as an acidic extractant of alkali cations in liquid-liquid extraction have been studied.

### EXPERIMENTAL

#### Synthesis of the PBPS acid and identification of the product

The PBPS acid was prepared from 4-butyl-anilin by Bart-Scheller reaction (Doak, Steinmann, 1946).  $CuCl$  was used as a catalyser to decompose the diazonium salt and the evolution of nitrogen required about 48 hours. The crude stibonic acid was purified through its pyridinium salt precipitating from the mixture of hydrochloric acid and methanol (1:1). It was finally hydrolysed with distilled water and after filtration it was dried at room temperature. The yield was 12 %. The product is soluble in benzene, toluene and chloroform.

The IR spectrum of the PBPS acid was recorded in KBr pastille. The spectrum shows an absorption at  $3400\text{ cm}^{-1}$  for the  $OH^-$  group and a cluster at  $2850\text{ cm}^{-1}$ ,  $2925\text{ cm}^{-1}$ ,  $2950\text{ cm}^{-1}$  refers to the butyl group of the PBPS. The Sb content of PBPS was determined with AAS in 10% benzene 90% ethanol medium.  $44\pm 2\%$  antimony content was found, the theoretical value is 40 %.

#### Two phases titration of PBPS acid

30.5 mg ( $1\cdot 10^{-2}\text{ M}$ ) and 61 mg ( $2\cdot 10^{-2}\text{ M}$ ) PBPS was dissolved in  $10\text{ cm}^3$  benzene. Before titration it was washed twice with  $25\text{ cm}^3$  0.01 M HCl and subsequently twice with  $50\text{ cm}^3$  distilled water.

10 cm<sup>3</sup> 1 M NaCl solution was used as an aqueous phase. Phases were contacted (equilibrated) for 3 minutes in separating funnel after addition of 0.1 M NaOH solution in 0.1 cm<sup>3</sup> increments. After separation of the phases the pH of the aqueous phase was measured by combination glass electrode.

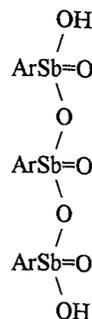
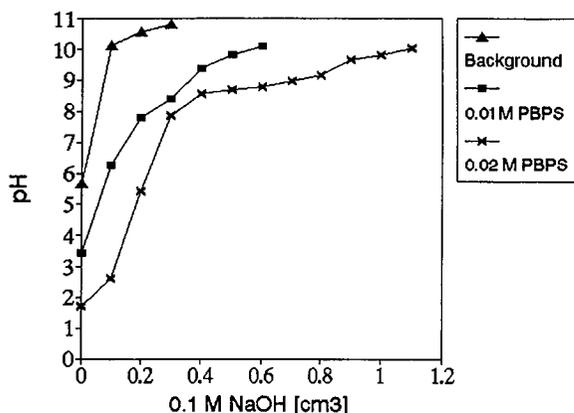
### Alkali metal extraction

Benzene was used in all experiments. In most cases the aqueous phase contained 10<sup>-3</sup> M alkali metal (Li, Na, K) hydroxide. The extraction was performed at room temperature, the shaking (equilibration) time was 3 minutes. The alkali metal concentration was measured by AAS. The organic phase was stripped with 0.01 M HCl and washed with distilled water.

## RESULTS AND DISCUSSION

### Two phases titration and distribution of the PBPS acid

The results of the two phases titration are shown in figure 1. According to the previous investigation of the structure of other arylstibonic acids, they exist in the solid state as trimers too, but dissociate to monomers in alkaline solution (Doak, 1946; Schmidt, 1920).



The structure of arylstibonic acids according to Doak, 1946.

PBPS acid conc., M	0.1 M NaOH expected	consumption, cm <sup>3</sup> found
1*10 <sup>-2</sup>	1.0	0.3
2*10 <sup>-2</sup>	2.0	0.63

Figure 1. Two phases titration of the PBPS acid

According to the data of figure 1. the PBPS acid dissolved in benzene may also exist as a trimer behaving as a weak monobasic acid in the studied pH range; the estimated value of the pK<sub>a</sub> is 8.5-9.

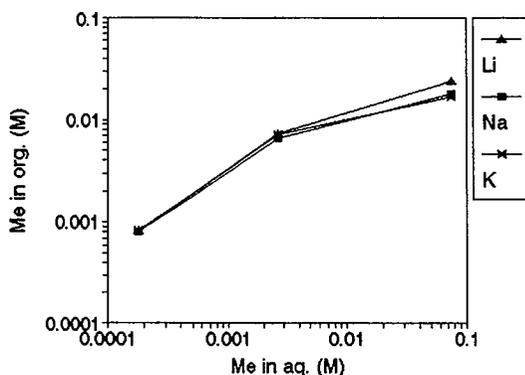
In connection with the two phases titration the distribution of the PBPS acid has been determined by measuring the antimony concentration of the aqueous and organic phases. The results are shown in the Table1.

**TABLE 1**  
Distribution coefficient of the PBPS acid as a function of equilibrium pH

Equilibrium pH	Sb concentration, mg/dm <sup>3</sup>		Distribution coefficient D
	in benzene phase	in aqueous phase	
4.1	5070	0.8	6340
7.6	4480	3.4	1320
11.3	5310	9	590
12.8	4180	12	350

### Alkali metal extraction with PBPS acid

The results of the individual alkali metal extraction with PBPS acid are shown in Figure 2. There is no significant difference between the individual extraction of the three different alkali metals. The efficiency of the extraction increases remarkably with increasing the pH of the aqueous phase.



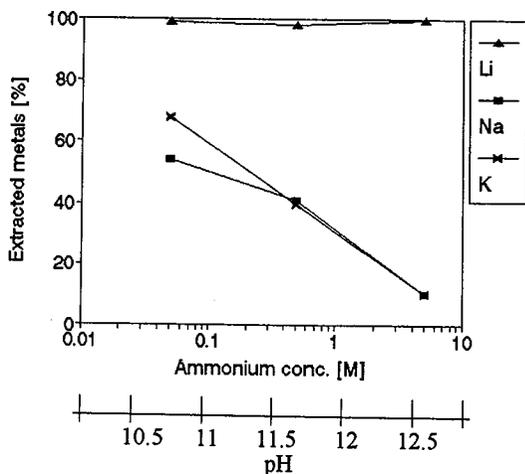
**Figure 2. Alkali metal extraction isotherms**

Organic phase contained  $5 \cdot 10^{-2}$  M PBPS acid in benzene, aqueous phase was  $1 \cdot 10^{-3}$  M,  $1 \cdot 10^{-2}$  M and  $1 \cdot 10^{-1}$  M MeOH.

### Alkali metal extraction in the presence of ammonium ion

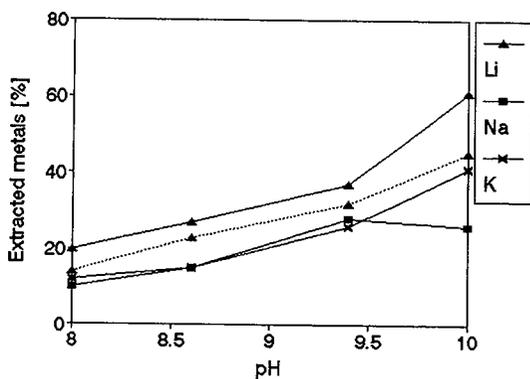
Addition of ammonium hydroxide allows not only the adjustment of the pH of the aqueous phase, but the ammonium ion acts as a competitive cation. According to our measurements the Li extraction from ammonium hydroxide medium is not influenced by the  $\text{NH}_4^+$  concentration, but the extractability of the Na and K is significantly decreased by the ammonium excess (figure 3.).

In order to separate the influence of the pH and the ammonium ion concentration on the alkali metal extraction, the pH dependence was studied at constant ammonium concentration using ammonium hydroxide ammonium chloride buffer solution (figure4.).



**Figure 3. Effect of the ammonium hydroxide concentration on the alkali metal extraction with the PBPS acid**

Aqueous phase:  $1 \cdot 10^{-3}$  M MeOH in ammonium hydroxide medium; organic phase:  $5 \cdot 10^{-2}$  M PBPS acid in benzene

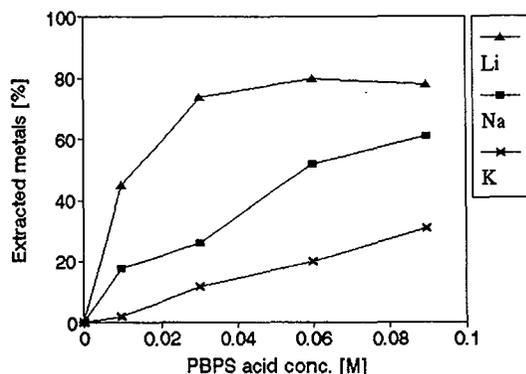


**Figure 4. Alkali metal extraction as function of pH at constant ammonium concentration**

Aqueous phase:  $1 \cdot 10^{-3}$  M MeOH and 10 fold (solid line) or 100 fold (dotted line) ammonium ion excess. The pH was adjusted by changing the proportion of ammonium hydroxide and ammonium chloride. Organic phase:  $1 \cdot 10^{-2}$  M PBPS acid.

Increasing the pH increases the extractability, but the presence of ammonium ion as a competitive cation decreases the efficiency of alkali metal extraction, even in the case of lithium ion. Influence of the anions (e.g. Cl) on the extraction has also been observed. According to figure 5, the extractability sequence in the presence of large excess of ammonium ion is  $Li > Na > K$  in contrast with the inorganic antimononic acid, which can selectively remove the sodium ions from dilute to concentrated

lithium chloride, potassium chloride brines using a hydroxide of the predominant alkali ion or ammonium hydroxide to adjust the pH 11 to 12 (Frianeza-Kullberg, Barnette, 1989).



**Figure 5. Alkali metal extraction as a function of the PBPS acid concentration at pH=10 and constant ammonium concentration (100 fold excess)**

Aqueous phase:  $1 \cdot 10^{-3}$  M MeOH. The pH was adjusted by using ammonium hydroxide ammonium chloride buffer.

#### Comparison of the PBPS acid with some extractants containing functional groups of different acidity

The PBPS acid shows a high selectivity for lithium in ammonium hydroxide medium compared with extracting agents, phase modifiers containing functional group of different acidity (Table 2). These functional groups can behave as cation exchangers, but the PBPS acid shows the highest selectivity for Li.

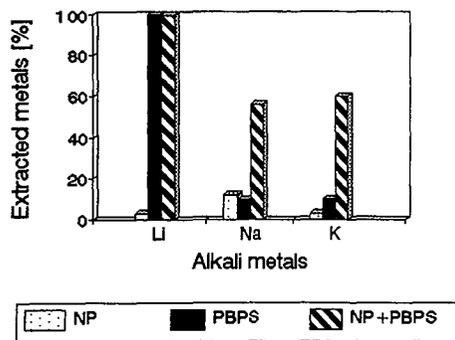
**TABLE 2**

Comparison of PBPS acid with some extractants containing functional groups of different acidity  
Organic phase:  $5 \cdot 10^{-2}$  M extractant in benzene, aqueous phase: 0.5 M  $\text{NH}_4\text{OH}$  and  $1 \cdot 10^{-3}$  M LiOH, equilibrium pH=11.4±0.5. Data in brackets refer to the results of the extraction from 5 M  $\text{NH}_4\text{OH}$  medium.

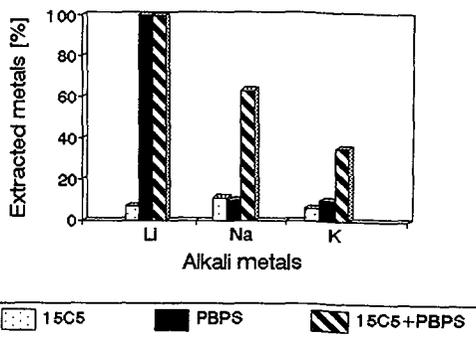
Extractant	pK <sub>a</sub>	Extracted Li, %
Synex DN 052	strongly acidic	86 (71)
D2EHPA	1.7	9
CYANEX 272	6.4	7
Versatic 10 acid	9.7	11
Nonyl-phenol	~10	9
PBPS acid	8.5-9	98 (99)

#### Synergistic extraction with 4-nonyl-phenol and 15-Crown-5

The equimolecular mixture of PBPS acid and 4-nonyl-phenol (NP) exhibits a synergistic effect on the extraction of sodium and potassium ions in presence of large excess of ammonium ions (figure 6.).



**Figure 6. Extraction of alkali metals with NP, PBPS acid and their mixture at pH=12.7**



**Figure 7. Extraction of alkali metals with 15C5, PBPS acid and their mixture at pH=12.7**

Aqueous phase:  $1 \cdot 10^{-3}$  M MeOH and 5M ammonium hydroxide, organic phase:  $5 \cdot 10^{-2}$  M extractant.

The crown ethers as ion pair extractants form stable complexes particularly with alkali and alkaline earth metal ions and the extractability of these complexes is largely governed by the chemical nature of the counter anion (Takeda, 1984). According to the size-selectivity rules of crown ethers, the cavity of the 15-Crown-5 fits the ion diameter of sodium ion. Substantial synergistic effect was observed in the case of the extraction of sodium from 5M ammonium hydroxide medium (figure 7.). The PBPS acid as an organic soluble aqueous insoluble cation exchanger helps to transfer the alkali metal cations to the organic phase meanwhile preserving electrical neutrality, thus avoiding the problem of anion transfer.

### CONCLUSION

The separation of alkali metal impurities from ammonium salts can be a difficult task, if the alkali metal is carried into the salt by a nonvolatile anion (e.g. sulphate etc.) and the usual ways of purification (e.g. crystallization) are not satisfactory. The hydrous antimonite, as a solid ion exchanger has been widely studied and suggested for such problems in the literature (Abe, 1969; Clearfield, 1982). Crown ethers have also been studied as extractants for similar purposes. Testing some typical representatives (Takeda, 1984) we could not observe satisfactory selectivity in the pH range 2-11 in excess of ammonium ions. A simple organic derivative of the antimonite has been prepared and tested as an alkali extractant in the presence of large excess ammonium ions with promising results for future development. Interesting synergism has also been observed with a crown ether and nonyl-phenol.

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## DESIGN OF NOVEL $\beta$ -DIKETONES OF HIGH SELECTIVITY: ROLE OF THE DISTANCE OF THE TWO DONATING OXYGENS

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### ABSTRACT

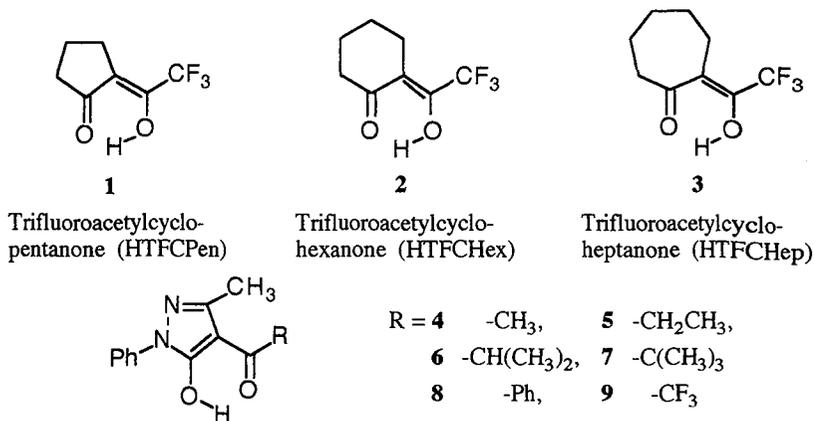
Some  $\beta$ -diketones in which the distance between the two donating oxygens is controlled by structural and steric effects have been synthesized and the role of the O-O distance on the intramolecular hydrogen bond, the acidity and the solvent extraction of metal ions has been investigated.  $^1\text{H-NMR}$  and IR data clearly indicate that the strength of the intramolecular hydrogen bond depends on the O-O distance. The O-O distances were estimated by an *ab initio* and a semi-empirical MNDO/H molecular orbital calculations. The  $\text{pK}_a$  value decreases as the O-O distance increases, that is, as the intramolecular hydrogen bond is weakened. The separation for lanthanides was found to improve as the O-O distance decreases.

The role of the O-O distance on the extractability and separability of Group 3A metals, Al and In, was also examined. Data proved that when the O-O distance is narrowed by modifying the ligand structure, the separation of Al over In is improved significantly. It is known that Al and In can be extracted with  $\beta$ -diketones such as acetylacetone and benzoylacetone. In the meanwhile, In is not extractable with  $\alpha$ -phenylacetylacetone or  $\alpha$ -phenylbenzoylacetone in which the O-O distance is narrowed by the substituent at the  $\alpha$ -position, although Al is readily extracted. It has also been found that the extraction order of Al and In is governed by intracomplex ligand-ligand interaction, which affects remarkably the complexation of Al with  $\beta$ -diketones.

### INTRODUCTION

Individual separation of lanthanides till now has been a hot subject for a lot of papers concerning separation chemistry. Separation of lanthanides using solvent extraction is based on the ability of complexation of each metal with suitable chelating reagent. The results of our recent studies on the solvent extraction of lanthanides using acylpyrazolones (Umetani (1987)) or 3-phenyl-4-benzoyl-5-isoxazolone (Le (1993)) primarily revealed a relation among the distance between two donating oxygens in its structure (O-O distance), the acidity of the ligands and the selectivity for lanthanides. In the present paper, a further study has been conducted to confirm this relation by modelling and working on two types of  $\beta$ -diketones: the cyclic group, 2-trifluoroacetylcyclopentanone (1), -cyclohexanone (2) and -cycloheptanone (3) in which the O-O distance is controlled by ring-structure, and acylpyrazolones, 1-phenyl-3-methyl-4-acetyl- (4), -4-propionyl- (5), 4-isobutyryl- (6) and 4-pivaloyl-5-pyrazolone (7) in which the O-O distance is controlled by the steric effect between 3-methyl and bulky 4-acyl substituents. Structures for these are shown in Figure 1. Molecular orbital calculations were adopted to obtain the optimized structures.

An attempt was made to introduce methyl or bromo group to the  $\alpha$ -position of  $\beta$ -diketones with a view to control the O-O distance. It was found that methyl and bromo group at the  $\alpha$ -position markedly increases the content of the keto form which is not able to complex metal ions. On the contrary, phenyl group at the  $\alpha$ -position increases the content of the enol form. In fact,  $\alpha$ -phenylacetylacetone and  $\alpha$ -phenylbenzoylacetone exist quantitatively as enol form in  $\text{CDCl}_3$  as confirmed by  $^1\text{H-NMR}$ . The extraction of Group 3A metals, Al and In, with several  $\beta$ -diketones has been investigated in the present paper and the extractability and selectivity are evaluated in terms of the role of the O-O distance and the interligand contact.



**Figure 1**  $\beta$ -Diketones with a controlled O-O distance.

### EXPERIMENTAL

Trifluoroacetyl cycloalkanones (Moor (1964)), acylpyrazolones (Jensen (1959)),  $\alpha$ -phenylbenzoylacetone (Levine (1949)), and  $\alpha$ -methylbenzoyltrifluoroacetone (Berkley (1953)) were synthesized according to the literature. Their purities were checked by elemental analysis, <sup>1</sup>H NMR, IR and mass spectrometry.

Molecular orbital calculations were performed on a CRAY Y-MP2E/264 using MNDO93 and Gaussian92. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

Extraction experiments were made in a 30 mL centrifuge tube in a similar manner as described previously (Umetani (1983)). The metal concentration in the aqueous phase was determined by inductively coupled plasma atomic emission spectrometry and that in the organic phase was determined after stripping with hydrochloric acid solution.

### RESULTS AND DISCUSSION

#### Extraction of lanthanides.

The variation of the O-O distance due to the two effects was detected by <sup>1</sup>H-NMR and IR spectrometry, probing the existence and strength of intramolecular hydrogen bond. The distance between the two donating oxygens was estimated by a semi-empirical MNDO/H calculation together with *ab initio* method (RHF/3-21G).

**TABLE 1**  
Structural and spectral data of HTFCPen, HTFCHex and HTFCHeP

	HTFCPen (1)	HTFCHex (2)	HTFCHeP (3)
O-O distance (Å) <sup>a</sup>	2.62	2.52	2.53
O-O distance (Å) <sup>b</sup>	2.55	2.43	2.42
IR (C=O, cm <sup>-1</sup> )	1695	1570	1600
<sup>1</sup> H-NMR (-OH, ppm)	12.9 (vb)	15.05 (s)	15.91 (s)
pK <sub>a</sub> <sup>c</sup>	6.9	8.1	8.8

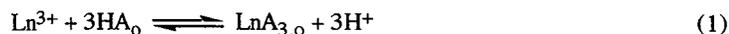
<sup>a</sup> *ab initio* (RHF/3-21G). <sup>b</sup> MNDO/H. <sup>c</sup> approximate values in 30% 1,4-dioxane/water.

**TABLE 2**  
Structural and spectral data of aliphatic substituted acylpyrazolones

-R	-CH <sub>3</sub> (4)	-CH <sub>2</sub> CH <sub>3</sub> (5)	-CH(CH <sub>3</sub> ) <sub>2</sub> (6)	-C(CH <sub>3</sub> ) <sub>3</sub> (7)
O-O (MNDO/H, Å)	2.60	2.56	2.54	2.48
<sup>1</sup> H-NMR (-OH, ppm)	—	—	—	14.9
pK <sub>a</sub>	3.94	4.15	4.18	4.26

Due to the partial decomposition of the reagents, the pK<sub>a</sub>'s of **1**, **2** and **3** were measured quickly by potentiometric titration method in 30% dioxane-water, while those of 4-substituted acylpyrazolones were obtained by the liquid-liquid distribution method.

The extraction equation of lanthanides (Ln<sup>3+</sup>) with acidic reagents (β-diketones, HA) is described as follows:



The validity of equation (1) was confirmed through the effect of pH and concentration of the extractant on the extraction of lanthanides. From this equation, the extraction constant can be deduced:

$$K_{\text{ex}} = [\text{LnA}_3]_o [\text{H}^+]^3 / [\text{Ln}^{3+}] [\text{HA}]_o^3 = D [\text{H}^+]^3 / [\text{HA}]_o^3 \quad (2)$$

$$\log K_{\text{ex}} = \log D - 3\text{pH} - 3\log [\text{HA}]_o \quad (3)$$

D is the distribution ratio defined as [LnA<sub>3</sub>]<sub>o</sub> / [Ln<sup>3+</sup>]. Extraction data are shown in Table 3 and Table 4 for cycloalkanones and acylpyrazolones, respectively.

**TABLE 3**  
Extraction parameters of cycloalkanones for lanthanides

	HTFCPen (1)			HTFCHex (2)			HTFCHeP (3)		
	pH <sub>1/2</sub> <sup>a</sup>	log K <sub>ex</sub>	SF	pH <sub>1/2</sub> <sup>a</sup>	log K <sub>ex</sub>	SF	pH <sub>1/2</sub> <sup>a</sup>	log K <sub>ex</sub>	SF
La <sup>3+</sup>	5.72	-13.26							
Pr <sup>3+</sup>	5.24	-11.80	1.46	(7.06) <sup>b</sup>	-17.27		(7.15) <sup>b</sup>	-17.55	
Eu <sup>3+</sup>	4.90	-10.81	0.99	6.81	-16.52	0.75	6.71	-16.23	1.32
Ho <sup>3+</sup>	4.75	-10.34	0.47	6.55	-15.74	0.78	6.50	-15.60	0.63
Yb <sup>3+</sup>	4.51	-9.62	0.72	6.17	-14.61	1.13	6.16	-14.56	1.04
SF (Yb-Pr)			2.18			2.66			2.99

<sup>a</sup> [HA]<sub>o</sub> = 0.05 M in chloroform. <sup>b</sup> [HA]<sub>o</sub> = 0.158 M in chloroform.

**TABLE 4**  
Extraction parameters of aliphatic substituted acylpyrazolones for lanthanides

	-CH <sub>3</sub> (4)			-CH <sub>2</sub> CH <sub>3</sub> (5)			-CH(CH <sub>3</sub> ) <sub>2</sub> (6)			-C(CH <sub>3</sub> ) <sub>3</sub> (7)		
	pH <sub>1/2</sub> <sup>a</sup>	log K <sub>ex</sub>	SF	pH <sub>1/2</sub> <sup>a</sup>	log K <sub>ex</sub>	SF	pH <sub>1/2</sub> <sup>a</sup>	log K <sub>ex</sub>	SF	pH <sub>1/2</sub> <sup>a</sup>	log K <sub>ex</sub>	SF
La <sup>3+</sup>	5.28	-9.84		5.33	-10.00		5.41	-10.24		6.74	-14.22	
Pr <sup>3+</sup>	4.76	-8.27	1.57	4.83	-8.51	1.49	4.93	-8.80	1.44	6.16	-12.48	1.74
Eu <sup>3+</sup>	4.35	-7.04	1.23	4.40	-7.20	1.31	4.44	-7.34	1.46	5.71	-11.13	1.35
Ho <sup>3+</sup>	4.08	-6.25	0.79	4.15	-6.46	0.74	4.15	-6.47	0.87	5.44	-10.33	0.80
Yb <sup>3+</sup>	3.78	-5.35	0.90	3.86	-5.59	0.87	3.83	-5.50	0.97	5.10	-9.32	1.01
SF (Yb-La)		4.49			4.41			4.74			4.90	

<sup>a</sup> [HA]<sub>0</sub> = 0.01 M in chloroform.

From the data, it can be seen lanthanides are extracted into chloroform much easier by **1** than by **2** and **3**. This fact, reflected in the considerably larger extraction constant (about 10<sup>4</sup> times) of **1**, is due to its strong acidity (pK<sub>a</sub> = 6.9 < 8.1 < 8.8). In the case of acylpyrazolones, although the extraction constant decreases as their acidity decreases from **4** to **7**, the K<sub>ex</sub> values of **7** are notably small compared to those of **4**, **5** and **6**. This could be explained by the strong interaction between 3-methyl and bulky 4-pivaloyl group which causes a great torsion in β-diketone moiety. This can be also observed in a optimized structure of lithium complex with **7** by a MNDO calculation.

The decrease in acidity of the extractants is unambiguously ascribed to the diminution of the O-O distance from **1** to **3** and from **4** to **7**. The smaller the distance is, the stronger the intramolecular hydrogen bond is, resulting in a lower acidity. <sup>1</sup>H-NMR and IR data clearly indicate that the strength of the intramolecular hydrogen bond depends on the O-O distance.

The separability of the extractant for two metals M1 and M2 is evaluated by the separation factor (SF), defined as

$$SF = \log K_{ex,M2} - \log K_{ex,M1} = \log (K_{ex,M2} / K_{ex,M1}) \quad (4)$$

Separation factor data proved that **2** and **3** with the smaller O-O distances separate lanthanides better than **1** (SF<sub>Pr-Yb</sub> = 2.18 < 2.66 < 2.99). This tendency is repetitive for the acylpyrazolone group. As a whole, the separability of the extractant for lanthanides enhances as the O-O distance is reduced.

The obtained results satisfy our prediction quoted above on the role of O-O distance of β-diketone type extractant. It is reasonable to say that there should be a direct and systematical relationship between its O-O distance and acidity, separability, that is, a short O-O distance brings fine SF value for lanthanides while diminishing acidity. A similar result was observed from another class of β-diketone, benzoyltrifluoroacetone (BFA) and its derivative, α-methylbenzoyltrifluoroacetone (MBFA), the O-O distance of which is governed by a steric effect of a substituent at the α-position. Figure 2 shows the plots of SF<sub>La-Yb</sub> vs. O-O distance. Notice that in chloroform, bulky acylpyrazolones provides best selectivity for La and Yb, according to our results so far.

In separation chemistry, choosing suitable ligand (host) is the main requirement for separation of metals (guest). Our results have confirmed the decisive role of the distance between two donating oxygens in the structure of β-diketone on the separation of lanthanides. This may contribute to ligand design process for molecular recognition and applied separation procedure.



The extraction equilibrium and the extraction constant are written similarly as equations (1)-(3), and the results are summarized in Table 5.

A similar reaction was seen for benzoyltrifluoroacetone (BFA) and  $\alpha$ -methylbenzoyltrifluoroacetone (MBFA). In is extracted better than Al with BFA which has bulky terminal groups. The extraction of Al moved slightly to a higher pH region with MBFA as compared to BFA, while a significant shift was seen for In with MBFA whose O-O distance (2.42 Å) is shorter than that of BFA (2.51 Å). Two factors mentioned above are combined in the extraction of Al and In with BFA and MBFA.

**TABLE 5**  
Extraction of Al and In with  $\beta$ -diketones

ligand	O-O <sup>a</sup> (Å)	pK <sub>a</sub> <sup>b</sup>	log K <sub>ex</sub> <sup>c</sup>		pH <sub>1/2</sub> <sup>d</sup>	
			Al	In	Al	In
AA <sup>e</sup>	2.50	12.65	-6.48	-7.20	3.30	3.95
PAA	2.44	12.85	-9.03	N.E.	4.01	N.E.
BA <sup>c</sup>	2.51	12.66	-7.60	-9.30	3.30	4.15
PBA	2.44	12.90	-9.72	N.E.	4.24	N.E.
BFA	2.51	8.10	-6.00	-4.53	3.00	2.51
MBFA	2.42	10.86	-7.41	-11.94	3.47	4.98

<sup>a</sup> Calculated by MNDO/H. <sup>b</sup> in 75 % dioxane water ([NaClO<sub>4</sub>] = 0.1 M).

<sup>c</sup> Extraction into benzene. <sup>d</sup> [HA]<sub>0</sub> = 0.1 M. <sup>e</sup> Stary, J. "The Solvent Extraction of Metal Chelates", Pergamon Press, London, 1964.

## Conclusion

The present paper could reveal the decisive role of the distance between the two donating oxygens in the  $\beta$ -diketone type extractants in the solvent extraction of lanthanides, aluminum and indium. The concept derived from the present paper could be further applicable to the design of organic ligands of high selectivity.

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# MECHANISM OF SYNERGISTIC EXTRACTION OF RARE METALS WITH ORGANOPHOSPHORUS COMPOUNDS

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## ABSTRACT

The synergistic extraction of rare metals, La, Gd and Ga, with mixed extractants of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) and 8-hydroxyquinoline (oxine) or 1,10-phenanthroline (phen) was carried out. An effect of synergism was observed in the extractions of La and Ga. In the La extraction, EHPNA-phen extractant system gave a higher extent of synergistic extraction compared with EHPNA-oxine extractant system. On the other hand, a large synergistic extraction of Ga was observed in the EHPNA-oxine extractant system contrary to that in the former. The extracted species of each metal ion was clarified and the mechanism of the synergistic extraction was elucidated.

## INTRODUCTION

Solvent extraction has been extensively applied to the practical separation of rare metals using acidic organophosphorus extractants. It is well known that this technique requires a large number of stages for the preparation of high-purity products, because the chemical and physical properties among rare metals are very similar to each other. To enhance the separation factor, some new extractants have been developed (Ohto (1993)), and a method of solvent extraction in the presence of a water- or oil-soluble chelating reagent has been proposed (Weaver (1968), Goto (1992)).

Synergistic coefficient (S.C.) is defined as  $D_{12}/(D_1+D_2)$ , where  $D_1$ ,  $D_2$  and  $D_{12}$  denote the distribution ratios of a metal ion between an aqueous and an organic phase containing respective extractant (1), extractant (2) and a mixture of (1) and (2). It is called that a synergistic extraction occurs when  $S.C. > 1$ . When extents of the synergism depend on metals (Kondo (1995)), to utilize the synergistic extraction is considered to be a simple method of separation among rare metals. However, few studies on the mechanism of synergistic extraction of rare metals has been reported (Kondo (1995)).

In the present study, the synergistic extraction of rare metals, La, Gd and Ga, with mixed extractants of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) and 8-hydroxyquinoline (oxine) or 1,10-phenanthroline (phen) was carried out to elucidate the mechanism of the synergistic extraction.

## EXPERIMENTAL

The main extractant and the synergists used are EHPNA and phen or oxine, respectively. EHPNA was supplied by Daihachi Chemical Co. Other organic and inorganic chemicals used were guaranteed reagent grade. First the extraction equilibria of the metals with EHPNA alone were measured at 303K. The organic phase was prepared by dissolving EHPNA in toluene. The aqueous solution was prepared by dissolving the metal chloride in 100 mol/m<sup>3</sup> hydrochloric acid-sodium acetate solution whose pH was adjusted. Then measurements of the synergistic extraction of the rare metals were carried out. The organic phase was prepared by further dissolving phen or oxine in the diluent containing EHPNA. The concentration of metal ion in the aqueous solution was determined by ICP-Atomic Emission Spectroscopy (Shimadzu ICPS 8000).

## RESULTS AND DISCUSSION

### Extraction Equilibria of Metal Ions with EHPNA Alone

Figure 1 shows the effect of pH on the extraction of the metal ions with EHPNA in toluene. The extent of extraction increased with atomic number. Assuming that the metal ion is extracted as a complex of composition,  $MR_{3-x}HR$  into the organic solution with the dimer of EHPNA,  $(HR)_2$ , the extraction equilibrium can be expressed as follows:



The distribution ratio,  $D$ , is given by equation (2)

$$D = C_{M,org}/C_{M,aq} \quad (2)$$

Using the extraction equilibrium constant,  $K_{ex}$ , equation (2) is rewritten as follows:

$$\log(DC_H^3) = \frac{3+x}{2}\log C_{(HR)_2} + \log K_{ex} \quad (3)$$

The experimental results were plotted according to equation (3) as shown in Figure 2. The straight lines were obtained and it was confirmed that a complex of composition,  $MR_{3-x}HR$  assumed was valid. The extraction equilibrium constants,  $K_{ex}$ , and the numbers of solvation,  $x$ , obtained from the intercepts and the slopes of these plots are listed in Table 1.

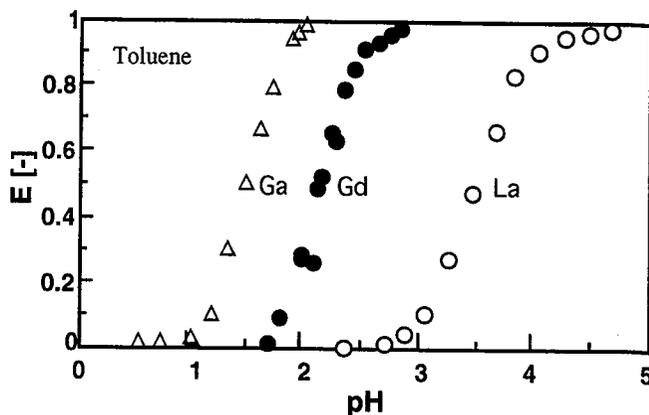


Figure 1 Effect of pH on metal extracted

**TABLE 1**  
Extraction equilibrium constants and solvation numbers

Metal	$K_{ex}$	$x$
La	$8.1 \times 10^{-6}$	4
Gd	0.071	3
Ga	2.81	1

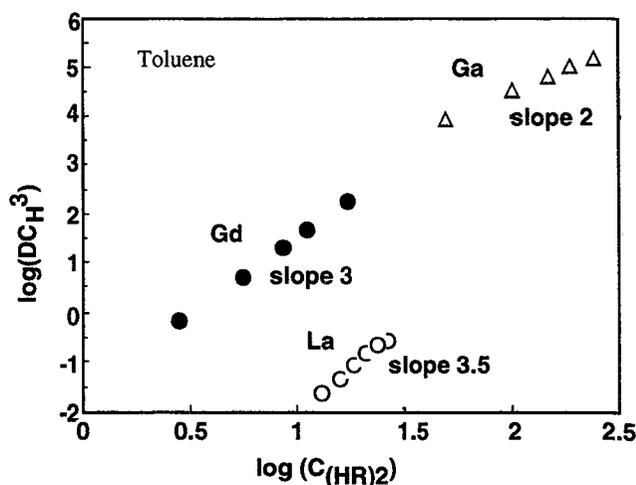


Figure 2 Determination of x values

#### Extraction Equilibria of Metal Ions with Mixed Extractants

The synergistic extractions of La, Gd and Ga were carried out using the EHPNA-oxine or EHPNA-phen extractant system. In the preliminary experiments, it was confirmed that the extraction of the metal ions with the synergist alone is negligibly small. An effect of synergism was observed in the extractions of La and Ga. The occurrence of the synergism for the extraction of the specified metal causes the enhancement of the separation factor, depending on metal separation system. Figures 3 and 4 show the effects of synergist on the extractions of La and Ga, respectively. In these figures, the ordinate shows the ratio of the extent of metal extracted in the synergistic extraction system,  $E$ , to that in the EHPNA extraction system,  $E(O)$ . And the abscissas show the initial concentration of synergist,  $C_{AD}$ . In the La extraction, the EHPNA-phen extractant system gave a higher extent of synergistic extraction compared with the EHPNA-oxine extractant one. On the other hand, the effect of synergist in the Ga extraction was contrary to that in the former. The cause of the difference in the synergistic extraction behavior may be due to the property of the metal and this interesting problem is now under consideration.

Assuming that the metal ion is extracted as a monomer complex of composition,  $MR_3 \cdot xHR \cdot yAD$  ( $AD$ , synergist) with the mixed extractants, the extraction equilibrium can be expressed as follows:



From the slope analysis of the experimental results for the concentration dependencies of the distribution ratio of La on EHPNA and, phen or oxine, it was found that  $x=4$  and  $y=1$  for the La extraction and  $x=1$  and  $y=1$  for the Ga extraction. In this procedure, the concentration of synergist in the organic solution,  $C_{AD,org}$ , was estimated using the values of the distribution ratio of the synergist (Kondo (1995)). From these results, equation (4) is written as follows:

$$\log D = \log C_{(HR)_2}^{\frac{3+x}{2}} C_H^{-3} C_{AD,org}^{-y} + \log K_{ex, syn} \quad (5)$$

The experimental data were arranged according to equation (5) and were plotted in Figure 5, from which the synergistic extraction equilibrium constants,  $K_{ex,syn}$ , were obtained as shown in Table 2. In the high range of D for the La-phen system in Figure 5, the plot was deviated from the slope of unity. We speculate that a formation of adduct-free complex,  $LaR_3 \cdot 4HR$ , is predominant in this range because of the relatively high solubility of phen to the aqueous solution.

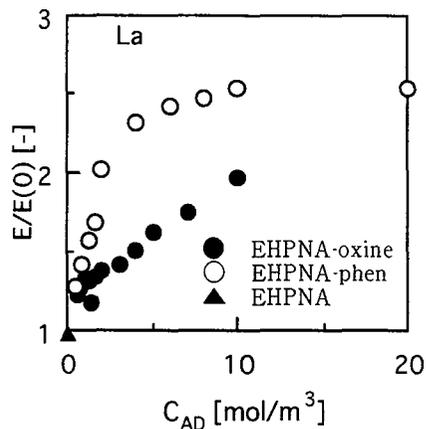


Figure 3 Effect of synergist on extraction of La

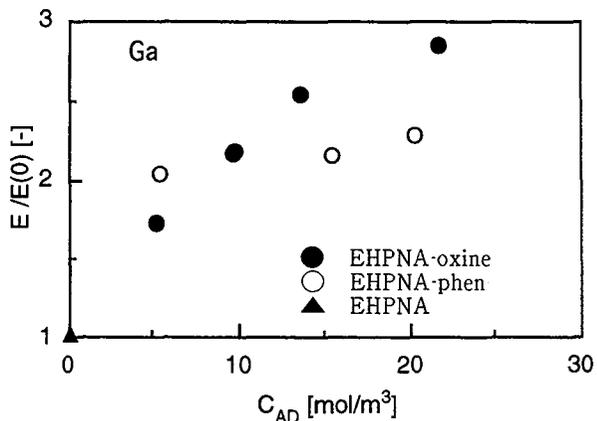


Figure 4 Effect of synergist on extraction of Ga

TABLE 2  
Synergistic extraction equilibrium constants

System	La-phen	La-oxine	Ga-oxine
$K_{ex,syn}$	$2.2 \times 10^{-4}$	$2.4 \times 10^{-6}$	1.6

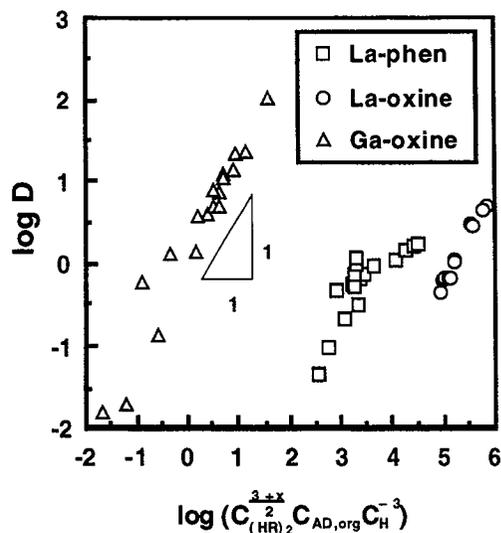


Figure 5 Determination of extraction constants for synergistic extraction

### CONCLUSION

The synergistic extractions of rare metals, La, Gd and Ga with the mixed extractants of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) and 1,10-phenanthroline or 8-hydroxyquinoline were carried out. An effect of synergism was observed in the extractions of La and Ga. The extracted species with EHPNA and the mixed extractant were clarified, and the extraction equilibrium constants were determined.

An occurrence of synergism for the extraction system of a specific metal, which can not be predicted, causes the separation factor to enhance depending on the metal separation system. The separation of the rare metals by the synergistic extraction system was found to be possible.

### ACKNOWLEDGMENTS

The authors wish to express their thanks to Mr. K. Yano for his valuable experimental assistance. We thank Daihachi Chemical Co. for supplying sample of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester.

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## EXTRACTION OF METAL IONS BY MEANS OF POLYDENTATE $\mu$ -IMIDO ORGANOPHOSPHORUS COMPOUNDS

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### ABSTRACT

38 bi- and tridentate  $\mu$ -imido organophosphorus compounds were synthesized and investigated for the study of structure-reactivity relations in solvent extraction of metal ions. These compounds are Brønsted acids, HA. Most of them are able to form neutral chelate complexes  $MA_2$  with metal ions  $M^{z+}$ . Some complexes of rare earth elements (Ln), Co, Ni, Pd, Cu, Zn, and Na were isolated and investigated by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR, IR, and EPR spectroscopy, and characterized by ESCA-technique, X-ray crystal structure analysis, and magnetic measurements. The extraction of the metal ions Mg(II), Ca(II), Sr(II), Ba(II), Ln(III) (Sc, Y, La...Lu), Hf(IV), Fe(II), Co(II), Ni(II), Pd(II), Cu(II), Ag(I), Au(III), Zn(II), Cd(II), Hg(II), Pb(II), and Bi(III) depends not only on the kind of donor atoms (O, S, N), the acidity and dimerization constants of the organophosphorus compound, but in some cases steric effects are dominant.

### INTRODUCTION

Polydentate organophosphorus compounds of the type  $G(G^1)P(X)-NH-Z(Y)G^2$  ( $Z = C, PG^3$ ;  $X, Y = O, S$ ;  $G, G^1 = OR$ ;  $G^2 = OR, NR_2$ ;  $G^3 = OR, OH, NH_2, NH-P(X)(OR)_2$ ;  $R = \text{alkyl, aryl}$ ) containing an acidic  $\mu$ -imido group are rarely used in liquid-liquid extraction of metal ions. Beginning with tetraphenyl  $\mu$ -imido-diphosphate **1a** (Herrmann 1984, 1988, 1990; Navrátil 1983, 1987, 1989, 1990) systematic studies of structure - reactivity relations in solvent extraction of metal ions and the mode of coordination of the metal in the extracted complex were carried out with following 38 compounds:  $(RO)_2P(X)-NH-P(Y)(OR^1)_2$  ( $X, Y = O$ : **1a-e, 1g-h**;  $X = O, Y = S$ : **2a-d**;  $X, Y = S$ : **3a, 3b, 3d-f**,  $R, R^1 = Ph$ : **a**;  $R, R^1 = 2\text{-Me-Ph}$ : **b**;  $R, R^1 = 3\text{-Me-Ph}$ : **c**;  $R, R^1 = 4\text{-Me-Ph}$ : **d**;  $R = 4\text{-Me-Ph}, R^1 = Ph$ : **e**;  $R = Ph, R^1 = 2\text{-Me-Ph}$ : **f**;  $R, R^1 = Oc$ : **g**;  $R, R^1 = Hex$ : **h**),  $(PhO)_2P(O)-NH-P(O)(OPh)OH$  **4**,  $(RO)_2P(O)-NH-P(O)(OR)NH_2$  **5**,  $(RO)_2P(X)-NH-P(X)(OR)-NH-P(X)(OR^1)_2$  ( $X = O$ : **6a, 6c, 6e**;  $X = S$ : **7a**),  $Ph_2P(S)-NH-P(S)Ph_2$  **8**,  $(PhO)_2(S)-NH-C(CH_3)=CH-CN$  **9**,  $(PhO)_2P(S)-NH-C(S)-NR^2R^3$  **10i-u** ( $R^2 = R^3 = Et$ : **i**,  $n\text{-Pr}$ : **k**,  $i\text{-Pr}$ : **l**,  $n\text{-Bu}$ : **m**,  $i\text{-Bu}$ : **n**, *cyc*-Hex: **o**, *Oc*: **p**, *Ph*: **q**;  $R^2 = Me, R^3 = Ph$ : **r**;  $R^2 = H, R^3 = t\text{-Bu}$ : **s**;  $R^2 = H, R^3 = n\text{-Hep}$ : **t**;  $R^2 = H, R^3 = 4\text{ Me-Ph}$ : **u**).

### RESULTS AND DISCUSSION

All the compounds of the types **1 - 10** are Brønsted acids, HA. Some  $pK_a$  values determined by potentiometric titration are presented in Table 1. The acidity of the derivatives **1 - 6** of the  $\mu$ -imido diphosphoric acid increases with rising electronegativity of the substituents. Sulfur donor atoms decrease the acidity.

The tetraaryl compounds crystallize and form dimers via hydrogen bonds as shown by X-ray crystal structure analysis of **1a** (Kulpe 1984), **1b, 2b, 2c, 2d** (Herrmann 1994), and **3a** (Nouaman

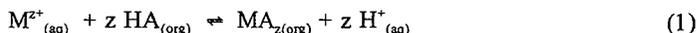
1993). Dimers are also formed in nonpolar diluents. The dimerization constants  $K_{dim}$  and distribution constants  $K_D$  (Distribution of HA between aqueous and organic phases) were determined for some compounds (see Table 1). No dimerization was found for **3a** in benzene.

TABLE 1

Acidity exponents  $pK_a$  in ethylenglycole monomethylether/water (4:1), constants  $K_D$  for distribution of HA between aqueous and organic solvents (<sup>a</sup>benzene, <sup>b</sup>CHCl<sub>3</sub>, <sup>c</sup>CFC-113, <sup>d</sup>CFC-213, <sup>e</sup>CFC-214, <sup>f</sup>CFC-112/benzene 10:1), and dimerization constants  $K_{dim}$  in the organic phase

Com- pound	$pK_a$	$\log K_D$	$\log K_{dim}$	Com- pound	$pK_a$	$K_D(HA)$	$\log K_{dim}$		
<b>1a</b>	2.4	1.1(1) <sup>a</sup>	3.3(5) <sup>a</sup>	<b>2b</b>	3.0				
		2.2(2) <sup>b</sup>	4.0(3) <sup>b</sup>					<b>2c</b>	3.0
		1.0(2) <sup>c</sup>	4.3(3) <sup>c</sup>						
		2.3(2) <sup>d</sup>	3.6(2) <sup>d</sup>						
		1.7(1) <sup>e</sup>	4.0(3) <sup>e</sup>						
2.1(3) <sup>f</sup>	4.3(3) <sup>f</sup>	<b>3a</b>	3.2	4.8(2) <sup>a</sup>	no dim.				
<b>3e</b>	3.4								
<b>1b</b>	2.7	1.7(2) <sup>a</sup>	4.6(5) <sup>a</sup>	<b>4</b>	2.2, 10.8	0.3(1) <sup>a</sup>			
<b>1d</b>	2.8	3.1(1) <sup>a</sup>	2.8(5) <sup>a</sup>	<b>5</b>	4.4	2.0(1) <sup>a</sup>			
		2.7(1) <sup>f</sup>				1.5(2) <sup>b</sup>			
<b>1e</b>	2.6			<b>6e</b>	2.4, 9.4				
<b>2a</b>	2.8	4.6(2) <sup>a</sup>	2.2(3) <sup>a</sup>	<b>9</b>	9.9				

Most of the compounds **1-10** are able to form neutral chelate complexes according to equation (1) by extraction of metal ions from aqueous solution.



Some complexes of rare earth elements (Ln), Co, Ni, Pd, Cu, Zn, and Na were isolated and investigated by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR, IR, and EPR spectroscopy, ESCA-techniques and characterized by X-ray crystal structure analysis, and magnetic measurements. The mode of coordination depends on the set of donor atoms and on the kind of metal ion. Yb<sup>3+</sup> is surrounded by six oxygen atoms in form of a slightly distorted octahedron in the complex with **1a** (Kulpe 1981). Pd<sup>2+</sup>, and Ni<sup>2+</sup> are coordinated via 4 sulfur atoms in a square planar complex with **3a** (Nouaman 1993), and **10k** (Navrátil 1989; Žák 1990). Six-membered chelate rings are formed in both complexes. The reaction of Pd<sup>2+</sup> with **2a** also yields a square planar complex. However the coordination of the metal ion occurs via sulfur and nitrogen atoms, and four-membered chelate rings are observed (Žák 1989). A three-nuclear copper(I) complex is yielded in the reaction of **10** with copper(II) (Richter 1995). The sodium complex with **1a** is six-nuclear both in the crystal and in benzene (Bock 1995).

By means of NMR spectroscopy it is possible to study complexes in solution as well as the interaction of the extractant, and metal complexes with different diluents. The determination of equilibrium constants leads e.g. to the value  $8.3(1) \times 10^2$  L/mol for the reaction of the dimer of **1a** with trioctylphosphine oxide (TOPO) in benzene yielding HA•TOPO. Paramagnetic ions have a

significant influence on chemical shifts. Individual signals between +37 ppm ( $\text{NdA}_3$ ) and 135 ppm ( $\text{ErA}_3$ ) are observed in  $^{31}\text{P}$  NMR spectra for every  $\text{Ln(III)}$  complex with **1a**. It is even possible to distinguish between  $\text{Ce(III)}$  (+9 ppm) and  $\text{Ce(IV)}$  (-7 ppm) in solution. The rate of exchange of  $\text{A}^-$  between  $\text{LnA}_3$  and  $\text{HA}$  (**1a**) depends on the size of the metal ion as well as on the diluent. By NMR technique in solution (0.10 M  $\text{HA}$ , 0.03 M  $\text{LnA}_3$ ) the following  $\log(1/\tau \times \text{sec})$  values were obtained at 292 K:  $\text{LaA}_3/\text{HA}$  in toluene 3.6;  $\text{LuA}_3/\text{HA}$  in toluene 2.8;  $\text{LaA}_3/\text{HA}$  in acetone 2.0;  $\text{LuA}_3/\text{HA}$  in acetone 1.8. The rotation barrier along C-N bond increases in compounds of the type **10** by complex formation.

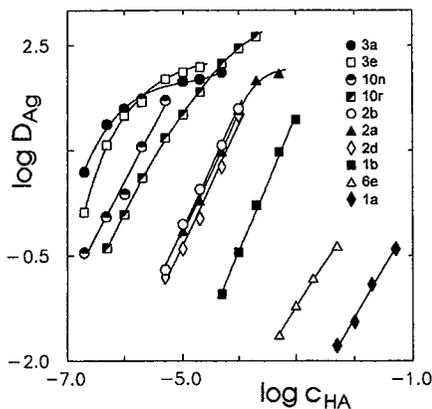


Figure 1. Log D of silver at 1.0 M  $\text{HNO}_3$  vs. logarithm of initial extractant molarity in benzene ( $c_{\text{Ag}} = 6 \times 10^{-8}$  M).

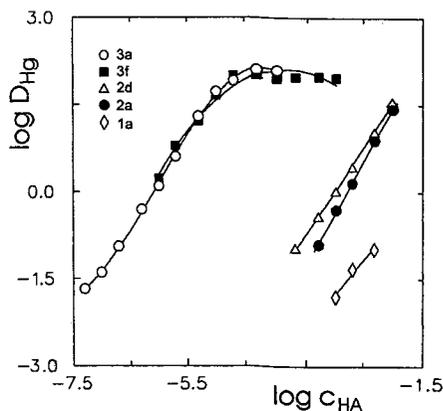


Figure 2. Log D of mercury at 0.5 M  $\text{HCl}$  vs. logarithm of initial extractant molarity in benzene ( $c_{\text{Hg}} = 2.3 \times 10^{-7}$  M).

The slope analysis of the dependence of distribution ratios  $D$  of  $\text{Ln(III)}$ ,  $\text{Hf(IV)}$ ,  $\text{Fe(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Pd(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Au(III)}$ ,  $\text{Zn(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Hg(II)}$ ,  $\text{Pb(II)}$ , and  $\text{Bi(III)}$  on the concentration of  $\text{HA}$  in the organic phase, and mineral acid in the aqueous phase shows that complexes  $\text{MA}_2$  are formed in most cases in the organic phase. An additional solvation of  $\text{MA}_2$  in the extracted complex by  $\text{HA}$  is observed for silver. It forms  $\text{AgA(HA)}$ . Figure 1 shows the extraction of silver ions with extractants of types **1**, **2**, **3**, **6**, and **10**. Silver is quantitatively extracted ( $\log D > 4$ ) from 1.0 M  $\text{HNO}_3$  with **8**, even if the concentration of  $\text{HA}$  in the organic phase is only  $10^{-7}$  M. According to the HSAB concept of Pearson the strength of the extractants for silver increases with the set of donor atoms  $\text{OO} < \text{OS} < \text{SS}$ . Distribution ratios decrease in the sequence of extractants: **8** > **3a** > **3e** > **10n** > **10r** > **2b** > **2a** > **2d** > **1b** > **6e** > **1a**. Silver is extracted very selectively by compounds of type **3**, **8**, and **10**. Unexpected, higher  $D$  values are observed with ortho-tolyl esters than with meta- and para-tolyl or phenyl esters.

A similar influence of the set of donor atoms is found in the extraction of mercury. The distribution ratios are more than 4 orders of magnitude higher with compounds of type **3** (SS) than with compounds of type **2** under given conditions (Figure 2).

A remarkable lower dependence on the kind of extractant is observed with zinc(II) which is situated on the borderline between hard and soft metal ions. As shown in Figure 3 in most cases

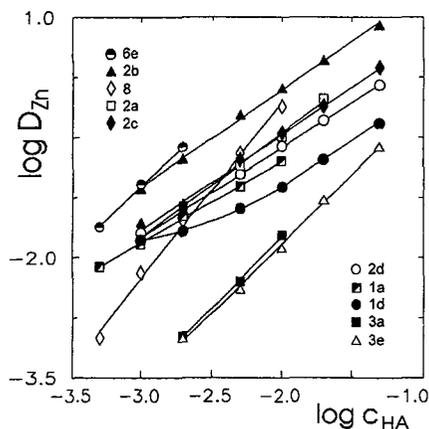


Figure 3. Extraction of zinc from 0.01 M HCl in dependence on the initial concentration of HA in benzene ( $c_{Zn} = 5 \times 10^{-6}$  M).

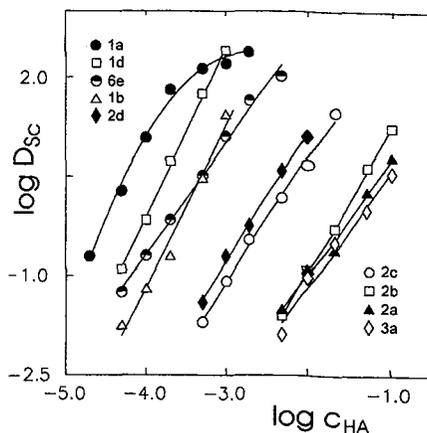


Figure 4. Log D of scandium at 0.1 M HCl vs. logarithm of initial extractant molarity in benzene ( $c_{Sc} = 6.3 \times 10^{-8}$  M).

D values decrease with the set of donor atoms OS > OO > SS. An effective extractant is 6e with three oxygen donor atoms. This is a hint to the formation of a sixfold coordinated zinc atom in the complex  $ZnA_2$ , of 6e. The slopes of the curves for the compounds 3a, 3e, and 8 are steeper than those for the compounds of the type 1 or 2, due to the fact that only the last compounds dimerize in benzene.

The curves for the extraction of Sc and Ce are shown in Figure 4, and Figure 5, respectively. Complexes of the composition  $LnA_3$  are formed only. As expected, the extraction ability for these typical hard metal ions decreases with increasing number of sulfur donor atoms in the compound HA. Due to the stronger acidity higher D values are obtained with the phenyl ester 1a than with the tolyl esters 1b, 1c, and 1d.

However the extraction of metal ions depends not only on the kind of donor atoms, and the acidity and dimerization constant of the organophosphorus compound, respectively. In some cases steric effects are dominant. The steric hindrance caused by the methyl group in the ortho position in 1b effects for Sc a remarkable decrease of distribution ratios. Due to steric effects, the sequences of distribution ratios of Ln ions are different e.g. for 1, and 6. Whereas D rises with decreasing radius of the lanthanoid ion from

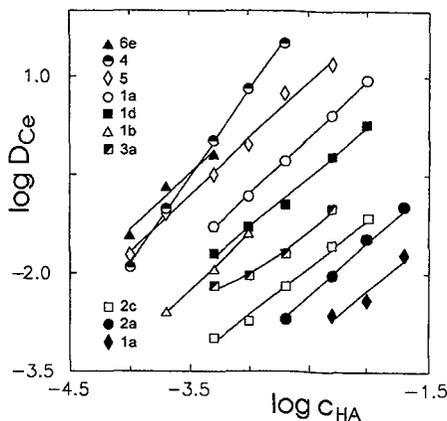


Figure 5. Log D of cerium at 0.1 M HCl vs. logarithm of initial extractant molarity in benzene ( $c_{Ce} = 1 \times 10^{-10}$  M).

lanthanum to lutetium using e.g. **1a**,  $D$  increases from Ce to Eu, and then it drops in the row of lanthanoids with **6e** as extractant, so that  $D_{Tm} < D_{Ce}$ . Sc is extracted about two orders of magnitude better by the bidentate **1a** than by the potential tridentate **6e**. For Tm no significant difference exists between these two extractants. Eu and Ce are extracted much better by **6e** than by **1a**. It is possible to understand this behaviour taking into account the ionic radius of the given metal atom. The extreme small scandium ion and also the thulium ion are not able to coordinate all the nine oxygen donor atoms of three ions of **6e**, whereas the bigger ions of europium and cerium are able to do this.

Distribution ratios of rare earth ions drop as well as separation factors in the sequence **1a** > **1g** > **1h** (Figure 6).

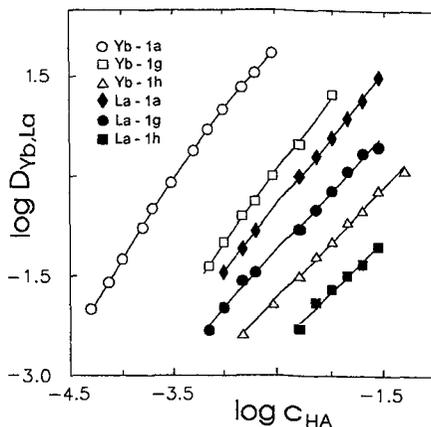


Figure 6. Log  $D$  of Yb and La at 0.1 M  $HClO_4$  vs. logarithm of initial extractant molarity in benzene

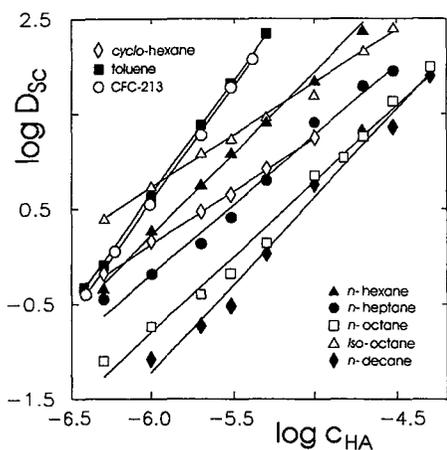


Figure 7. Log  $D$  of scandium at 0.1 M  $HNO_3$  vs. logarithm of initial molarity of **1a** in different diluents ( $c_{Sc} = 1.8 \times 10^{-7}$  M).

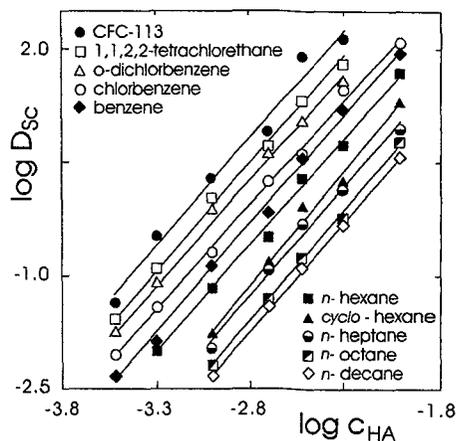


Figure 8. Log  $D$  of scandium at 0.1 M  $HNO_3$  vs. logarithm of initial molarity of **10h** in different diluents ( $c_{Sc} = 1.8 \times 10^{-7}$  M).

A very high influence of the kind of diluent has been observed in the extraction of rare earth ions e.g. with **1a** or **10a**. The highest distribution ratios are observed using chlorofluorocarbon diluents as shown in Figure 7 and Figure 8. Distribution ratios of scandium increase remarkably with decreasing number of carbon atoms in the chain of *n*-alkane diluents. They are about two orders of magnitude higher in *iso*-octane than in *n*-octane. The influence of the diluent decreases

somewhat with rising radius of the rare earth ion. So the difference between  $\log K_{ex}$  values changed from 2.6 for Sc, 2.3 for Tm to 2.2 for Eu, measured with solutions of **10a** in CFC-113 and *n*-decane, respectively.

### CONCLUSIONS

The results of this paper have shown, that the extraction behaviour of an organophosphorus compound depends on many factors. Not all of them are understood very well and it needs further investigation.

### ACKNOWLEDGEMENTS

The authors thank the FONDS DER CHEMISCHEN INDUSTRIE, the KONFERENZ DER DEUTSCHEN AKADEMIEN DER WISSENSCHAFTEN, and the BUNDESMINISTERIUM FÜR BILDUNG, WISSENSCHAFT, FORSCHUNG UND TECHNOLOGIE for financial support.

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## EQUILIBRIA AND EFFECT OF DILUENT IN THE SOLVENT EXTRACTION OF LITHIUM SALTS BY HIGHLY ALKYLATED 14-CROWN-4 ETHERS

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### ABSTRACT

As shown by survey experiments, 14-crown-4 ethers bearing certain aliphatic substituents exhibit strong selectivity for lithium. Both selectivity and overall extraction efficiency depend markedly on the type of ring substituents and on the diluent properties. To understand such effects in greater detail, extraction of LiCl by the crown ether 2,2,3,3,6,9,9,10,10-nonamethyl-14-crown-4 (NM14C4) was subjected to equilibrium analysis. By use of the program SXLSQL (a solvent-extraction modeling program), the extraction behavior as determined by ion chromatography has been modeled quantitatively in terms of four equilibria in 1-octanol. The following neutral and ionic organic-phase species have been considered: LiCl, Li<sup>+</sup>, Cl<sup>-</sup>, LiCECl, and LiCE<sup>+</sup> (CE = crown ether). Parallel measurements of the same system by <sup>7</sup>Li NMR techniques agree with the ion-chromatography results. The NMR experiment affords the advantage of distinguishing between free and bound lithium and thus provides a check on the species indicated by the modeling. Extraction of LiCl by NM14C4 correlates with diluent properties, including the Shmidt-Marcus diluent parameter and Reichardt's *E<sub>T</sub>* parameter; as diluent polarity increases, LiCl extraction increases steeply.

### INTRODUCTION

The nature of the diluent strongly influences the strength of extraction of metal salts by crown ethers. Thus, the role of solvation and its relationship with speciation must be understood to establish a foundation for designing improved crown ethers for ion recognition. We have reported that certain highly alkylated members of the 14-crown-4 family of crown ethers (Figure 1) extract lithium salts with high selectivity in liquid-liquid extraction systems (Sachleben, (1993)). A striking dependence of the extraction efficiency and selectivity on the nature of the aliphatic substituents has led us to examine in more detail the role of solvation and speciation in these systems. 2,2,3,3,6,9,9,10,10-Nonamethyl-14-crown-4 ether (NM14C4) was selected as a representative 14-crown-4 ether for in-depth equilibrium modeling and characterization of the effect of diluent properties on extraction behavior.

### EXPERIMENTAL SECTION

In all extraction experiments, equal volumes of aqueous and organic phases were placed in vials, which were subsequently mounted on a vertical disk and rotated at ca. 40 rpm for at least two hours at 25 ± 1 °C. Good phase separation was ensured by centrifugation at 3000 rpm for 5 minutes. Aliquots of the organic phase were then stripped by a 10-fold excess of deionized water and analyzed by ion chromatography. The small volume changes caused by water solubilization in 1-octanol were taken into account in data manipulation; volume changes in the other diluents were neglected.

The concentration of lithium in the organic phase employing 1-octanol as the diluent was also determined by <sup>7</sup>Li NMR. The NMR spectra were obtained on a Bruker MSL-400 NMR

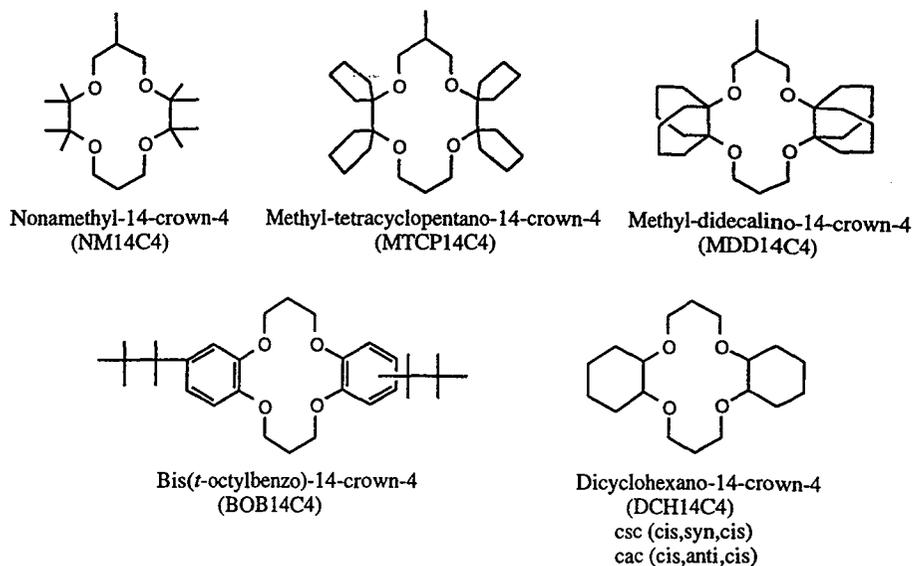


Figure 1. Structures and abbreviations of substituted 14-crown-4 ethers.

spectrometer operating at 155.503 MHz. Due to the slow exchange rate of free and complexed lithium species, two corresponding lithium peaks were observed. Concentrations were determined from integrated peak areas relative to an external standard; relaxation delays were in excess of  $5T_1$  in all cases.

The extraction data from ion-chromatography analyses were fitted with the solvent-extraction modeling program SXLSQI, which is a version of SXLSQA (Baes, (1988); Baes, (1990)) capable of handling ionic species in the organic phase. SXLSQI calculates ionic activity coefficients using either an extended form of the Debye-Hückel equation for the organic phase or the Pitzer equations for the aqueous phase; the activity coefficients of neutral species are calculated by the Hildebrand-Scott treatment, though they are close to unity here because of the low organic-phase solute concentrations.

## RESULTS AND DISCUSSION

Although metal salts exist predominantly as ion pairs in low-polarity organic solvents, ion-pair dissociation becomes increasingly important as the dielectric constant increases. Taking the salt extraction by the diluent alone into account, the applicable system of equilibria for the extraction of LiCl by crown ether (CE) can be expressed as equations 1-4:

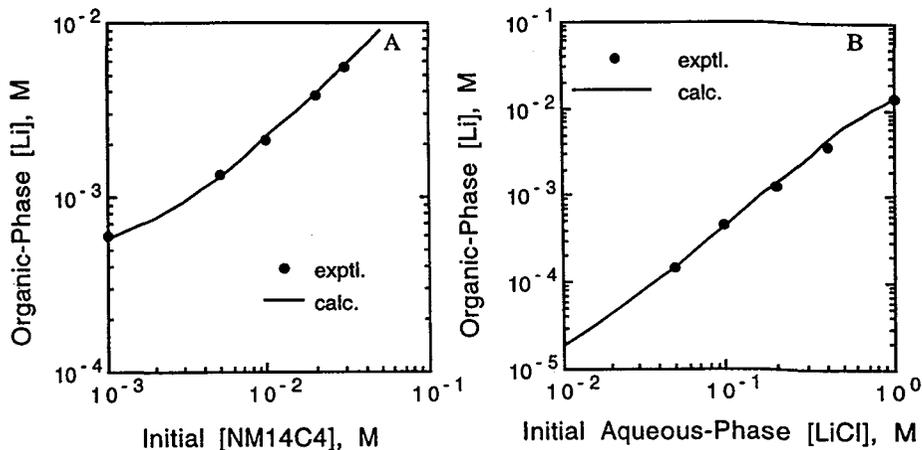


Figure 2. The dependence of organic-phase lithium concentration on crown-ether concentrations at 0.4 M LiCl (A) and on aqueous LiCl concentration at 0.02 M crown ether (B) for LiCl extraction with nonamethyl-14-crown-4 into 1-octanol. Symbols represent data as obtained by ion-chromatographic analysis. Solid lines were calculated from the model (equations 1-4), where  $\log K_{dij} = -2.74 \pm 0.03$ ,  $\log K_{dij\pm} = -6.85 \pm 0.08$ ,  $\log K_{ex} = 0.20 \pm 0.02$ ,  $\log K_{ex\pm} = -3.53 \pm 0.02$ .

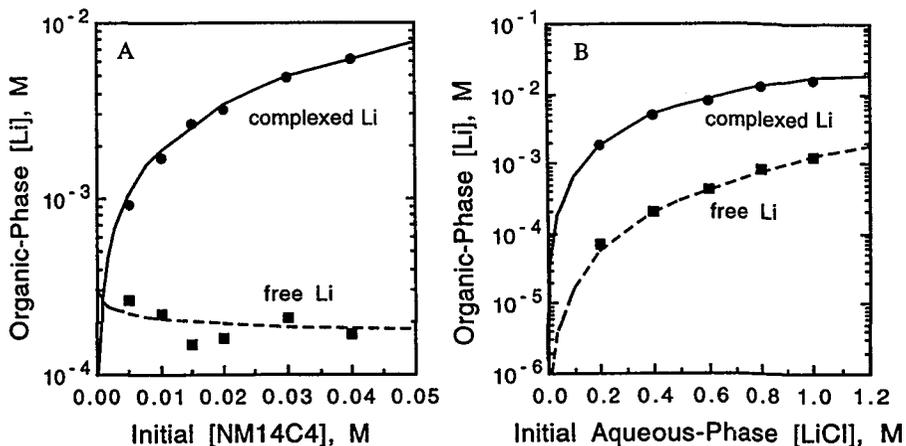


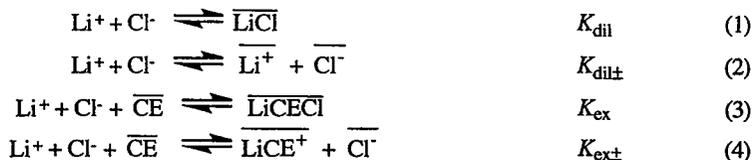
Figure 3. NMR-measured free and complexed lithium concentrations (symbols) compared with the SXLSQI model; the  $\log K$  values used in the model were those determined from the ion-chromatography data (Figure 2). (A): [LiCl] = 0.4 M; (B): [NM14C4] = 0.03 M.

TABLE 1

Simultaneous extraction of alkali metal chlorides or nitrates with 14-crown-4 ethers in 1-octanol at 1:1 volume ratio. [CE] = 20 mM, [Li<sup>+</sup>] = [Na<sup>+</sup>] = [K<sup>+</sup>] = [Rb<sup>+</sup>] = [Cs<sup>+</sup>] = 0.4 M; 25 °C. \*

Crown Ethers	Anions	logD					Li loading %
		Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	
none	Cl <sup>-</sup>	-2.51	-3.07	-3.25	-3.18	-3.11	
	NO <sub>3</sub> <sup>-</sup>	-2.35	-2.92	-3.14	-3.14	-3.04	
BOB14C4	Cl <sup>-</sup>	-2.38	-2.99	-3.16	-3.12	-3.07	1.7
	NO <sub>3</sub> <sup>-</sup>	-2.19	-2.82	-3.07	-3.07	-3.02	3.0
cacDCH14C4	Cl <sup>-</sup>	-2.46	-3.06	-3.25	-3.22	-3.13	0.6
	NO <sub>3</sub> <sup>-</sup>	-2.28	-2.95	-3.18	-3.16	-3.08	1.5
cscDCH14C4	Cl <sup>-</sup>	-1.79	-2.95	-3.22	-3.18	-3.11	21
	NO <sub>3</sub> <sup>-</sup>	-1.57	-2.74	-3.15	-3.13	-3.06	37
MDD14C4	Cl <sup>-</sup>	-1.25	-2.78	-3.22	-3.16	-3.08	87
	NO <sub>3</sub> <sup>-</sup>	-1.21	-2.67	-3.15	-3.11	-3.04	93
MTCP14C4	Cl <sup>-</sup>	-2.42	-3.01	-3.26	-3.20	-3.12	1.0
	NO <sub>3</sub> <sup>-</sup>	-2.31	-2.92	-3.16	-3.15	-3.08	0.9
NM14C4	Cl <sup>-</sup>	-1.53	-2.91	-3.20	-3.12	-3.05	44
	NO <sub>3</sub> <sup>-</sup>	-1.40	-2.73	-3.10	-3.06	-3.01	59

\*  $D = [Li]_{org}/[Li]_{aq}$ , where  $[Li]_{org}$  and  $[Li]_{aq}$  are respectively the analytical lithium concentrations in the organic and aqueous phases at equilibrium. Loading =  $100\% \times ([Li]_{org} - [Li]_{dil})/[CE]_{total}$ ; where  $[Li]_{dil}$  is the concentration of Li extracted by 1-octanol alone. Since  $[Li]_{dil}$  depends slightly on  $[Li]_{org}$  (see below), the loading expression only approximately represents the degree of saturation of the crown ether.



Overbars indicate species in the organic phase.

14-Crown-4 ethers are generally good lithium extractants, but their efficiency and selectivity can be greatly modified by varying the ring substituents. As shown by Table 1, substituted 14-crown-4 ethers in 1-octanol extract lithium selectively from an aqueous solution containing sodium and other alkali metals. Among the six 14-crown-4 ethers investigated, MDD14C4 and NM14C4 have the highest lithium extraction efficiency and selectivity. Isomers MDD14C4 and MTCP14C4 differ markedly in lithium extraction ability, as do the isomers cacDCH14C4 and cscDCH14C4. The tested crown ethers in general extract sodium and the other alkali metal ions weakly, with little increase over the background extraction by 1-octanol alone. In all cases, the observed order is  $Li^+ > Na^+ > K^+, Rb^+, Cs^+$ . Further, nitrate promotes extraction better than chloride, which follows from nitrate's larger size and lower Gibbs energy of transfer from water to various diluents (Marcus, (1988)).

To understand the underlying extraction equilibria more clearly, we have conducted a series of LiCl extraction studies involving NM14C4 in 1-octanol (analysis by ion chromatography). In this case, the usual treatment of ion-pair extraction according to equation 3 did not yield satisfactory results, and nonideality could not explain the systematic deviations. Consideration of ion-pair dissociation (equation 4), however, greatly improved the fitting. Since 1-octanol is known to extract metal salts by itself (Westall, (1990)), equations 1 and 2 were also taken into account. Refinement of  $\log K$  values corresponding to the four equilibria by SXLSQI gave excellent agreement between the calculated and experimental results (Figure 2). Speciation calculations based on the obtained equilibrium constants show that dissociated ions can be the dominant species in 1-octanol (and similar polar diluents) at low organic-phase electrolyte concentrations.

Direct  $^7\text{Li}$  NMR measurements were carried out to test the speciation model given by equations 1-4 in the extraction of LiCl by NM14C4 in 1-octanol. The  $^7\text{Li}$  NMR experiments show clearly the presence of free and complexed lithium species in 1-octanol, although NMR in this case does not distinguish ions from ion pairs. As shown in Figure 3, the organic-phase concentrations of free

lithium ( $[\text{Li}^+] + [\text{LiCl}]$ ) and complexed lithium ( $[\text{LiCE}^+] + [\text{LiCECl}]$ ) determined by NMR are well represented by the SXLSQI model based solely on the ion-chromatography data. It may also be noted that the NMR results (Figure 3A) indicate a slight downward trend in the free lithium concentration as a function of the crown-ether concentration. This effective suppression of the extraction of free lithium by the 1-octanol diluent arises in the model as a consequence of the common-ion effect (equations 2 and 4); that is, the increasing extraction of LiCl by NM14C4 increases the concentration of dissociated  $\text{Cl}^-$  anions in the organic phase, thereby driving equation 2 to the left.

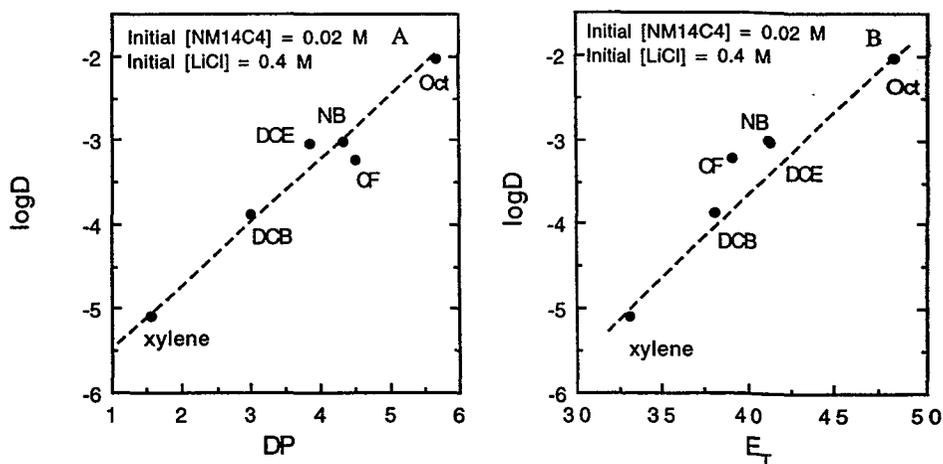


Figure 4. The dependence of LiCl distribution ratios on the Schmidt-Marcus diluent parameter (DP) (A) and Reichardt  $E_T$  value (B). Key: DCE = 1,2-dichloroethane, DCB = 1,2-dichlorobenzene, NB = nitrobenzene, Oct = 1-octanol, CF = chloroform.

The extraction of LiCl by NM14C4 increases steeply as the polarity of the diluent increases. Diluent polarity may be represented by the Schmidt-Marcus diluent parameter (DP) (Schmidt, (1978); Marcus, (1989)) or Reichardt's  $E_T$  value (Dimroth, (1963); Reichardt, (1990)). Distribution ratios ( $D$ ) for

LiCl extraction by NM14C4 into six different diluents are shown in Figure 4, as a function of either DP or  $E_T$ . Only for 1-octanol is extraction by the diluent important (equations 1 and 2). It may be expected that little or no ion-pair dissociation occurs in 1,2-xylene or chloroform, but ion-pair dissociation is important for nitrobenzene and, to a lesser extent, for 1,2-dichloroethane. It may be seen that the extraction strength as given by  $\log D$  increases with either of the indices of diluent polarity. Dielectric constant gives a poor correlation, whereas  $\log D$  correlates nearly linearly with DP or  $E_T$ .

### CONCLUSIONS

Compared with other crown ethers, some members of the 14-crown-4 ether family extract lithium salts efficiently and selectively. The extraction strength depends upon the type of ring substitution and diluent properties. Modeling of LiCl extraction data for the case of NM14C4 supports extraction via equations 1-4. In polar diluents, dissociation of ion pairs must be considered as well as the extraction by the diluents alone. NMR experiments support the speciation model and directly prove the existence of free and complexed lithium species in 1-octanol. Extraction data correlate well with established diluent parameters. It is to be expected that the understanding developed in these studies will support the design of more effective lithium extraction systems, which could find use (adding value) in process or analytical applications.

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### ACKNOWLEDGMENTS

This research was funded by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Lockheed Martin Energy Systems. We thank Donald A. Palmer for assistance with ion chromatography.



## CALIXARENE TYPE EXTRACTANTS FOR METAL IONS WITH IMPROVED PROPERTIES

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### ABSTRACT

The extractability of several transition and heavy metal ions was tested by using a calix[4]arene carrying carboxylic acid groups. The distribution factors of lanthanides increase by about 20 and the extracted complexes with lanthanide ions have a 1:1 stoichiometry when the calixarene carries octadecyl groups rather than *t*-butyl groups at the upper rim. Kinetic data on diffusion coefficients and the mass flow of uranyl complexes are given.

### INTRODUCTION

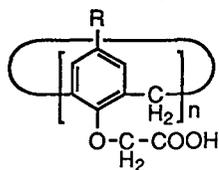
From the variety of macrocyclic compounds, calixarenes (Gutsche 1989 and 1990, Vicens 1990, Linnane 1994) are preferable for metal extraction (i) because of the easy synthesis of a great number of derivatives which allows comparison of the impact of cavity size, conformation, functional groups, and other factors on the extraction behaviour, and (ii) the flexibility to design a proper ligand to selectively recognize a metal ion.

Previous studies concerned the lanthanide extraction by using calix[4]- and calix[6]arenes bearing carboxylic acid groups, at the lower rim and *tert*-butyl (compounds 1, and 3, Ludwig 1993) or *tert*-octyl groups (Ohto 1991 and 1992) at the upper rim and the findings of the present study will be compared with these results. It was established that (i) *t*-butylcalix[4]arene 1 extracts lanthanides as sandwich complexes because a 1:1 complex is not hydrophobic enough to be extracted, and (ii) the selectivity and extractability is increased by co-extracting sodium ions which rigidify the molecule through intramolecular binding to the ethereal oxygens. In this work the competitive extractability of metal ions having different charges is tested for 1, as well as the extraction of lanthanide ions by using the more hydrophobic calix[4]arene 2 bearing carboxylic acid and octadecyl groups.

### EXPERIMENTAL

Chemicals used for synthesis were of grade 'for synthesis' and those used for metal extraction of grade p.a.. Metal stock solutions were made by dissolving the corresponding sulfates (elements in Figure 1) and by dissolving lanthanide oxides (99.99%) in HClO<sub>4</sub>. Extraction was carried out batchwise at 298 K followed by stripping with 0.1 M HCl. The equilibria were attained in less than one hour. In order to increase the solubility of 1 to 4 (Scheme 1), octanol as modifier was added to the solvent as indicated in the figure captions. Both aqueous phases were analyzed using ICP-AES (elements in Figures 1, 2), ICP-MS (Figures 3-5) and a  $\gamma$ -spectrometer (for Eu-152, 10  $\mu$ M Ln<sup>3+</sup> in Figure 2). Solutions were freshly prepared. An analytical ultracentrifuge model Beckmann E equipped with UV-VIS scanner as well as with an optical system connected to a video device was used for kinetic studies. Compounds 1 to 3 were in a *cone* conformation; with the 4 acid groups looking into one direction and the alkyl groups into the other, as concluded from the NMR spectra. The rotation of the phenyl rings around -CH<sub>2</sub>-Ar-CH<sub>2</sub>- is sterically hindered in 1 to 3 and the conformation is therefore fixed.

Scheme 1: Compounds used for this study



- 1: n = 4, R = *tert*-butyl
- 2: n = 4, R = n-octadecyl
- 3: n = 6, R = *tert*-butyl
- 4: n = 8, R = *tert*-butyl

The compounds 1 and 2 were synthesized according to known procedures (Gutsche 1989, Arnaud 1989, Nakamoto 1989) and identified by means of t.l.c., m.p., <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and FAB-MS, and elemental analysis.

RESULTS AND DISCUSSION

Extraction Equilibria

Figure 1 shows the distribution coefficients for competitive metal ion extraction with compound 1 (25 mM) between pH 2.3 and pH 2.5. The highest extractability is observed for Th<sup>4+</sup>, Fe<sup>3+</sup>, and UO<sub>2</sub><sup>2+</sup>, while the extractability of Ni<sup>2+</sup>, Co<sup>2+</sup>, and Mn<sup>2+</sup> is very low. The metal ions have diameters which are comparable or smaller than the cavity size of 1, but no relationship is observed between extractability and ion size. The distribution coefficients depend on the pH of the aqueous phase, which is typical for a cation exchange mechanism for the extraction under these conditions.

The extractability of compounds 1 and 2 towards Eu<sup>3+</sup> in the absence and presence of other lanthanides and excess sodium is compared in Figure 2. The distribution coefficients increase by about 20 when 2 is used instead of 1 under similar conditions (0.5 mM extractant) as a result of the increased hydrophobicity. The slope of 3 for compound 1 decreases in the presence of excess sodium ions, while the slope of 3 remains constant in case of 2. Furthermore, the presence of excess sodium ions no longer increases the distribution coefficients as it does in case of 1. It is therefore concluded that the stoichiometry (lanthanide:ligand) of the complex extracted by 2 is the same in the absence and presence of excess Na<sup>+</sup>.

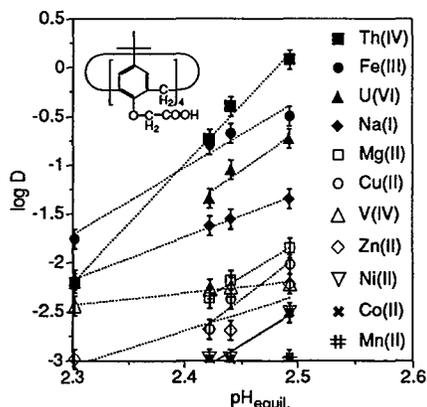


Figure 1. Competitive extraction of metal sulfates into toluene using calixarene compound 1 at 298 K  
 Aqueous Phase: 0.01 M Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> and 0.001 Moles Liter<sup>-1</sup>(M) of each other metal ion  
 Organic Phase: 0.025 M 1 in toluene containing 5% 2-octanol

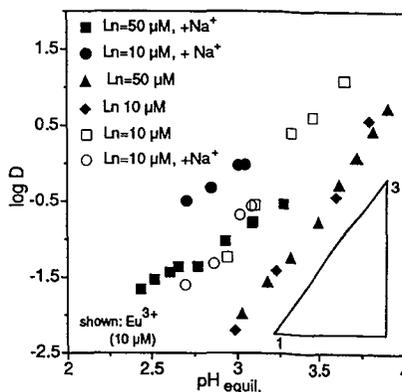


Figure 2: Extraction of Eu<sup>3+</sup> into chloroform at 298 K  
 Aqueous Phase: 10 μM Eu(ClO<sub>4</sub>)<sub>3</sub>, HClO<sub>4</sub> (●, ◆, □, ○) and 40 μM Ln(ClO<sub>4</sub>)<sub>3</sub> (■, ▲); (Ln = La + Nd + Er + Yb) and 0.05 M NaClO<sub>4</sub> (■, ●, ○)  
 Organic Phase: 0.5 mM ligand 1 (closed symbols) or 2 (open symbols)

The distribution coefficients of 6 lanthanide ions are plotted in Figure 3 as a function of the concentration of **2** dissolved in chloroform. The extractability at pH 4 decreases in the order: Eu, Dy, Tb > Er > Nd, La. Above 0.1 mM, a slope of about 1 indicates the extraction of 1:1 complexes. This is different from the extraction using **1**, where 1:2 metal:ligand complexes are extracted. The difference is ascribed to the higher hydrophobicity of **2** as well as of the 1:1 complex with Ln<sup>3+</sup>, so that no second ligand molecule is necessary for the phase transfer. At extractant concentrations below 0.1 mM, the slope is 2 indicating the extraction of 'sandwich'-complexes.

Figure 4 depicts the plot of distribution coefficients of lanthanides at various pH values using compound **2** at a 0.2 mM concentration. The slope of about 2 decreases above pH 3.3 in the presence of excess Na<sup>+</sup>. That phenomenon was previously found for **3** and may be caused by partial dissociation of the extracted complex. The selectivity order: Dy, Er, Tb ≥ Eu > Nd > La is comparable to the order: Er > Eu > Yb > Nd > La found for **1** under similar conditions. The preference for the medium and heavy lanthanides disappears in the absence of excess sodium ions. That effect was also observed for **1**: There, a sodium ion is complexed to the ethereal oxygen atoms and and co-extracted deep inside the calixarene cavity, rigidifying the molecule while simultaneously weakening the intramolecular hydrogen bonding between the carboxylic groups.

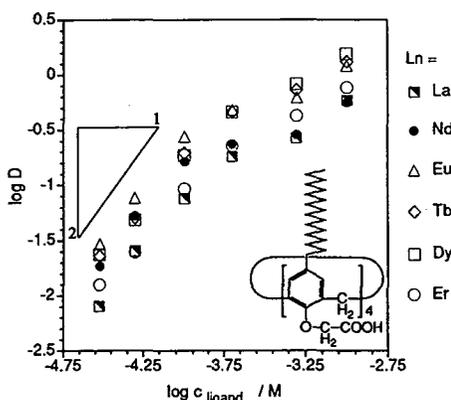


Figure 3. Extraction of Ln<sup>3+</sup> into CHCl<sub>3</sub> at 298 K  
Aqueous Phase: Ln(ClO<sub>4</sub>)<sub>3</sub>, each 5 \* 10<sup>-6</sup> M  
pH 4.02 (0.024 M KH<sub>2</sub>C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>),  
Organic Phase: calixarene compound **2**

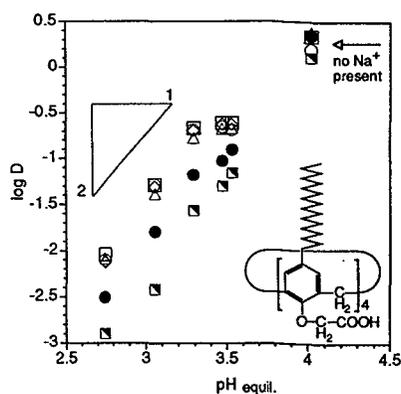
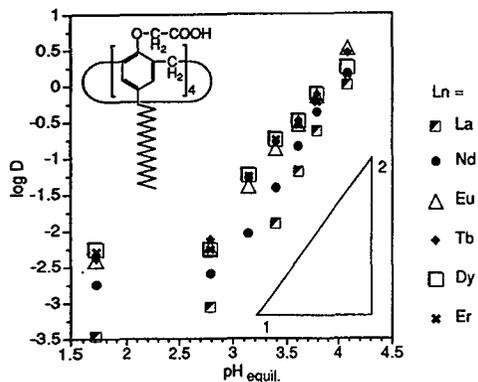


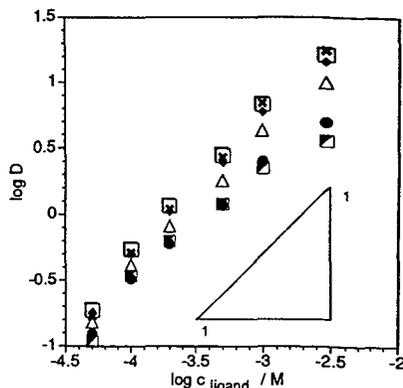
Figure 4. Extraction of Ln<sup>3+</sup> into CHCl<sub>3</sub> at 298 K  
Aqueous Phase: Ln(ClO<sub>4</sub>)<sub>3</sub>, each 5 \* 10<sup>-6</sup> M  
0.05 Na(H)NO<sub>3</sub> (except at pH 4.0)  
Organic Phase: 0.2 mM calixarene compound **2**

The extraction behaviour of **2** dissolved in toluene is depicted in Figures 5 and 6. The distribution coefficients depend on the pH (Figure 5) with a slope of 2 between pH 2.8 and 4. No decrease of this slope is found as compared with the chloroform system. The minimum extractability is observed below pH 2.7, but from previous studies it is known that an ion-pair extraction occurs at more acidic conditions (above 1 M acid). The distribution coefficients are of the same order of magnitude in chloroform and toluene. In case of **1**, there is a difference under comparable conditions, with toluene resulting in D-values higher by about one order of magnitude. The different behaviour of **2** is interpreted as a result of the higher hydrophobicity of the complex, which reduces the influence of the solvent on the distribution coefficients.

Figure 6 shows the distribution coefficients of the same metals as a function of the ligand concentration in toluene. The slope is 1 for Tb, Dy, and Er, indicating that a 1:1 complex is extracted. For La and Nd, the slope decreases to 0.8 and for Eu to 0.9 at higher extractant concentration, leading to an improved selectivity towards the heavy lanthanides.



**Figure 5.** Extraction of  $\text{Ln}^{3+}$  into toluene at 298 K  
 Aqueous Phase:  $\text{Ln}(\text{ClO}_4)_3$ , each  $5 \times 10^{-6}$  M,  
 0.05 M  $\text{Na}(\text{H})\text{NO}_3$   
 Organic Phase:  $2 \times 10^{-4}$  Moles Liter $^{-1}$  calixarene 2  
 in toluene containing 3% 1-octanol



**Figure 6.** Extraction of  $\text{Ln}^{3+}$  into toluene at 298 K  
 Aqueous Phase:  $\text{Ln}(\text{ClO}_4)_3$ , each  $5 \times 10^{-6}$  M,  
 0.05 M  $\text{Na}(\text{H})\text{ac}$ , pH 4.00  
 Organic Phase: calixarene 2 in toluene containing  
 3% 1-octanol

### Extraction Kinetics

The diffusion coefficients ( $d$ ) of the uranyl complexes of ligands **1**, **3**, and **4** in toluene/1-octanol were determined. For that purpose, the complexes were prepared by batchwise extracting uranyl ions from 0.1 M  $\text{UO}_2(\text{NO}_3)_2$  solutions which contained 0.001 M  $\text{HNO}_3$ . The distribution coefficients  $D$  were measured to be 6.25, 4.76, and 3.85 for **1**, **3**, and **4**, respectively. The loaded organic phase was then contacted in an analytical ultracentrifuge with fresh solvent which was equilibrated with  $\text{HNO}_3$ . The results are summarized in Table 1.

The integral mass flux  $I$  was studied for the same uranyl complexes. The values of  $I$  are depicted in Figure 7 as a function of the phase contact time. The maximum mass flux  $\vec{J}_{t \rightarrow 0}$  was determined by differentiation of the integral mass flux density curves followed by extrapolation to  $t = 0$ , the moment of the first phase contact (Gauglitz 1995). The values of  $\vec{J}_{t \rightarrow 0}$  are summarized in Table 2.

**TABLE 1**

Diffusion coefficients of uranyl complexes in the organic phase at 298 K

Compound	Solvent composition (vol.%)	$d$ , $\text{cm}^2 \text{s}^{-1}$
<b>1</b> (Tetramer)	toluene/1-octanol (70/30)	$2 \times 10^7$
<b>3</b> (Hexamer)	toluene/1-octanol (95/5)	$(0.7 \pm 0.2) \times 10^7$
<b>4</b> (Octamer)	toluene/1-octanol (80/20)	$4 \times 10^7$

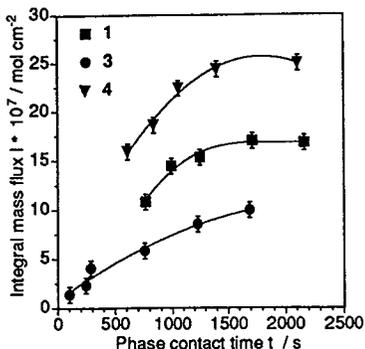


Figure 7. Integral mass flux at 298 K, measured in an ultracentrifuge

Aqueous Phase: 0.1 M  $\text{UO}_2(\text{NO}_3)_2$   
0.001 M  $\text{HNO}_3$

Organic Phase: 25 mM extractant in toluene containing 1-octanol (30 vol.% for L1, 5 vol.% for L2, 20 vol.% for L3)

TABLE 2  
Maximum mass flow  $\bar{J}_{t \rightarrow 0}^*$  during extraction of uranyl ions

Compound	$\bar{J}_{t \rightarrow 0}^* / \text{mol cm}^{-2} \text{ s}^{-1}$
1	$1.4 \times 10^{-9}$
3	$(1.45 \pm 0.15) \times 10^{-9}$
4	$2.5 \times 10^{-9}$

### Next studies

Next studies deal with the synthesis of new calixarene-type extractants aiming at better separation factors as well as with kinetic modeling.

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## SELECTIVE EXTRACTION OF PRECIOUS METALS WITH ALKYLPYRIDINE DERIVATIVES FROM HYDROCHLORIC ACID

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### ABSTRACT

Bidentate ligand of N-N, 2-ethylhexylaminomethylpyridine(=EHAP) and bidentate ligand of N-S, t-dodecylthiomethylpyridine(=DTMP) were synthesized to investigate the extraction behaviors for precious metals. EHAP and DTMP have selectively extracted palladium(II), platinum(IV) and rhodium(III) over copper(II), nickel(II), cobalt(II), cadmium(II), zinc(II), and iron(III) from hydrochloric acid. In order to elucidate the extracted species of palladium(II), the extraction equilibria of palladium(II) with EHAP and DTMP were measured 303K, and the extraction mechanisms were discussed. The loading test of palladium(II), platinum(IV) and rhodium(III) with EHAP and DTMP were examined. This result suggested that these precious metals have been extracted as the 1:1 chelate complexes with EHAP and DTMP, respectively.

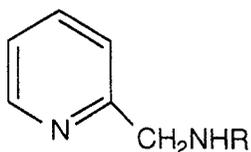
### INTRODUCTION

The platinum group metals, especially, palladium(II), rhodium(III), and platinum(IV) are very important metals in industry. The high prices of these metals have stimulated investigations of their separation, concentration and purification by solvent extraction techniques(Gindin, 1981; Ritcey, 1988). These metals occur in nature associated with the major base metals, copper, nickel and cobalt. Both technical and commercial considerations demand that the individual platinum group metals are separated not only from the other metals but also from each other to a high purity, with a high yield and with a high percentage of recovery. From such point of view, it is desired to develop new extracting reagents with high selectivity for these metals. Thus far, a number of extractants for platinum group metals have been developed, however, the majority of them are those of the sulfur atom donating ligand type(Cleare, 1979; Edwards, 1979; Moiski, 1979; Charlesworth, 1981; Barns, 1982; Inoue, 1990). Few studies on extractants which contain plural nitrogen atoms as ligating ones have been reported on the solvent extraction of platinum group metals.

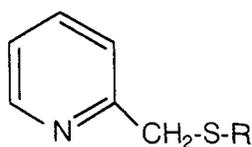
In the present paper, the novel type of pyridine derivatives, 2-ethylhexylaminomethylpyridine (EHAP) and t-dodecylthiomethylpyridine (DTMP), which were expected to exhibit the specific extraction behaviors for platinum group metals, were newly synthesized, and measured the extraction equilibria of precious metals, especially palladium(II), from hydrochloric acid.

## EXPERIMENTAL

EHAP and DTMP were synthesized from 2-ethylhexylamine and chloromethyl pyridine and from t-octylthiol and chloromethyl pyridine, respectively, according to a conventional method (Romary, 1968). Their chemical structures were shown below.



EHAP (R=2-Ethylhexyl)



DTMP (R=tert-Dodecyl)

Identification of the purified products, EHAP and DTMP were carried out by using NMR spectra and elemental analysis. Their purities were verified to be 98% and 97%, respectively, by gas chromatography. An analytical grade of 1,2-dichloroethane or toluene was used as a diluent.

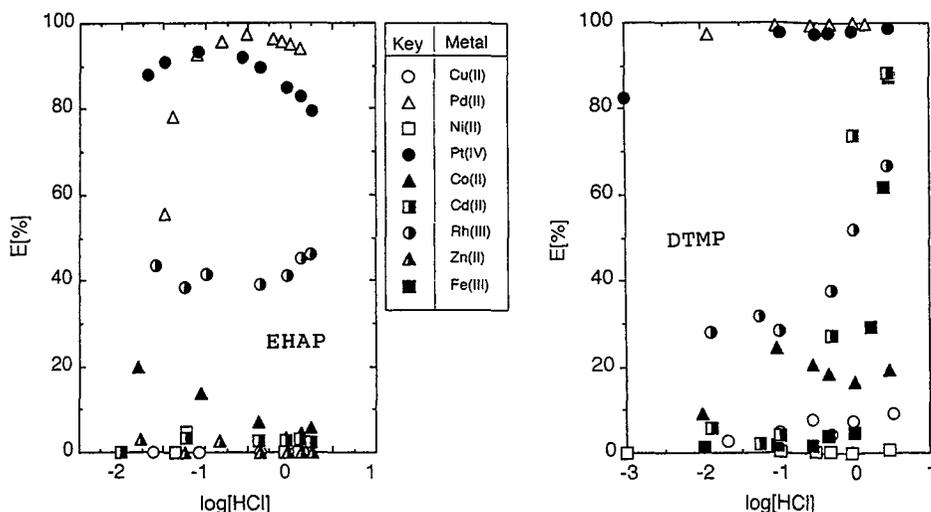
Equal volumes of aqueous and organic phases were shaken in a flask immersed in a thermostated water bath maintained at 30 °C overnight to attain equilibrium. The equilibration had been confirmed to be attained within 5 hours in a preliminary experiment for platinum group metals. The initial concentration of each metal was about 5 mmol  $\text{dm}^{-3}$ . The initial and equilibrium concentrations of the metal in the aqueous phase were determined by using a Nippon Jarrell-Ash model AA-782 atomic absorption spectrophotometer. The metal concentration in the organic phase was calculated from the mass balance of the metal contents in the aqueous phase before and after equilibrium.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the percent extracted of metal ions with EHAP and DTMP, respectively, from hydrochloric acid. As seen

from figure.1, EHAP can extract only platinum group metals such as palladium(II), rhodium(III), and platinum(IV) from hydrochloric acid. Base metals such as copper(II), nickel(II), cobalt(II), zinc(II), and cadmium(II) can not be extracted from hydrochloric acid with EHAP. Thus, EHAP was found to be a highly selective extractant for palladium(II), rhodium(III), and platinum(IV) from the hydrochloric acid containing the base metal ions as mentioned above.

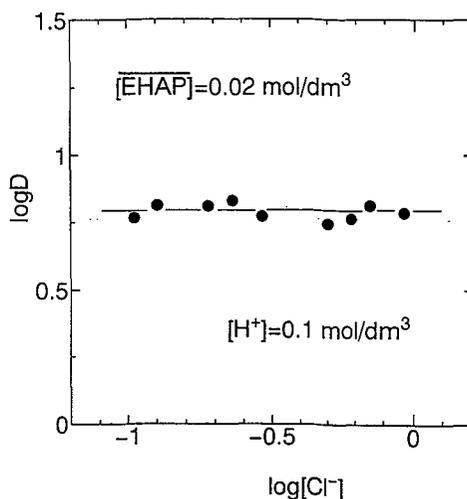
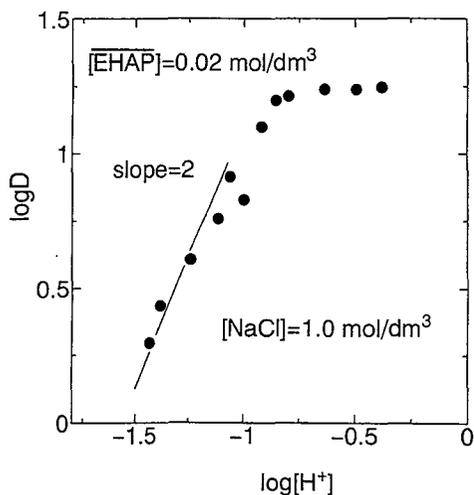
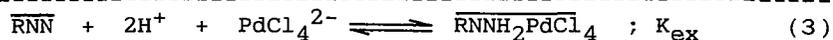
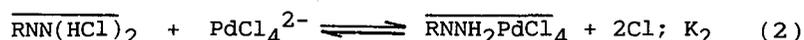
As is evident from figure. 2, base metals such as Copper(II), cadmium(II), nickel(II), zinc(II), and cobalt(II), which were not extracted with EHAP in the whole concentration region of hydrochloric acid, were extracted with DTMP in the high concentration region of hydrochloric acid. Accordingly, compared with the extraction behavior of EHAP, DTMP exhibited a lower selectivity for precious metals than that of EHAP in the high concentration region of hydrochloric acid.



Figures 1 and 2. Effect of the concentration of hydrochloric acid in the extraction of various metal ions with EHAP and DTMP ( $[EHAP]=[DTMP]=0.02 \text{ mol dm}^{-3}$ ).

Thus, since both EHAP and DTMP exhibited especially the high selectivity for palladium(II), the effects of the hydrogen ion and chloride ion concentration on the extraction behaviors of palladium(II) were investigated in the extraction with EHAP. Figure 3 shows the effects of the hydrogen ion concentration on the distribution ratio of palladium(II) at the constant chloride ion concentration of  $1 \text{ mol/dm}^3$ . The distribution ratio of

palladium(II) monotonously increases with an increase of the hydrogen ion concentration in its low concentration region. On the other hand, figure.4 shows the effect of chloride ion concentration on the distribution ratio at a constant hydrogen ion concentration of 0.1 mol/dm<sup>3</sup>. It was found that the distribution ratio of palladium(II) was dependent on the hydrogen ion concentration, and that it was independent of the chloride ion concentration. These results suggest that palladium (II) was extracted according to the following extraction reaction.



Figures 3 and 4 Effect of concentrations of chloride ion and hydrogen ion on the distribution ratio of palladium(II)(EHAP).

The loading test of palladium(II), platinum(IV), and rhodium(III) with EHAP and DTMP was examined. As an example, the experimental results with EHAP were shown in figure.5. The mole ratios of the extractant to metal ions extracted in the organic phase were plotted as a function of the concentration of metal ions. These results show that the molar ratio of EHAP to palladium(II),

rhodium(III), and platinum (IV) in the organic phase asymptotically approaches unity, respectively. Accordingly, palladium (II), rhodium(III) and platinum(IV) were considered to be extracted as 1:1 complexes.

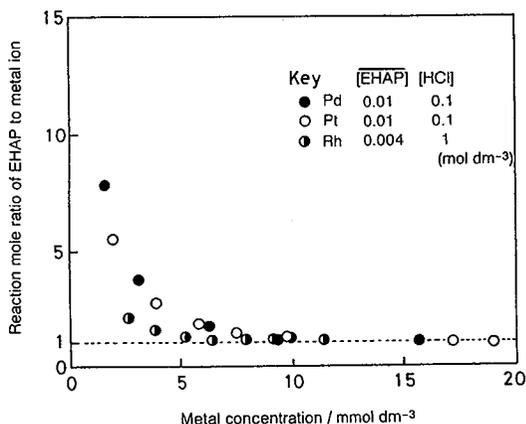


Figure.5 Determination of the reaction mole ratio by a loading test(EHAP).

Since palladium(II) and platinum(IV) are so strongly extracted by EHAP or DTMP, it is predicted that these metals are hard to strip with a conventional stripping solution, such as hydrochloric acid or ammonia. The stripping of palladium(II) was examined on EHAP. Aqueous ammonia solution(1 or 2 mol dm<sup>-3</sup>), which is usually used for stripping palladium(II), could strip neither palladium(II) nor platinum(IV) from the organic phase containing 4 mmol dm<sup>-3</sup> of palladium(II) or platinum(IV). Only 16.7% or 35.6% of palladium (II) could be stripped with 1 or 2 mol dm<sup>-3</sup> aqueous ammonium thiocyanate solutions, respectively, from the organic phase containing 4 mmol dm<sup>-3</sup> of palladium(II) and 20 mmol dm<sup>-3</sup> of EHAP. The 99.3% of palladium(II) could be stripped using 1 mol dm<sup>-3</sup> aqueous thiourea solution from the organic phase containing the about same concentrations of palladium(II) as EHAP.

## CONCLUSION

It was found that EHAP and DTMP, which are newly synthesized in the present paper, have excellent selectivity to precious metals. EHAP selectively extracted palladium(II), rhodium(III), and platinum(IV) over base metals such as copper(II), nickel(II), cobalt(II), cadmium(II) and zinc(II) from hydrochloric acid.

While, DTMP also selectively extracted palladium(II) and platinum(IV) over base metals mentioned above in the range of low concentration of hydrochloric acid, however, among these base metals, all metals except for nickel(II) were extracted DTMP in the high concentration region of hydrochloric acid. EHAP exhibited the higher selectivity for precious metals such as palladium(II) and platinum(IV) than that of DTMP. The extraction equilibrium of palladium(II) with EHAP was measured. It was found that palladium(II) was extracted with two hydrogen ions as a 1:1 complex with EHAP.

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## SOLVENT EXTRACTION OF CESIUM BY SUBSTITUTED CROWN ETHERS

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### ABSTRACT

*"Dedicated to the memory of our friend and colleague, W. J. McDowell, 1925-1994."*

The extraction of alkali metal nitrates by 18-crown-6, 21-crown-7, and 24-crown-8 ethers, bearing cyclohexano, benzo-, *t*-alkylbenzo, and furano- substituents, in 1,2-dichloroethane has been surveyed. Introduction of a furano substituent onto the macrocyclic ring of 18-crown-6 or 21-crown-7 ethers causes a significant reduction in both extraction efficiency and selectivity. Addition of an additional benzo group to dibenzo-21-crown-7, to give tribenzo-21-crown-7, decreases both extraction efficiency and selectivity, whereas addition of one or two additional benzo groups to dibenzo-24-crown-8 increases the extraction efficiency and selectivity for the larger ions Rb<sup>+</sup> and Cs<sup>+</sup>. Detailed equilibrium modeling of the extraction by lipophilic 21-crown-7 ethers indicates that the addition of *t*-alkyl substituents onto the benzo groups has only a minor effect on the extraction of cesium nitrate by dibenzo-21-crown-7 ethers.

### INTRODUCTION

The removal of cesium from radioactive wastes resulting from the reprocessing of nuclear fuels continues to be an important technological problem (Cecille, 1991). A variety of different separation methods have been studied, including solvent extraction, ion exchange, and precipitation (Schultz and Bray, 1987). Among the solvent extraction systems studied, the use of crown ethers as ion-selective complexants has received significant attention (Blasius, 1984; Gerow, 1979; Gerow, 1981; McDowell, 1992). However, a detailed understanding of how substituents affect cesium extraction by crown ethers has yet to be developed. As part of our continuing program to elucidate the physical and structural principles underlying efficiency and selectivity in solvent extraction (Chem.Div., 1993), we have surveyed the extraction of alkali metal nitrates by the series of large-ring crown ethers bearing cyclohexano and multiple aryl substituents, as shown in Figure 1. This study was undertaken to determine how substituent groups affect the selectivity and efficiency of cesium nitrate extraction by crown ethers. In addition, we have studied in detail the extraction of cesium nitrate by the three substituted dibenzo-21-crown-7 ethers (**2b-d**) and have developed a model to describe speciation in the organic phase using the computer program **SXLSQI** (Deng, submitted).

### EXPERIMENTAL

**Materials.** The crown ethers **1a**, **1b**, **2a**, **3a**, and **3b** were purchased from commercial sources (Parish Chemical/Aldrich Chemical). The remaining crown ethers (**1c**, **2b-g**, and **3c-g**) were prepared as described elsewhere (Deng, submitted). Dibenzo-18-crown-6 (**1b**) was recrystallized from dioxane. Dicyclohexano-21-crown-7 (**2e**) and dicyclohexano-24-crown-8 (**3c**) were purified by bulb-to-bulb distillation (180 °C @ 0.02 torr). Alkali metal nitrate salts were purchased as analytical reagents and dried at 110 °C for 3 days before use. 1,2-Dichloroethane (DCE) was of spectrophotometric grade. Distilled/de-ionized water was used for all of the experiments.

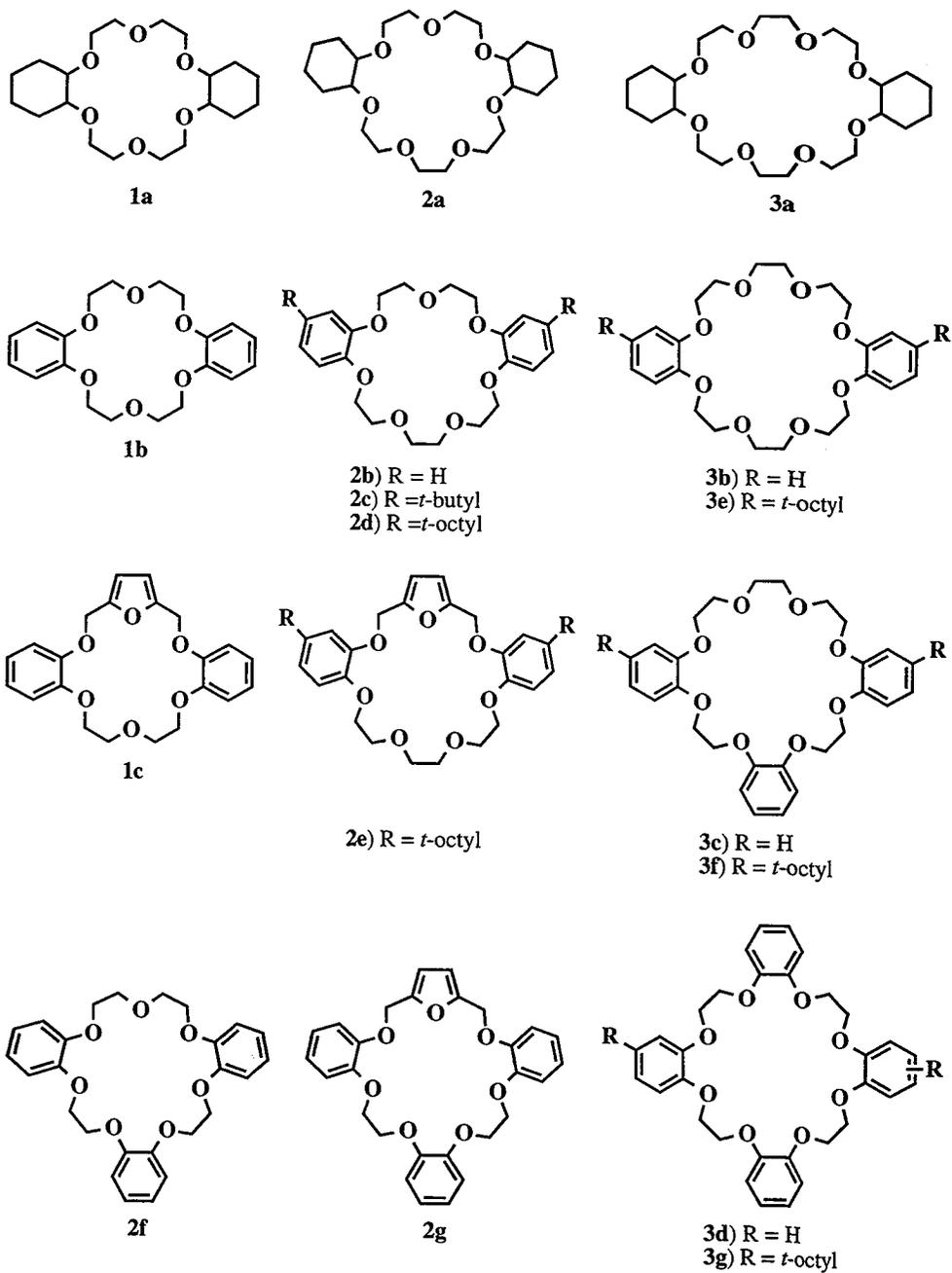


Figure 1. Structures of crown ethers.

**Solvent Extraction.** Equal volumes (0.5 mL each) of organic phase (0.025 M of crown ether) and aqueous phase (mixture of metal nitrate salts,  $MNO_3$ , each at 0.4 M where  $M = Li^+, Na^+, K^+, Rb^+$ , and  $Cs^+$ ) were equilibrated by repeated inversion on a rotating device in a thermostatic air box at  $25.0\text{ }^\circ\text{C}$  ( $\pm 0.5\text{ }^\circ\text{C}$ ) for 2 to 15 hours; this procedure was determined previously to be sufficient to ensure equilibrium. The samples were centrifuged for 5 to 10 minutes. An aliquot of the organic phase (0.3 mL) was removed and contacted with 3.0 mL of water, following the same procedure as for the extraction. This back-extraction sample was centrifuged, and 2.0 mL of the aqueous phase was removed for analysis. A second back extraction showed that essentially all of the metal salts are removed from the solvent in the first back-extraction. The final metal ion concentrations in the organic phase were calculated on the basis of the first stripping results. Multiple (3 - 5) extraction runs were performed for each crown ether solution.

Metal cation analysis of aqueous solutions was performed on a Dionex 2020i ion chromatography system equipped with an autosampler, AI-450 workstation, and conductivity detector, using a Dionex IonPac CS12 cation exchange column with 0.02 M methanesulfonic acid as the eluent. Calculations were based on an average of three injections for each sample using the external standard method. Lower detection limits for  $Li^+, K^+, Rb^+$  and  $Cs^+$  were  $[M^+] \geq 3 \times 10^{-6}$ ; the lower limit for  $[Na^+] \geq 10^{-4}$  resulted from the high background of  $Na^+$  in the controls. Acid-treated polypropylene vials and containers were used for both extraction and storage of aqueous solutions. All organic solutions were stored in Teflon<sup>®</sup> containers.

## RESULTS AND DISCUSSION

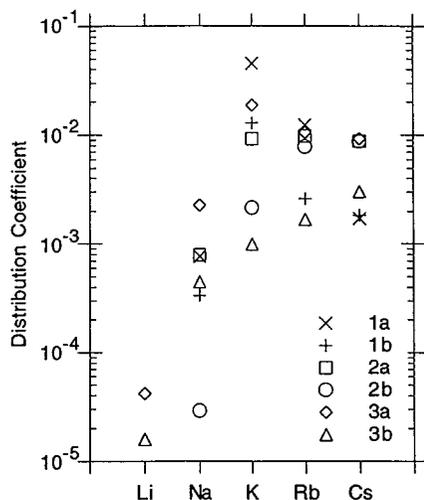


Figure 2. Extraction of alkali metal nitrates by dicyclohexano and dibenzo crown ethers in DCE. (Values for  $D_{Na}$  below  $10^{-4}$  are approximate, see experimental.)

The extraction of alkali metal nitrates by the commercially available dicyclohexano (**1a**, **2a** and **3a**) and dibenzo (**1b**, **2b** and **3b**) crown ethers in DCE is shown in Figure 2. These data are consistent with previous studies indicating that the 18C6 ethers **1a** and **1b** extract the intermediate sized  $K^+$  ion most strongly while the dicyclohexano 21C7 (**2a**) and 24C8 (**3a**) ethers extract  $K^+, Rb^+$ , and  $Cs^+$  ions similarly. Only the dibenzo-substituted 21C7 (**2b**) and 24C8 (**3b**) ethers exhibit a preference for the larger  $Rb^+$  and  $Cs^+$  ions. In general, the dibenzo crown ethers (**1b**, **2b**, and **3b**) extract more weakly than their dicyclohexano counterparts, reflecting the reduced basicity of the aryl ether oxygens in these macrocycles. In particular, **2b** exhibits notably weaker extraction of  $Na^+$  ion, consistent with previous attributions of high cesium/sodium selectivity to this crown ether (Blasius, 1984).

In an effort to determine if improved cesium selectivity can be obtained by simple modification of the crown ether structure, we obtained data for the extraction of alkali metal nitrates by 21C7 and 24C8 ethers bearing multiple (2-4) benzo substituents (Figure 3) and by 18C6 and 21C7 ethers bearing furano substituents (Figure 4). Both benzo and furano substituents act as rigid spacer groups and reduce the electron-donating properties of the ether oxygens to which they are attached. The results shown in Figure 3 suggest that the effect of adding benzo substituents is most significant for the extraction of the larger  $Rb^+$  and  $Cs^+$  ions. In the case of the 21C7 ethers (Figure 3a), the addition of one benzo substituent to dibenzo-21-crown-7 (**2b**  $\rightarrow$  **2f**) suppresses the extraction of  $Cs^+$  ion by a factor of 4.0; thus, whereas **2b** extracts  $Rb^+$  and  $Cs^+$  ions similarly, **2f** exhibits  $Rb^+$  selectivity. Conversely, the addition of benzo substituents to dibenzo-24-crown-8 (Fig 3b) increases the extraction of  $Cs^+$  ion by a factor of 1.8 in going from **3b** to **3c** and by a factor of 4.2 in going

from **3c** to **3d**. Consequently, **3d** is unique among the crown ethers in this study in that it exhibits selectivity for  $\text{Cs}^+$  ion over all of the other alkali metal cations and it exhibits the largest  $D_{\text{Cs}}$ . The addition of furano groups to benzo crown ethers (Figure 4) significantly decreases the extraction of the larger cations ( $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ ), consequently reducing the selectivity for these cations.

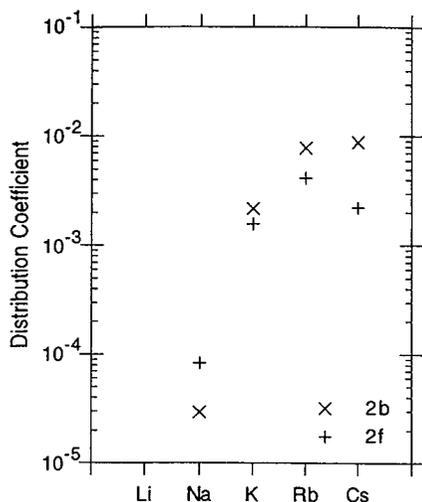


Figure 3a. Extraction of alkali metal nitrates by dibenzo- and tribenzo-21-crown-7 ethers. (Values for  $D_{\text{Na}}$  below  $10^{-4}$  are approximate, see experimental.)

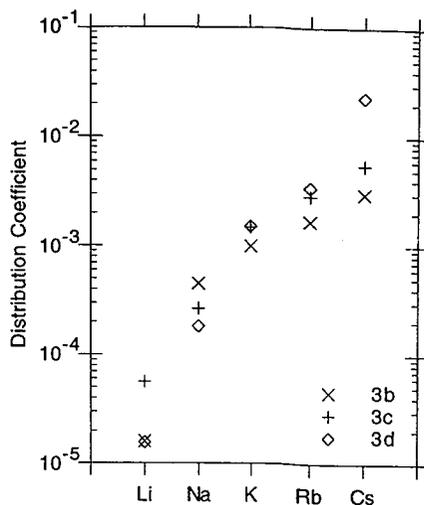


Figure 3b. Extraction of alkali metal nitrates by dibenzo-, tribenzo-, and tetrabenzo-24-crown-8 ethers.

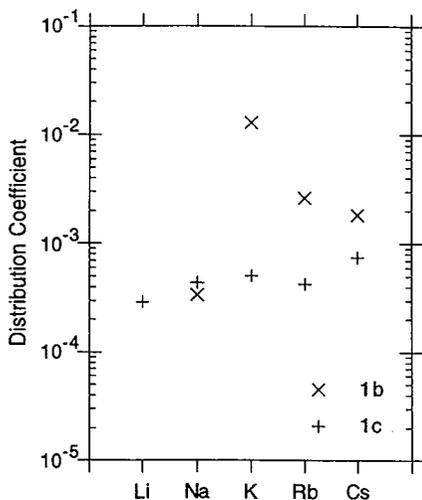


Figure 4a. Comparison of the extraction of alkali metal nitrates by dibenzo-18-crown-6 and furanodibenzo-18-crown-6. (Values for  $D_{\text{Na}}$  below  $10^{-4}$  are approximate, see experimental.)

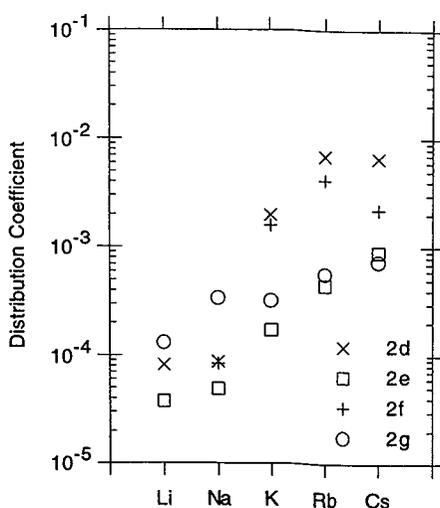


Figure 4b. Comparison of the extraction of alkali metal nitrates by benzo-21-crown-7 ethers and furano-substituted benzo-21-crown-7 ethers.

Generally, benzo-substituted crown ethers exhibit low solubility in non-polar organic diluents; addition of alkyl substituents, particularly tertiary alkyl groups, increases both the solubility and lipophilicity of benzo crown ethers. The effect this type of substitution has on extraction properties has not yet been studied in detail by others. In Figure 5, we compare the extraction of alkali metal nitrates by benzo-crown ethers (**2b** and **3b-3d**) to that of their derivatives bearing *t*-alkyl groups on the benzene rings (**2c**, **2d** and **3e-3g**).

For the series of 21C7 ethers, no significant differences are observed in the extraction of the larger cations  $K^+$ ,  $Rb^+$ , and  $Cs^+$  (vide infra). Increases in the extraction of the smaller  $Li^+$  and  $Na^+$  ions by the *t*-alkylbenzo crown ethers result in minor decreases in extraction selectivity. Similar trends were observed for the 24C8 ethers, except in the case of the tetrabenzo-24-crown-8 ethers **3d** and **3g**. The addition of *t*-octyl substituents to two of the four benzo groups of **3d** (to produce **3g**) appears to decrease the extraction of  $Cs^+$  by a factor of 2, while increasing the extraction of  $K^+$  and  $Rb^+$  ions by a similar amount. The reasons for these unique observations are not well understood and suggest the need for further study.

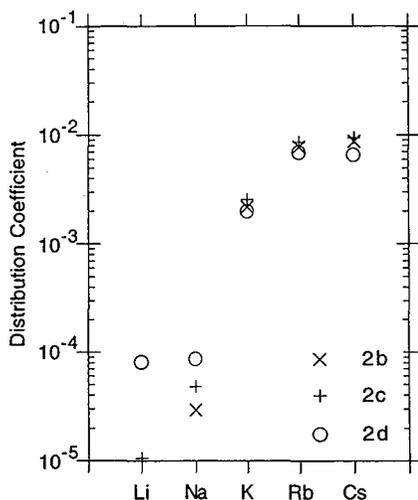


Figure 5a. Comparison of the extraction of alkali metal nitrates by benzo-21-crown-7 and *t*-alkylbenzo-21-crown-7 ethers. (Values for  $D_{Na}$  below  $10^{-4}$  are approximate, see experimental.)

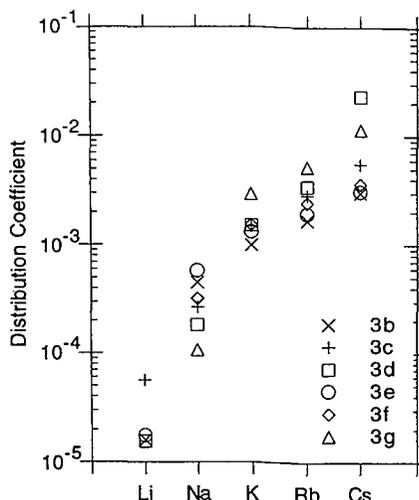


Figure 5b. Comparison of the extraction of alkali metal nitrates by benzo-24-crown-8 and *t*-alkylbenzo-24-crown-8 ethers

Finally, with the goal of relating crown ether structure to equilibrium constants for the formation of distinct extraction complexes, the extraction of cesium nitrate was determined over a range of conditions for four 21-crown-7 ethers in the partially ionizing diluent DCE at 25 °C. The crown ethers included **2a-2d**. Variation of aqueous cesium nitrate concentration up to 0.4 M and organic-phase crown ether concentration up to 0.025 M was modeled by the program *SXLSQI* (Deng, submitted). Formation of the species  $CsBNO_3$  (B = crown ether) and partial dissociation to the ions  $[CsB]^+$  and  $NO_3^-$  in the organic phase satisfactorily account for the observed behavior of the benzo-crown ethers. As shown in Table 1, differences in alkylation of the benzo groups give only minor differences in the extraction behavior. By contrast, **2a** exhibits much stronger extraction than the benzo crowns. On addition, **2a** entails behavior that can best be explained by formation of the higher complexes  $CsB_2NO_3$  and  $[CsB_2]^+$ .

**Table 1**

Constants for the Extraction of CsNO<sub>3</sub> by 21-Crown-7 Ethers in 1,2-Dichloroethane at 25 °C.<sup>a</sup>

Crown Ether	log <i>K</i> <sub>ex</sub> CsBNO <sub>3</sub>	log <i>K</i> <sub>ex±</sub> CsB <sup>+</sup>	log <i>K</i> <sub>ex</sub> CsB <sub>2</sub> NO <sub>3</sub>	log <i>K</i> <sub>ex±</sub> CsB <sub>2</sub> <sup>+</sup>	<i>R</i>
2a	0.57(6)	-3.97(24)	1.6(3)	-1.59(6)	0.066
2b	0.12(2)	-4.71(6)			0.058
2c	0.15(2)	-4.97(12)			0.081
2d	0.05(3)	-4.31(5)			0.075

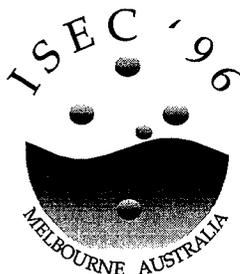
<sup>a</sup> In these experiments, CsNO<sub>3</sub> was the only aqueous salt present. *R* is the approximate standard relative error of the models compared with the data. **SXLSQI** corrects for the ionic activity by the Pitzer treatment for the aqueous phase and an extended Debye-Hückel equation for the organic phase. The Hildebrand-Scott treatment is employed for the nonideality of the neutral organic-phase species, although this was negligible in the present case.

#### ACKNOWLEDGMENTS

We would like to especially acknowledge our friend and colleague, W. Jack McDowell (1925-1994), whose lifelong work in the area of solvent extraction and more recent interest in the use of crown ethers in solvent extraction helped inspire the work presented here. This research was funded by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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## ASSOCIATION OF HYDROXYOXIME EXTRACTANT WITH OXYGEN CONTAINING MODIFIERS

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### ABSTRACT

Association of salicylaldoxime with oxygen containing modifiers is discussed and structures of appropriate associates are given.

### INTRODUCTION

Commercial extractants often contain oxygen-containing modifiers, which affect the extraction abilities of extractants by formation of mixed associates. High molecular weight alcohols and nonylphenol are used in several copper extractions using extractants containing salicylaldoximes as the active substance, e. g. in ACORGA P5100 and ACORGA PT 5050 - Szymanowski (1992). The use of unknown esters as modifiers is also described, e. g. in ACORGA M5615, M5397 and M5640 and the better extraction properties of these extractants are claimed - Dalton (1986).

The association of hydroxyoximes with various modifiers, including alcohols, ketones, ethers and esters of various structure is discussed. The effect of these modifiers upon copper extraction with 2-hydroxy-5-alkylbenzophenone oxime was reported by Komasa and Otake (1983) and Dalton (1986).

The works of Sella and Bauer (1992a, 1992b) and Sella et al. (1993) has permitted not only to optimise the structures of sophisticated extractants but also of extracted complexes and to study the structural effects of extractants upon their extraction abilities. Molecular modelling has been recently used by us to study the association of hydroxyoximes with methanol and 4-methylphenol - Bogacki et al. (1994) and the hydration of non-chelating oximes - Kopczyński et al. (1994).

### EXPERIMENTAL

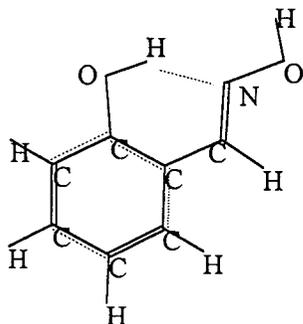
Salicylaldehyde oxime was considered as a low molecular compound of commercial hydroxyoxime extractants, while methanol, methyl ether, acetone and methyl acetate were the oxygen containing modifiers. In further studies, alcohols, ketones and esters of various structures were considered. The relatively low molecular mass of these compounds shortens the computing time without loss of accuracy and reproducibility. Semi-empirical PM3 calculations were carried out on IBM PC computer using the version 5.00 of MOPAC (Steward). The precise mode was used which set the convergence criteria for GNORM=0.01 and SCFRT=0.00001. Starting geometries for the calculations were obtained with Dreiding models and expressed in internal coordinates. The initial conformation used standard bond distances and bond angles. The angles of hydrogen bonded ligands were selected to produce tetrahedral association around a given oxygen atom, although these angles were always allowed to be optimised.

For each selected associate structure, i. e., number of associated modifier molecules, position and type of hydrogen bonding, the optimised geometry of associate was formed for which the minimum PM3 heats of formation ( $\Delta H$ ) were obtained.

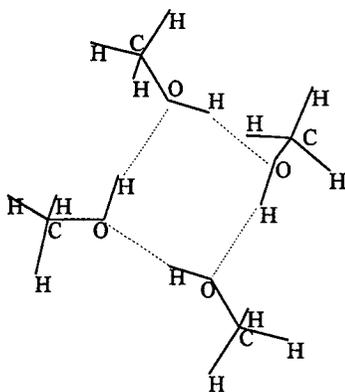
Stereo drawings of the optimised forms were displayed by the HyperChem™ Release 3 for Windows program (Autodesk, Inc.).

## RESULTS AND DISCUSSION

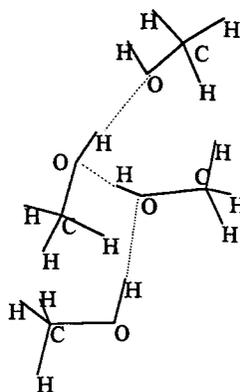
The phenolic group of salicylaldehyde is intramolecularly bonded with the nitrogen atom of the oximino group (OH...NOH) (Structure 1,  $\Delta H = -65.493$  kJ/mole).



Structure 1



Structure 2



Structure 3

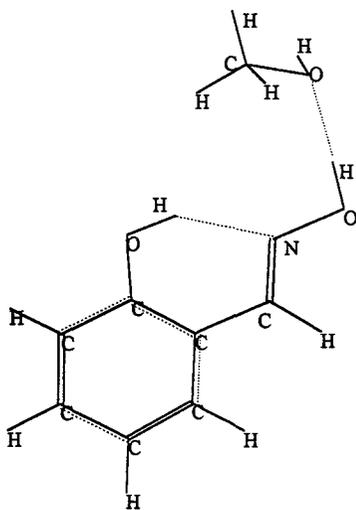
The hydroxyoxime molecules contain two oxygen atoms and one nitrogen atom which are capable of forming associates with modifiers containing a hydroxyl group. The hydroxyoxime molecule contains also the hydroxyl group capable of forming hydrogen bonds with the various modifiers containing oxygen, e. g. ethers, ketones and esters. Thus, the hydroxyoxime can act both as an electron donor and acceptor. Modifiers, e.g. alcohols, which contain hydroxyl group can also

act as an electron donor and acceptor (Szymanowski, 1994). However, when they contain an oxygen or a nitrogen atom, then they can only act as an electron donor. The possibilities of the formation of various associates by different molecules decrease in the following order:

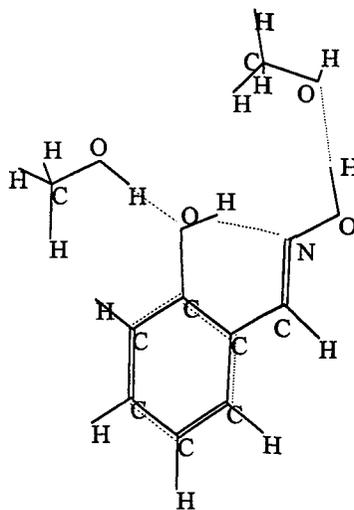
alcohols > esters > ketones  $\approx$  ethers.

The association becomes more complex when alcohols or alkylphenols are used as modifiers, because the hydroxyl group undergoes self-association. Alkylphenols form rather linear associates while alcohols can form both cyclic and linear associates (Structures 2,  $\Delta H = -929.088$  kJ/mole and 3,  $\Delta H = -919.956$  kJ/mole). Usually all these forms exist in equilibrium. However, the composition of the associate mixture depends upon the alcohol structure, i. e. the length and branching of the alcohol chain. The ease of association of the alcohols decreases from secondary to tertiary alcohols and with an increase in the alkyl chain branching. The cyclic-tetramer is the most stable associate of methanol.

Three different 1:1 methanol salicylaldehyde associates can be formed with different heats of formation. In the most stable structure 4, ( $\Delta H = -297.150$  kJ/mole) alcohol acts as an electron donor to the oximino group.



Structure 4

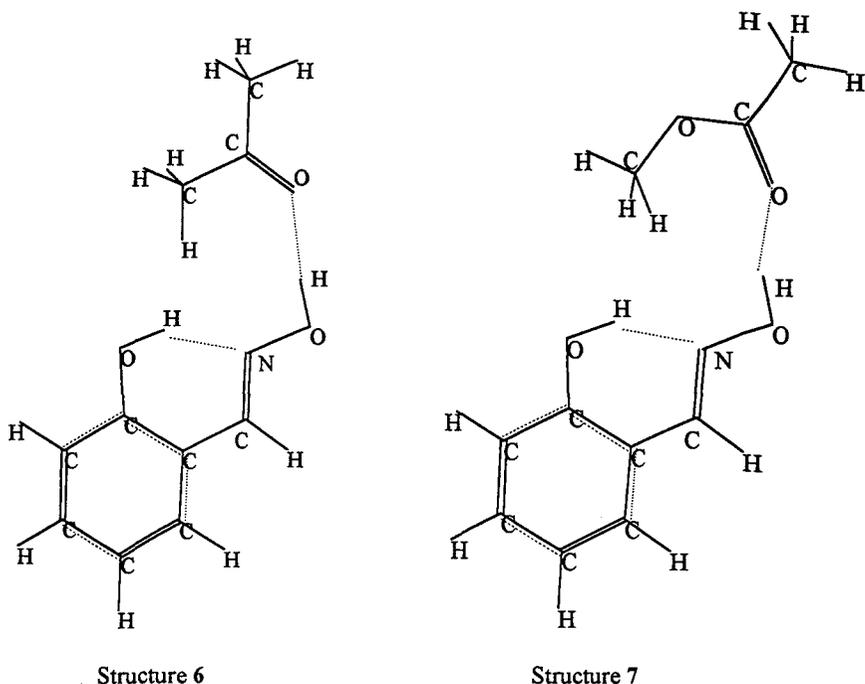


Structure 5

Alcohol can also act as the electron acceptor from the oxygen of the phenolic group. The formation of the hydrogen bond between the oxygen atom of the oximino group and hydrogen atom of the alcohol hydroxyl group is highly unlikely. Thus, the further association is very selective and 2:1 associate contains mainly the structure 5,  $\Delta H = -530.226$  kJ/mole.

Ketones, ethers and esters can only act as electron donors which form a hydrogen bond with the oximino group, as in the case of acetone (Structure 6,  $\Delta H = -307.887$  kJ/mole).

Esters form hydrogen bonds with oximino group mainly via the carbonyl group,  $C=O$ , (Structure 7,  $\Delta H = -476.916$  kJ/mole). The formation of the hydrogen bond via the second oxygen - OR is almost negligible (about 5%).



The self-association of alcohols decreases their ability to associate with hydroxyoximes which is indicated in the heats of associate formation. (Table 1). The modifiers which do not contain the hydroxyl group seem to be more active in hydrogen bond formation with hydroxyoximes than alcohols. This statement supports the results of Dalton (1986) about the effect of various esters on extraction properties of ACORGA reagents.

**TABLE 1.**  
PM3 heat of formation ( $\Delta H$ ) and dipole moment ( $\mu$ ) for various associates of salicylaldehyde oxime and various modifiers ( $\Delta H_{\text{relative}} = \Delta H_{\text{associate}} - (\Delta H_{\text{oxime}} + \Delta H_{\text{modifier}})$ )

Modifier	Type of hydrogen bonds	$-\Delta H$ associate kJ/mole	$-\Delta H$ relative kJ/mole	$\mu$ Debye
Acetone	(Me) <sub>2</sub> C=O...HON=	307.887	19.214	2.354
Methyl acetate	Me(O)C=O...HON=	476.916	15.529	2.104
	MeCOO...HON=	467.716	8.329	2.307
Methyl ether	(Me) <sub>2</sub> O...HON=	280.324	12.605	1.709
Methanol self-association	Cyclic-tetramer	929.088	14.119	1.849
	Linear-tetramer	919.956	12.836	5.268

The association of esters with salicylaldoximes depends on the structure of the alkyl group of both the acid and the alcohol (Table 2 and 3).

The association of butyl acetates with salicylaldoxime rises in the order:

n-butyl < 1-methylpropyl < t-butyl.

The opposite order is obtained in the series of methyl pentates. Similar effects of the alkyl structure are also observed for the association of ketones, ethers and alcohols with salicylaldoxime. However, in the latter case it is difficult to interpret results because of the self-association of the alcohol which depends upon the alcohol structure. The association of alcohols, e.g. of methanol towards cyclic-tetramer, is a competitive process which hinders the alcohol association with hydroxyoximes. As a result, low values of  $\Delta H_{\text{relative}}$  relative are observed in this case (Table 1).

**TABLE 2.**  
PM3 heat of associate formation ( $\Delta H_{\text{relative}} = \Delta H_{\text{associate}} - (\Delta H_{\text{oxime}} + \Delta H_{\text{modifier}})$ )  
\* in relation to cyclic-tetramer of methanol

Modifier	Type of hydrogen bonds	$-\Delta H$ associate kJ/mole	$-\Delta H$ relative kJ/mole	
Butyl acetate				
	n-butyl	Me(O)C=O...HON= MeCOO...HON=	540.020 532.955	16.120 9.055
1-methyl propyl				
		Me(O)C=O...HON= MeCOO...HON=	542.429 529.470	20.179 7.220
t-butyl				
		Me(O)C=O...HON= MeCOO...HON=	540.836 530.102	22.907 12.173
Methyl pentate				
	n-butyl	But(O)C=O...HON= ButCOO...HON=	540.143 511.215	16.243 -11.317
1-methyl propyl				
		But(O)C=O...HON= ButCOO...HON=	534.552 523.162	15.696 4.306
t-butyl				
		But(O)C=O...HON= ButCOO...HON=	515.610 520.413	0.605 5.408
Methanol				
		Me(H)O...HON=	297.150	0.386*
		Me(H)O...HON= and MeOH...OH	530.226	2.191*

The computing of salicylaldoxime association with various models of modifiers indicate that the association depends significantly upon the modifier type (alcohol, ester, ketone, etc.) and the structure of the alkyl chain. It is possible to modify the associate formation of hydroxyoximes and then their extraction properties by an appropriate selection of modifiers.

#### ACKNOWLEDGEMENT

The work was supported by KBN donation for Institute activity No. 32/221.

**TABLE 3**  
Length of intra- and intermolecular bonds in salicylaldehyd oxime - modifier associates  
\* the angle of the O...H-O hydrogen bond

Modifier	Intramolecular bond		Intermolecular bond		
	Length, A	Angle*, deg	Type	Length, A	Angle*, deg
Acetone	1.855	142.2	(Me) <sub>2</sub> C=O...HON=	1.799	172.7
Methyl acetate	1.837	143.5	Me(O)C=O...HON=	1.811	166.1
	1.840	143.4	MeCOO...HON=	1.829	176.3
Methyl ether	1.836	143.4	(Me) <sub>2</sub> O...HON=	1.814	177.1
Butyl acetate n-butyl	1.853	142.5	Me(O)C=O...HON=	1.794	173.0
	1.847	142.9	MeCOO...HON=	1.841	158.8
1-methyl propyl	1.853	142.5	Me(O)C=O...HON=	1.793	173.7
	1.835	143.7	MeCOO...HON=	1.838	170.3
t-butyl	1.834	143.9	Me(O)C=O...HON=	1.792	174.2
	1.862	141.7	MeCOO...HON=	2.540	175.4
Methyl pentate n-butyl	1.834	144.1	But(O)C=O...HON=	1.798	175.5
	1.834	143.7	ButCOO...HON=	1.838	164.6
1-methyl propyl	1.832	143.4	But(O)C=O...HON=	1.801	169.3
	1.845	142.9	ButCOO...HON=	1.837	155.9
t-butyl	1.832	143.5	But(O)C=O...HON=	1.801	162.9
	1.844	142.9	ButCOO...HON=	1.840	155.0
Methanol	1.820	143.3	Me(H)O...HON=	1.808	179.4
			and MeOH...OH	1.823	178.1

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## PHOSPHOR-ORGANIC EXTRACTANTS ASSOCIATION AND PHASE STATE IN THE TOLUENE MEDIA

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### ABSTRACT

Phase behaviour and aggregational pattern in the water/oil systems, containing phosphor-organic extractants were studied by dielectric, dynamic light scattering and surface tension measurements. The thermodynamic parameters both extractant adsorption at the water/oil interfaces and their association in the toluene medium were determined. The concentration and temperature ranges of the water/extractant/toluene microemulsions have been found. The aggregation of microemulsion droplets at various temperatures, alcohol/extractant ratios and water contents have been discussed.

### INTRODUCTION

Phosphor-organic compounds are widely used in extraction of rare earth elements (Yagodin G.A. et al. 1981, Fomin V.V. 1960). It is known that in some cases the third equilibrium phase formation takes place. Modifiers (aliphatic alcohols or phenols) being introduced into a system can prevent the third phase formation (Sergievskii V.V. et al. 1966). The effect of the modifiers on the phase state of the system can be related to formation of stable colloidal structures like micelles and microemulsions (Liu Huizhu et al. 1990). The later can affect the selectivity of extraction separation (Sawistowski et al. 1963). The regulation of association processes in the system gives a possibility to control the selectivity of elements extraction at the cost of "effective" changing of partition coefficient. The quantitative description of the association, micelle and microemulsion formation allows to predict the phase behaviour of multicomponent two-phases systems, intensify the extraction process, increase the selectivity of the process.

The associational properties of phosphor-organic extractants are of interest in connection with structure which is similar to the phospholipid structure. Biological activity and biochemical process features are closely related to the structural organisation of phosphor-organic amphiphilic compounds.

### EXPERIMENTAL

In this connection we have studied the association and micelle formation of typical phosphor-organic extractants (POE): tributyl phosphate (TBP); di(2-ethylhexyl)phosphoric acid (D2EHPA); tri-n-tolyl phosphate (TTP); tri-iso-amyl ester of phosphoric acid (TIAEPA) and trioctylphosphine oxide (TOPO) in the toluene

medium. Dielectric measurements (increment of dielectric permeability ( $\Delta\epsilon$ ) and dielectric losses tangent) of solutions under investigation were carried out by the resonance method using "Tesla BM-560" instrument, using a cylindrical cell of the coaxial type. The light scattering study carried out by the photon-correlation spectroscopic method using 15 milliwatt He-Ne laser as an incident light source.

## RESULTS AND DISCUSSION

It was established that the dependencies  $\Delta\epsilon$ -C had a complicated nature due to association and micelle formation processes of examined compound in the liquid phase. An increment of dielectric permeability is increased sharply when a surface-active agent (surfactant) concentration that is equal to the critical micelle concentration (CMC). In the region of low surfactant concentration peaks on the concentration dielectric permeability curve asymmetric premicelle associates forms. Thus by deviations on the curves  $\Delta\epsilon$ -C it is possible to determine the values of critical concentration of association (CAC) and CMC. In table 1 obtained values of CAC and CMC are presented. Using temperature dependencies of CAC and CMC, values of Gibbs energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of association (index "a") and micelle formations (index "b") were calculated.

TABLE 1

Thermodynamic parameters of association and micelles formation of some phosphor-organic compounds.

Surfactant	n*	CAC, $\text{mole/dm}^3 \cdot 10^3$	CMC, $\text{mole/dm}^3$	$-\Delta G_a$ , kJ/mole	$-\Delta G_b$ , kJ/mole
TBP	12	0.7	0.034	17.6	8.6
TiAEPa	15	3.6	0.072	13.9	6.5
D2HEPA	16	6.0	0.076	12.6	6.3
TTP	21		0.14		4.9
TOPO	24		0.17		4.5

n\*- the number of carbon atoms of hydrocarbon chains

Analyses of the data indicated a significant influence of the phosphor-organic compounds structure on their associative state in liquid phase. The higher solubility of the compound in nonpolar medium the higher values of CAC and CMC. Among studied compounds, TBP the most easily associates due to its low solubility. It should be pointed out that TBP might form hydrogen bonds in presence of water in the organic solvent with formation of a rich variety of different complexes. It is necessary to emphasize that the interrelation between found thermodynamic parameters is closely related to the nature and energy of the mutual interaction of the polar groups of extractants, their solvation by toluene and the hydrogen bonds formation. At extractant concentration more than CMC the concentration increment of dielectric permeability comes to 2-3 that indicates about chain associates (micelle) formation.

In table 2 thermodynamic parameters of association and micelle formation of TBP and D2EHPA are shown. Calculation of thermodynamic parameters of association and micelle formation for D2EHPA was carried out using of CAC and CMC temperature dependence. Closeness of values found for thermodynamic parameters for TBP and D2EHPA association reflects the fact that the main reason is hydrogen bonds formation between phosphate groups of compounds, and in general hydrophilic- lipophilic of compound (HLB).

**TABLE 2**

Thermodynamic parameters of association and micelle formation of TBP and D2EHPA.

Surfactant	$-\Delta H$ , kJ/mole	$-\Delta G$ , kJ/mole	$-\Delta S$ , J/mole
		Association	
D2EHPA	41.5	12.6	64.0
TBP	39.4	17.6	60.0
		Micelles formation	
D2EHPA	8.3	6.3	6.4

The values of CAC and CMC (tables 1, 2) depend on the hydrophilic nature of the compounds. In the row of similar compounds it is possible to use the number of methylene groups (n) in the hydrocarbon chains for characterising the compound HLB. It is found that values of Gibbs energy (of association ( $\Delta G_a$ ) and micelle formation ( $\Delta G_b$ )) are in linear correlation with n. This gives an opportunity to evaluate the associative state of the wide range of phosphor-containing extractant in organic media. It is necessary to pay attention to the fact that thermodynamic parameters of TOPO micelle formation are close to those these of corresponding esters of the phosphoric acid. This fact confirms once more the suggestion about weak ionisation of alkyl esters of the phosphoric acid in the toluene. Influence of extractants structure on the Gibbs energy of micelle formation reflects a decreasing contribution of electrostatic effects and hydrogen bonds on increasing the number and length of hydrocarbon chains. The antitate relationship between Gibbs energy values of micelle formation or association and n magnitude is confirmation of a significant contribution of hydrogen bonds in the state of POE in the toluene media. Essential differences between  $\Delta H_a$  and  $\Delta H_b$  indicate that association is dealing with interactions between phosphate groups of POE whereas for micelle formation interactions between associates are more important.

Thus, in the presence of water POE forms micelles in toluene media. In this case associative behaviour of the compounds is related to the polar group nature and by the hydrocarbon chains structure.

In order to reveal the mutual phases solubilization role in the effectiveness of the liquid extraction the phase behaviour of the system Water/sodium salt of

D2EHPA(SEHP)/oil was considered. In the aliphatic alcohol presence microemulsion formation was observed. Microemulsification took place only under definite relations  $r=[\text{alcohol}]/[\text{extractant}]$  that apparently is related to changing of the packing parameters ( $K_{\text{pack}}$ ) of POE molecule in the surfactant monolayer (Izraelashvili J.N.1976). The  $K_{\text{pack}}$  value is dependent on the factors that determine the state of a amphiphilic compound at the water-oil interface. On increasing of  $K_{\text{pack}} > 1$  formation of microemulsions in hydrocarbon dispersion media takes place. The  $K_{\text{pack}}$  values of extractants in the alcohol presence can be evaluated on the base surfactant tension measurements.

It was found that the isotherms of surface tension ( $\sigma$ ) have a shape that is typical for surfactant whereupon the deviations on concentration dependence curves for surface tension and specific conductivity are in good agreement with each other. Analysis of surface tension isotherms (Sheludko A., 1984) of water solution of POE containing octanol-1 gives the possibility to set up the adsorption ( $G$ ), the adsorption constant ( $k$ ) and surface area in the saturated surfactant monolayer ( $S = 1/G$ ).

**TABLE 3**  
Adsorption and micelle formation parameters of SEHP.

$r=[\text{alcohol}]/[\text{extractant}]$	$G \cdot 10^6$ , M/m <sup>2</sup>	$k \cdot 10^{-3}$ , dm <sup>3</sup> /mole	$S \cdot 10^{20}$ , m <sup>2</sup>	$\text{CMC} \cdot 10^3$ , mole/dm <sup>3</sup>	$K_{\text{pack}}$
0	3.3	7.6	50	2.5	0.95
0.8	4.1	4.5	40	3.4	1.15
1.0	3.7	8.7	45	6.2	1.05
1.2	3.5	12.9	47	7.4	1.01

\* without taking into account changing of hydrocarbon chains volume.

At constant temperature (table 3) increasing of  $r$  values, the magnitude of the maximal adsorption  $G$  is diminished which is related to forming of mixed monolayers: aliphatic alcohol - POE. As a result of increasing the  $r$  value, the packing parameter has a tendency to decrease. At increased concentrations of alcohol, formed microemulsion is destroyed due to increasing POE solubility in the organic phase. At the same time, increasing the temperature increase the solubility of alcohol in oil which leads to shifting of microemulsion domain in the direction of higher temperature. Thus the aggregational pattern and stability of microemulsion water/SEHP/toluene are nicely explained within the frame of well-known structural models (Mitchell D. J. et al. 1981).

The structure and aggregative stability of extraction systems containing POE depend both on modifier (alcohol, cosurfactant) and extractant concentrations. An investigation of system Water/ D2EHPA /toluene in the presence of octanol -1 and sodium salt of D2EHPA by dielectric and photon-correlation measurements indicate that the apparent hydrodynamic radius of particles change considerably with temperature raising or alcohol concentration in the system. In particular, at total concentration  $[\text{SEHP}]+[\text{D2EHPA}]=10^{-2}$  mole/dm<sup>3</sup> with  $r$  increase it is observed growth of dielectric permeability increment ( $\Delta\epsilon$ ) and hydrodynamic radius of particles

(decreasings of diffusion coefficient  $D$ ). However at  $r > 2.6$  dielectric permeability stays practically constant and  $D$  is diminished. Increase of total concentration of extractant and its salt in systems studied the  $\Delta\epsilon$  (and  $D$ ) dependencies from  $r$  have more complicated. The found regularities of changing of hydrodynamic radius and dielectric parameters can be explained by influence of the investigated factors on processes of microemulsion drops aggregatuon (similarly to descibed by Baker R. C. in 1984). Study of microemulsion viscosity dependence on dispersed phase content is in good accord with data of dielectrometry and light scattering.

Analysis of dependencies set up allows a conclusion that at low volume fraction of dispersed phase microemulsion represents water drops in hydrocarbon media. With increasing of weakly dissociated D2EHPA concentration in a system its relative concentration grows at the water-oil interface. As a result the effective surface charge of the drops is diminished and correspondingly their polarizability also (as well as  $\Delta\epsilon$ ) Decreasing in this case of the diffusion coefficient reflects increasing the microemulsion drop size.

Increasing of volume fraction of dispersed phase is accompanied by corresponding structural changes in the system. Diffusion coefficient and dielectric permeability considerably depend on the values the  $r$  due to both changing of drop size and their aggregation. The higher D2EHPA content in the system the larger is the microemulsion drops capacity to aggregation (due to interface electric potential decrease). It leads to decreasing of summary dipole moment of aggregates and correspondingly to  $\Delta\epsilon$  reduction. In this condition the diffusion coefficient does not in this case reflect mobility of the single particle but is characteristics of the aggregate drops. Introduction of phosphorous acid ester influences on equilibrium size of aggregates and on parameters of interparticle interactions which is characterised by  $\Delta\epsilon$  increasing. Diffusion coefficient changes reflect alteration of separate kinetic stable elements of forming structural network in the microemulsion bulk. It is typical that the diffusion coefficients value passes through a minimum that indicates that at a definite value of  $r$  microemulsion particles have the most tendency to aggregate whereupon this capacity does not depend on total extractant concentration in the system.

## CONCLUSION

Thus the structure and character of aggregation processes in microemulsions formed in extraction are determined by such factors as total concentration of extractant and its extractable complex, presence of modifier (surface- active additions ), temperature, content of solubilized (microemulsion) water in organic phase. The further investigations will show the influence of the aggregation in microemulsions on the parameters of extraction process (coefficients of distribution and selectivity).

## ACKNOWLEDGMENTS

This investigation is supported by grants from Russian Fund of Fundamental Researchs

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## WATER PARTITION AND EQUILIBRIUM IN SYSTEM TBP-HCl-H<sub>2</sub>O

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### ABSTRACT

The experimental data in system TBP - HCl - H<sub>2</sub>O are described, assuming the formation of ionic pairs, monosolvate and semisolvate. Hydration of species in the organic phase and its effect on activities are also described.

### RESULTS AND DISCUSSION

When the strong mineral acids are extracted with oxygen containing organic solvents, significant amounts of water are transferred into the organic phase. It had been shown that water affects strongly the extraction equilibrium and it is necessary to take into account the change of activity coefficients of components due to hydration in order to describe the equilibrium. In this study we would try to use for this purpose the equation (Yagodin et al, 1980) connecting activities in dry solution  $a_{i0}$  and in wet solution  $a_i$  under water activity  $a_w$ .

$$a_i = a_{i0} \exp(-h a_w) \quad (1)$$

where  $h$  is the hydration ratio of the component  $i$ . When we pass from  $a_w = 1$  to some  $a_w$  the change of activity  $a_i$  can be expressed:

$$a_i = a_{i1} \exp[h(1 - a_w)] \quad (2)$$

where  $a_{i1}$  is the activity of component  $i$  for  $a_w = 1$ .

The system tri-*n*-butylphosphate (TBP) - HCl - H<sub>2</sub>O has been studied extensively. Experimental data were collected by Hardy, (1970). Attempts to describe the equilibrium assuming the formation of some

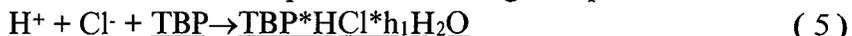
solvates failed when one ignored activity coefficients in the organic phase. Yagodin et al, (1978) offered to take into account the following interactions :



where underline shows the substance in the organic phase.

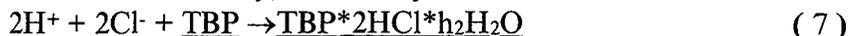
$$K_{0.5} = [\underline{Cl^-}] a_2^{0.5} \exp [ h_{0.5} (1 - a_1) ] \quad (4)$$

where  $a_1$  and  $a_2$  are activities of water and HCl respectively,  $h_{0.5}$  is a hydration ratio of ionic species in the organic phase .



$$K_{1.1} = [\underline{TBP*HCl}] a_2^{-1} a_3^{-1} \exp [ h_1 (1 - a_1) ] \quad (6)$$

where  $a_3$  is TBP activity,  $h_1$  is a hydration ratio of the monosolvate .



$$K_{2.1} = [\underline{TBP*2HCl}] a_2^{-2} a_3^{-1} \exp [ h_2 (1 - a_1) ] \quad (8)$$

where  $h_2$  is a hydration ratio of the semisolvate. But Yagodin et al (1978) ignored hydration of TBP.

The concentration of HCl in the organic phase  $c_{2o}$  is a sum of the concentration of three species :

$$c_{2o} = [\underline{Cl^-}] + [\underline{TBP*HCl}] + 2 [\underline{TBP*2HCl}] = K_{0.5} a_2^{0.5} \exp [ h_{0.5} (a_1 - 1) ] + K_{1.1} a_2 a_3 \exp [ h_1 (a_1 - 1) ] + 2K_{2.1} a_2^2 a_3 \exp [ h_2 (a_1 - 1) ] \quad (9)$$

Molar concentrations were chosen because it was necessary to know the sum of all the concentrations in order to use mole fractions or molality .

The treatment of experimental data by Ochkin et al (1992) resulted in the following values of the parameters :

$K_{0.5} = 0.0015$  ;  $h_{0.5} = 5$  ;  $K_{1.1} = 0.1302$  ;  $h_1 = 8.4$  ;  $K_{2.1} = 0.00064$  ;  $h_2 = 16.65$ . The relative error of calculation of  $c_{2o}$  was equal to 9.4% . The constants were chosen as the concentration of hydration water  $c_{1h}$  was less than the whole water concentration  $c_{1o}$  .

$$c_{1h} = h_{0.5} a_1 [\underline{Cl^-}] + h_1 a_1 [\underline{TBP*HCl}] + h_2 a_1 [\underline{TBP*2HCl}] < c_{1o} \quad (10)$$

The next step is taken to include the equations of material balance for TBP and water ;

$$c_3 = [\underline{Cl^-}] + [\underline{TBP*HCl}] + [\underline{TBP*2HCl}] + c_{3f} \quad (11)$$

$$c_1 = h_{0.5} a_1 [\underline{Cl^-}] + h_1 a_1 [\underline{TBP*HCl}] + h_2 a_1 [\underline{TBP*2HCl}] + c_{13} \quad (12)$$

where  $c_{3f}$  is the concentration of free TBP and  $c_{13}$  is the concentration of water related to free TBP. The kind of the

functions for  $c_3$  and  $c_{13}$  can be determined from the experimental data for binary system (Hardy et al, 1964). So the equation for  $c_3$  in binary system is found as:

$$c_3 = 3.50 a_3 \exp (0.619 a_1) \quad (13)$$

The results of calculation using equation (13) are given in table 1 and the standard error for this is 0.041 mole/l.

**TABLE 1**

Row	$a_1$ mole/kgH <sub>2</sub> O	$c_1$ mole/dm <sup>3</sup>	$a_3$ mole/kgTBP	$c_3$ mole/dm <sup>3</sup>	$c_3$ calc. mole/dm <sup>3</sup>
1	0.1104	0.20	0.9470	3.6343	3.5490
2	0.2244	0.44	0.8919	3.6170	3.5869
3	0.3298	0.68	0.8402	3.6038	3.6068
4	0.4273	0.97	0.7933	3.5839	3.6173
5	0.4997	1.15	0.7590	3.5751	3.6194
6	0.5286	1.20	0.7458	3.5683	3.6206
7	0.6183	1.48	0.7028	3.5488	3.6067
8	0.7996	2.17	0.6165	3.5064	3.5397
9	0.8421	2.44	0.5957	3.4860	3.5113
10	0.9019	2.78	0.5661	3.4687	3.4627
11	0.9799	3.42	0.5255	3.4212	3.3734
12	1.0000	3.58	0.5151	3.4207	3.3480

It is more complicated to find the equation for  $c_{13}$ . After many attempts the next equation is derived:

$$c_{13} = 6.65 a_1 a_3 \exp (0.619 a_1) / [c_3 (1 - 0.5 a_1)] \quad (14)$$

The equation (14) takes into account the change of volumes during the extraction.

The results of calculation depend on choice of hydration numbers. The function  $c_1 / (a_1 c_{2o})$  was calculated and its value passed through a minimum at  $c_{2o} = 2.005$  (value 7.44) and then increased to value 8.4. Therefore the optimum values of  $h_1$  fall between 7.2 and 8.0 and the optimum values of  $h_2$  fall between 16.0 and 17.0. The treatment of experimental data resulted in the next set of constants;  $K_{0.5} = 0.0018$ ;  $h_{0.5} = 5$ ;  $K_{1.1} = 0.098$ ;  $h_1 = 7.6$ ;  $K_{2.1} = 0.000514$ ;  $h_2 = 16.5$ . The results of calculation are given in the table 2. The

relative errors are equal to 7.5% for  $c_{20}$ , 10.0% for  $c_1$  and 2.5% for  $c_3$ .

**TABLE 2**

Row	$c_{20}$ mole/dm <sup>3</sup>	$c_{20}$ calc mole/dm <sup>3</sup>	$c_3$ mole/dm <sup>3</sup>	$c_3$ calc mole/dm <sup>3</sup>	$c_{10}$ mole/dm <sup>3</sup>	$c_{10}$ calc mole/dm <sup>3</sup>
1	0.00009	0.00008	3.420	3.345	3.590	3.708
2	0.00024	0.00023	3.420	3.349	3.590	3.705
3	0.00044	0.00041	3.420	3.347	3.590	3.697
4	0.00074	0.00069	3.420	3.351	3.590	3.694
5	0.00165	0.00158	3.420	3.359	3.590	3.688
6	0.00596	0.00499	3.420	3.367	3.590	3.667
7	0.02350	0.01599	3.420	3.383	3.640	3.658
8	0.03330	0.02427	3.420	3.389	3.670	3.665
9	0.03700	0.02894	3.415	3.393	3.690	3.683
10	0.09300	0.06769	3.405	3.403	3.840	3.780
11	0.20000	0.12746	3.380	3.408	4.200	3.989
12	0.35800	0.22048	3.330	3.374	4.790	4.345
13	0.49000	0.34599	3.285	3.348	5.300	4.839
14	0.68400	0.49489	3.220	3.267	6.060	5.377
15	0.90100	0.67766	3.160	3.199	6.900	6.019
16	1.12100	0.89112	3.110	3.129	7.440	6.718
17	1.34200	1.11807	3.075	3.045	7.720	7.358
18	1.56500	1.34123	3.040	2.947	8.000	7.859
19	1.78400	1.70658	3.005	3.123	8.240	8.999
20	2.00500	1.93422	2.960	3.039	8.490	9.226
21	2.22700	2.15389	2.935	2.941	8.700	9.305
22	2.45000	2.39251	2.900	2.872	8.900	9.322
23	2.67000	2.59382	2.865	2.806	9.060	9.137
24	2.89000	2.83607	2.845	2.804	9.100	9.053
25	3.11400	3.07705	2.830	2.802	8.980	8.828
26	3.34200	3.33275	2.820	2.818	8.750	8.582
27	3.56800	3.59045	2.830	2.834	8.400	8.279
28	3.79300	3.84436	2.835	2.849	7.970	7.887
29	4.01800	4.11964	2.840	2.881	7.560	7.471
30	4.24200	4.40772	2.850	2.911	7.040	7.036

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## PSEUDOCALIXARENES AND ITS APPLICATION FOR SOLVENT EXTRACTION OF METAL IONS

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### ABSTRACT

The pseudocalixarenes (PCA) have been proposed for solvent extraction of metal ions. An efficiency of nitrogen-containing PCA for solvent extraction of metal ions of the 3-rd group has been shown. The scandium solvent extraction has been taken as an example of the analysis for reasons of increased solvent extraction ability of nitrogen-containing PCA in comparison with the oxygen-containing one. The influence of phase contact time and contents of nitrogen in the structure of the nitrogen-containing PCA "Yarresin B" on scandium solvent extraction has been investigated. The solvent extraction isotherms have been obtained. The influence of solvents on scandium solvent extraction with "Yarresin B" have been studied.

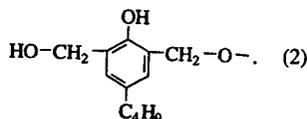
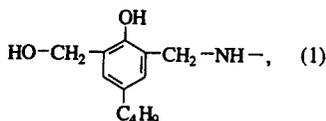
### INTRODUCTION

In recent years the attention of researchers is attracted by calixarenes as the compounds, capable to form the complexes with metal ions (Gutsche(1985)). However, these compounds are used mainly in scientific research and their solubility in organic solvents isn't sufficient for their use as extractants. In this study the solvent extraction of metal ions of the 3-rd group with a number of commercially accessible pseudocalixarenes (PCA) (Semenov(1994), Zhukovsky(1985), Bukin(1994)) have been investigated. The PCA are linear oligomers according to the terminology (Gutsche(1985)) and have a high solubility in organic solvents.

### EXPERIMENTAL

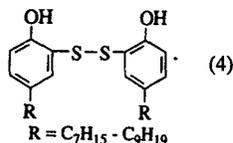
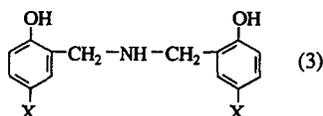
The following substances were used as extractants:

1. The PCA synthesized by polycondensation reaction of para-tert butyl phenol with formaldehyde in ammonia presence. Its Russian trade mark is "Yarresin B". PCA "Yarresin B" is a mixture of compounds, in molecules of which phenolic nuclei are bonded by methylene, o,o'-dimethylene-amine, o,o'-dimethylene-ether bridges. The free ortho-positions of compounds are partially occupied by methylol groups. Due to presence of (1) and (2) fragments PCA "Yarresin B" forms with metals the chelate compounds (Knop(1979)).



2. The PCA, synthesized by polycondensation reaction of para-tert.butyl phenol with formaldehyde in sodium hydroxide presence. Its trade mark is "101K". The PCA "101 K" is a mixture of compounds, in molecules of which phenolic nuclei are bonded by methylene or o,o'-dimethylene-ether bridges. The free ortho-positions of compounds are partially occupied by methylol groups. The PCA "101 K" also forms the chelate compounds (Knop(1979)) owing to the presence of fragment (2) in its molecule. The typical calixarenes (CA) cyclic structures are absent in PCA structure. It is confirmed by a low melting temperature of PCA (for example,  $t_{\text{Yarresin B}}^{\text{m.p.}} = 80\text{-}100^\circ\text{C}$  (our data),  $t_{\text{CAm.p.}} > 250^\circ\text{C}$  (Gutsche(1985)), as well as by a high solubility of PCA in organic solvents unlike CA. The linear oligomers owing to the inner molecular hydrogen bonds form the pseudo-cyclic structures - pseudocalixarenes.

3. Bis(2-hydroxy-5-octylbenzyl)amine. Its trade mark is "Octophor N" (3),  $x = \text{C}_8\text{H}_{17}$ .



4. Bis(2-hydroxy-5-alkylbenzyl)amine (HABA) (3),  $x = \text{C}_5\text{H}_{11} - \text{C}_8\text{H}_{17}$ .

5. Para-alkylphenol disulphide (APDS) (4).

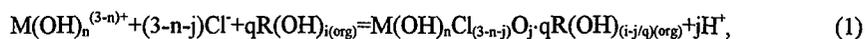
The extractants characteristics are summarised in table 1.

**TABLE 1**  
Extractant characteristics

Name	Molecular mass	Contents, %		
		Sulphur	Nitrogen	Methylol groups
PCA "Yarresin B"	460	-	2.1	1.5
PCA "101 K"	520	-	-	7-12
"Octophor N"	484	-	2.9	-
HABA	453	-	3.1	-
APDS	454	13.3	-	-

## RESULTS AND DISCUSSION

The data on the scandium, gallium and indium distributions between chloride aqueous solutions and one of "Yarresin B" in toluene are presented in table 2. The indium and scandium solvent extraction is increased with the increase of pH equilibrium values ( $\text{pH}_{\text{equil}}$ ). This is accounted for by the displacement of reaction (1) equilibrium under the decrease of hydrogen ions concentration.



where the subscript org denotes the organic phase. The gallium solvent extraction decreases with the  $\text{pH}_{\text{equil}}$  increase. The reason for the phenomenon is the decrease of free extractant concentration because of the extractant transition to the  $\text{R}(\text{OM})_i$  form, where  $\text{M}_1$  is an alkaline metal. The main attention in this research was given to the scandium solvent extraction.

The scandium distribution coefficient logarithm ( $\log D_{\text{Sc}}$ ) dependencies upon  $\text{pH}_{\text{equil}}$  of aqueous phase are presented in Figure 1. The initial scandium concentration in aqueous phase ( $\text{C}_{\text{Sc}}$ ) is 0.1 M. The 0.25 M extractant solutions in toluene were used.

**TABLE 2**  
 Scandium, indium and gallium solvent extraction with 0.1 M  
 "Yarresin B" solution in toluene.  $C_{Sc}=C_{In}=0.01$  M;  $C_{Ga}=4.3 \cdot 10^{-3}$  M.

$pH_{equil.}$	$D_{Sc}$	$pH_{equil.}$	$D_{In}$	$pH_{equil.}$	$D_{Ga}$
1.60	0.022	3.60	0.090	8.74	2.17
2.80	0.216	3.80	0.315	8.84	1.49
2.95	0.270	4.05	0.900	9.05	0.64
3.20	0.546	4.30	1.37	9.51	0.48
3.60	1.03	5.07	1.50	10.00	0.30
4.40	6.60	-	-	10.95	0.15

The Pearson's concept of Hard and Soft Acids and Bases (HSAB) (Pearson(1963)) was used for explanation of the various solvent extraction abilities of investigated reagents in relation to scandium. The scandium ion is a typical hard Lewis acid (Pearson(1963), Semenov(1991)). It is confirmed by a fact of thiocyanate ion coordination through the nitrogen (Komissarova(1967)). According to (Bjerrum(1977)), a way of formation of thiocyanate ion bond is indicative of the relative hardness or softness of Lewis acid. Therefore scandium should preferably form the coordination bond with a hard base. Sulphur in APDS is a soft base, therefore APDS practically doesn't extract the scandium ( $D_{Sc}=10^{-3}$ ). Oxygen in methylol and ether groups of PCA "101 K" is a hard base and for this extractant we can expect the highest scandium distribution coefficients. PCA "Yarresin B", "Octophor N" and HABA contain amine groups in which the nitrogen is an intermediate base (Spivakov(1980)). However, they extract the scandium better, than PCA "101 K". To explain this fact it is necessary to keep in mind that scandium coordinates the nitrogen, entering into a structure of above mentioned reagents, in kind of  $Sc(OH)_n Cl_{(3-n-j)} O_j \cdot qR(OH)_{(i-j/q)}$  compound, where  $n+j \leq 3$ . In this compound the scandium is less hard Lewis acid owing to the decrease of its effective charge. The higher donor activity of nitrogen in comparison with oxygen in these compounds introduces the contribution into the increased extraction ability of nitrogen containing extractants in comparison with the oxygen containing ones. This fact is confirmed by the lower energy of amines ionization in comparison with the ethers like them in structure (Guryanova(1973)). The best overlapping conditions of interacting acceptor and donor orbits are essential as well. Earlier (Guryanova(1973)) the relationship of overlapping conditions of acceptor and donor orbits, described by overlapping integral, with experimentally found sequence of change of amines and ethers donor properties was shown on example of acceptors: halogenides and element-organic compounds of gallium, aluminium, boron and compounds with hydrogen bond. It follows to note, that according to the data (Chikina(1975)), scandium chloride forms less strong complexes with oxygen contained ligands, than with amines. Since the most high  $D_{Sc}$  values were found for PCA "Yarresin B", the greatest attention was given to this extractant. It was found, that under increase of nitrogen contents in reagent the  $D_{Sc}$  values are increased, this testifies the considerable role of this element in formation of the extractable complex. This regularity confirms the conclusion about the formation of chelate compound under scandium extraction with PCA. The equilibrium in the mentioned system is complete for 1.5 hour, that is shown as on the example of scandium solvent extraction, as on its stripping. The isotherms of scandium solvent extraction with "Yarresin B" solutions of various concentration are obtained (Figure 2). It follows from these results, that the extractant capacity is 1 scandium mole per 1 "Yarresin B" one.

The solvent has considerable influence on the extraction process (Zolotov(1968)). In this research the octane, toluene, chloroform, octanol as well as kerosene, that are in wide use in hydrometallurgical processes (Voldman(1982)) are chosen for study of solvent nature

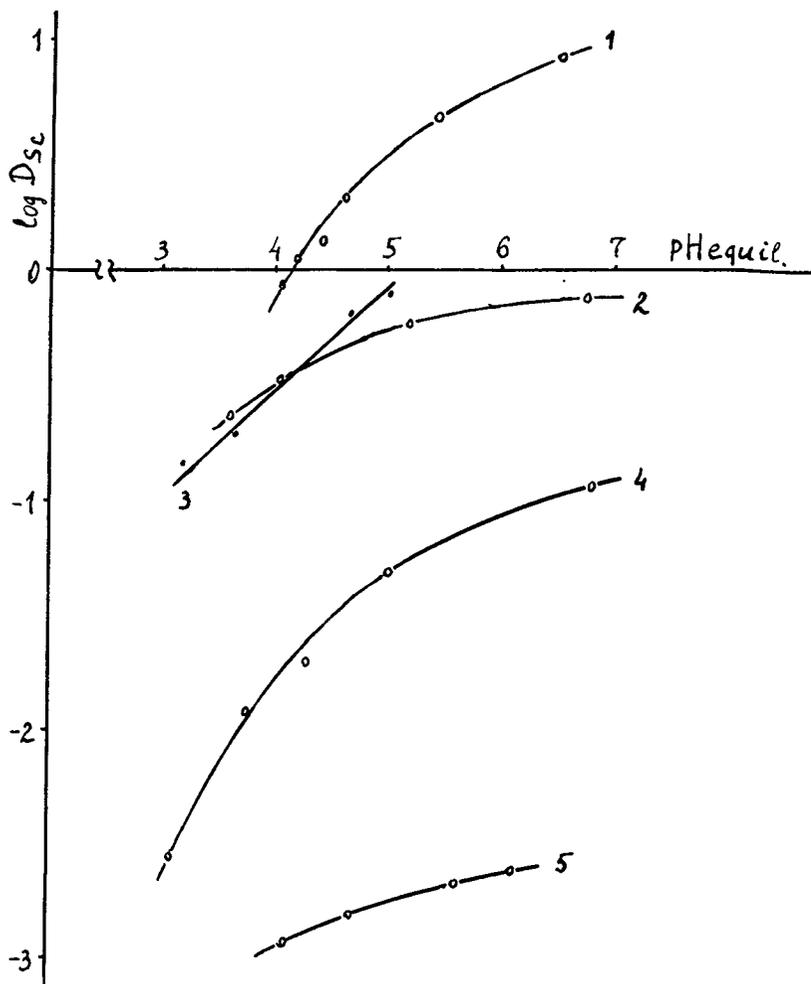


Figure 1. Plots of  $\log D_{sc}$  vs  $pH_{equil.}$   $C_{Sc}=0.1$  M;  $C_S=0.25$  M.  
 1-PCA "Yarresin B"; 2-"Octophor N"; 3-HABA; 4-PCA "101 K"; 5-APDS.

influence on scandium extraction with "Yarresin B" PCA. It was found, that the scandium extraction decreases in series: octane > kerosene > toluene > chloroform > octanol. The solvents influence on solvent extraction is determined by them solvating ability, which, in turn, basically depends on the solvent polarity. It is not possible to express the solvating ability or polarity of solvent through the properties of continuous uniform media (dipole moment, dielectric constant ( $\epsilon$ ), refractive index). Therefore any empirical parameter of polarity (Gurikov(1980), Reichardt(1988)) is chosen for quantitative evaluation of solvent influence on solvent extraction.

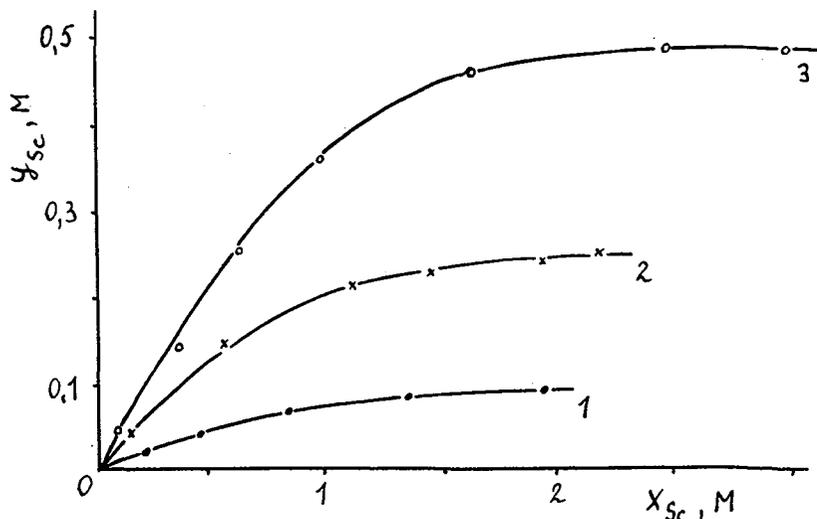


Figure 2. The isotherms of scandium solvent extraction with "Yarresin B" solutions of concentrations in toluene (M): 1-0.1; 2-0.25; 3-0.5;  $pH_{\text{equil.}}=4.5$ .

This parameter is calculated on the basis of equilibrium constants, kinetic or spectroscopic measurements (Reichardt(1988)), or from the fundamental constants of substance (evaporation heat, critical temperature, molar volume etc.) (Gurikov(1980)). The known from the literature solvent parameters and calculated correlation factors ( $r$ ) between them and  $D_{sc}$  under the solvent extraction with "Yarresin B" solution in pointed out solvents are presented in table 3.

TABLE 3  
The  $D_{sc}$  relation with solvent parameters.

Parameter	Solvent				Correlation factor $r$	Importance criterion $H= r \sqrt{N-1}$
	Octane	Toluene	Chloroform	Octanol		
$\epsilon$	1.948	2.379	4.806	10.34	0.816	1.41
$P$	39.00	33.46	44.57	90.08	0.685	1.19
$P/\epsilon$	20.02	14.06	9.28	6.13	0.981	1.70
$\delta, \text{MPa}^{1/2}$	15.1	18.2	19.0	21.1	0.996	1.73
$E_T, \text{kJ/mole}$	130	142	164	202	0.890	1.54
$P_{\text{coh.}}, \text{MPa}$	228	337	362	445	0.992	1.72

The verification of calculated  $r$  values on importance (Rumshisky(1971)) has not confirmed the correlation between such properties of substance, as dielectric constant, molar polarization ( $P$ )(Weissberger(1955)) and empirical parameter of polarity ( $E_T$ )(Reichardt(1988)) on the one hand, and  $D_{sc}$  on the other one (critical value of importance criterion of correlation factor  $H_{cr} = 1.65$  at importance level  $\alpha=0.1$  (Rumshisky(1971))). However, the distribution coefficient is in good correlation with the relation  $P/\epsilon$ , offered by (Kuznetsova(1970)). This parameter describes the solvating ability of organic solvents of various classes.

It indicates an opportunity of application of  $P/\epsilon$  parameter for forecasting of solvent influence on solvent extraction. The greatest value of correlation factor with  $D_{sc}$  is for solubility parameter  $\delta$  (Reichardt(1988)) and cohesive pressure  $P_{coh}$ . (Gurikov(1980)), that have dimension of energy density and are calculated on the base of physicochemical constants of substance. Thus the solvent influence on scandium solvent extraction with "Yarresin B" depends on mainly their polarity. Under an increase of solvent molecule polarity from octane to octanol the  $D_{sc}$  decrease is observed owing to the increase of interaction between extractant and solvent. Besides that in the case of octanol there is the opportunity of additional formation of inter molecular hydrogen bonds with extractant, that results in appreciable decrease of  $D_{sc}$  values.

### CONCLUSIONS

The carried out research shows the opportunity of nitrogen containing pseudocalixarenes use for solvent extraction of metal ions of 3rd group: scandium, gallium and indium. The various solvent extraction abilities of the nitrogen, oxygen and sulphur containing pseudocalixarenes in relation to scandium were explained with the use of the Pearson's concept of Hard and Soft Acids and Bases. The capacity of the nitrogen containing pseudocalixarene "Yarresin B" is 1 scandium mole per 1 "Yarresin B" one. The scandium extraction with "Yarresin B" solutions in various diluents decreases in series: octane>kerosene>toluene>chloroform>octanol. The scandium distribution coefficient is in good correlation with the next solvent parameters: relation of molar polarization and dielectric constant  $P/\epsilon$ , Hildebrand solubility parameter  $\delta$  and cohesive pressure  $P_{coh}$ .

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## ALUMINIUM AND IRON EXTRACTION BY DNNSA AND DNNSA-DEHPA REVERSE MICELLES

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### ABSTRACT

This paper investigates the liquid liquid extraction of aluminium and iron from nitrate media in the presence of supporting electrolyte by two different reverse micellar systems: (i) the surfactant dinonylnaphthalene sulfonic acid (DNNSA) in n-hexane and the mixture of di(2-ethylhexyl)phosphoric acid (DEHPA) and DNNSA in n-hexane.

The mixed system showed synergism in the extraction of both metals. This effect takes place after the C.M.C. is reached and tends to disappear as the concentration of DNNSA is increased. Although the extraction behaviour of the two metals is similar, there are some differences that can be attributed to the different conditions required for the extraction of each metal. As the pH for extraction of Fe and Al are different, the effect of pH as well as of ionic strength on interfacial tension was investigated. Metal distribution results are analysed in terms of interfacial activity.

### INTRODUCTION

The interactions of dinonylnaphthalene sulfonic acid (DNNSA) with other reactants in the extraction of metal ions, have been reviewed by Gallacher (1982). Van Dalen and Gerritsma (1971) were the first to report that the addition of di(2-ethylhexyl)phosphoric acid (DEHPA) to concentrated solutions of DNNSA suppressed the emulsifying property of DNNSA, and enhanced the extraction of  $Ce^{3+}$  and  $Am^{3+}$  solutions in perchloric acid. They suggested that this synergism was due to the inclusion of DEHPA molecules in the reverse micelles of DNNSA.

The same behaviour was observed by Osseo-Asare and Keeney (1980a) in the extraction of Ni with an organic solution containing variable amounts of DNNSA with and without LIX63. Synergism was observed when the mixture was used and was attributed to the ability of DNNSA reverse micelles to solubilize both the oxyme and the metal ion (Osseo-Asare and Keeney, 1980a and 1980b). A general thermodynamic model of liquid-liquid distribution in reverse micellar systems, consisting of a surfactant and a chelating agent (mixed system) has been presented by Osseo-Asare (1988). This model followed the micellar pseudophase model developed by Berezin et al. (1973) and Martinek, et al. (1973 and 1977), and it was further extended to the problem of liquid-liquid distribution equilibria in reverse micellar systems. A comparison between the theoretical model and experimental data (DNNSA/LIX63/ $Ni^{2+}$ ) showed good agreement.

The mechanism of solvent extraction for the system DNNSA + DEHPA in n-dodecane was studied by Van Dalen et al. (1978) for the extraction of a series of metal ions from 1N  $HClO_4$ . The authors suggested that only positively charged complex ions (metal + DEHPA) are included in the DNNSA reverse micelles; complex neutral species enter the organic phase without being included, and are solvated with DEHPA molecules.

As the formation of reverse micelles depends on the conditions of the system, in this work the behaviour of mixtures of DEHPA and DNNSA is investigated in the extraction of two metals that

extract at different pH. The metals selected are  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . The effect of ionic strength is also studied.

### EXPERIMENTAL

For distribution coefficient studies the two phases were gently shaken for 30 minutes in a thermostatic water bath at  $25 \pm 0.5$  °C. This time was long enough to achieve equilibrium. Vigorous shaking was avoided in order to prevent the formation of a coarse emulsion. After shaking, the samples were left in the water bath in order to reach phase separation. The time required varied with surfactant concentration and the ionic strength used; more concentrated samples at low ionic strength needed more time for phase separation.

The aluminium concentration was measured by atomic absorption spectrometry at a wavelength of 309.3 nm with acetylene-nitrous oxide flame. Iron was analysed at a wavelength of 248.3 nm with an acetylene-air flame. Interfacial tension measurements were conducted on a Krüss K10 digital tensiometer using the Du Nuoy ring method.

DNNSA was kindly given by King Industries as NACURE 1052 (50% solution in n-heptane) and was used without further purification. All DNNSA used was of the same batch. DEHPA was purchased from BDH and was purified according to the procedure recommended by Union Carbide(1972). The ionic strength was adjusted using  $\text{NaNO}_3$ . This and all other chemicals were of AnalaR quality.

### RESULTS AND DISCUSSION

All experiments with the mixed DNNSA-DEHPA system (from now onwards called the mixed system) were conducted using a concentration of DEHPA of  $0.01 \text{ kmol/m}^3$ .

#### Interfacial tension

The interfacial tension data for the single DNNSA system (in future called the single system) at pH 0.6 and 3.0 are given in Figure 1. It can be observed that below the C.M.C. the system is more interfacially active at pH 0.6 than at pH 3.0 and that the C.M.C. is reached at a lower DNNSA concentration. Interfacial tension measurements at constant pH show a slight increase of the interfacial tension with ionic strength (Lay, 1994).

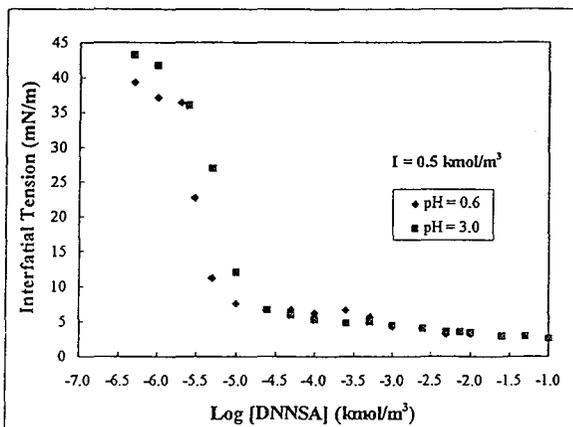


Figure 1. Interfacial tension data in the single system

Interfacial tension measurements for the mixed system at pH 0.6 and pH 3.0 are shown in Figures 2 and 3 respectively, where interfacial tension data is plotted versus Log [DNNSA] at different values of I. There is a shift of the C.M.C. to a higher DNNSA concentration for the mixed system, which indicates an association of DNNSA and DEHPA in the organic phase leading to a reduction of the DNNSA activity at the interface. Therefore, in order to obtain the activity required to reach micellization an increase in the DNNSA concentration is necessary. A similar shift of the C.M.C. to a higher concentration was observed by Osseo-Asare and Keeney (1980) and Savastano (1988) through the investigation of the system DNNSA/LIX63/hexane. However, the shift in their work was more pronounced because the hydroxyoxime is less interfacially active than DEHPA. By increasing the DNNSA concentration at a constant DEHPA concentration the values of interfacial tension for the single and mixed system begin to approach each other, i.e. DNNSA populates the interface in preference to DEHPA.

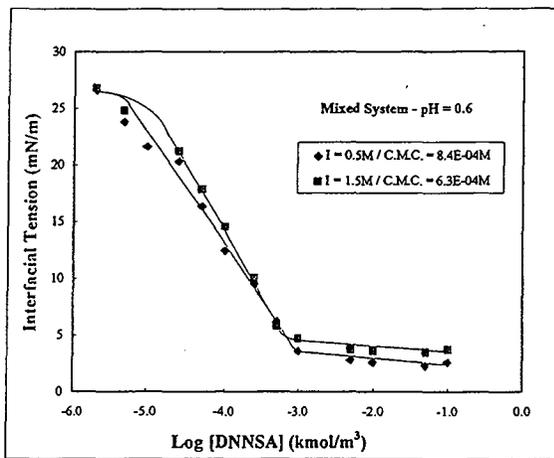


Figure 2. Interfacial tension data: Mixed system at pH 0.6.

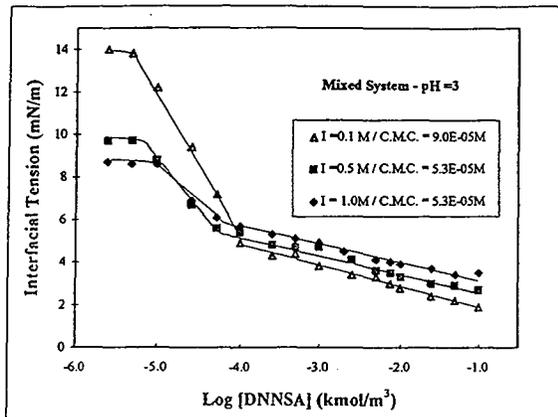


Figure 3 Interfacial tension data: Mixed system at pH 3.0

The interfacial tension of the mixed system decreases with increasing pH, thus indicating that anionic DEHPA is interfacially more active than its unionised form. Although DEHPA has been considered to be totally unionised at pH 3.0 (Vandegrift and Horwitz, 1980) results obtained by Gaonkar and Neuman (1987) indicate that ionisation is significant even at pH 2.0. Measurements of the interfacial tension vs DEHPA concentration in the pH range of 1.0 to 5.0 (Lay, 1994) show a decrease in interfacial tension with increasing pH. As expected the adsorption of DEHPA at the interface increase with pH as the acid becomes more ionised.

#### Distribution coefficients for Al and Fe

Figures 4 and 5 show the variation of the distribution coefficients of Al and Fe with DNNSA concentration and I in the mixed system. In Figures 6 and 7 the results for Al and Fe in the mixed system are shown together with those obtained with the single system. To facilitate the analysis of results Figures 6 and 7 also include the interfacial tension values for the mixed system and a plot of the addition of the distribution coefficients obtained for DEHPA alone and the single system at the conditions of the mixture.

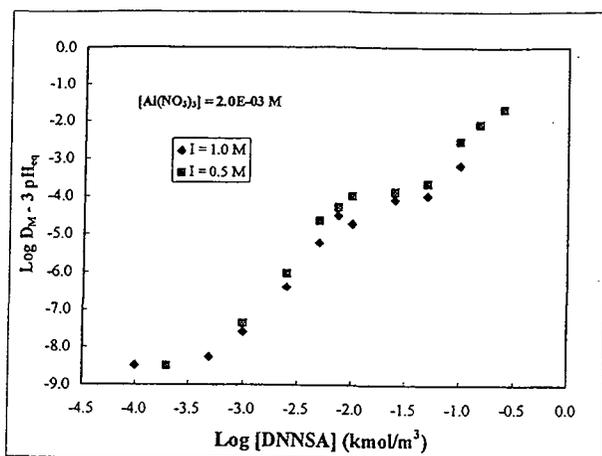


Figure 4. Mixed system: Effect of [DNNSA] and I on aluminium distribution. pH 3.0.

As can be seen in Figures 6 and 7 the distribution coefficients of both metals show a synergistic effect after the C.M.C. is reached; they first increase with DNNSA concentration, they reach a maximum and then decrease down to the value of the single system. Beyond this point they overlap with the single system values.

According to Van Dalen and Geritsma (1971), and Van Dalen et al. (1974 and 1978) the extraction of trivalent metal ions from an aqueous phase of 1 kmol/m<sup>3</sup> HClO<sub>4</sub> by a solution of DNNSA in n-hexane is enhanced by the addition of DEHPA due to the inclusion of one or two monomer DEHPA molecules in the DNNSA reverse micelle. The number of DEHPA molecules included depends on the concentration ratio of DEHPA : DNNSA. At a ratio of 0.74, one molecule of DEHPA is included, and at 1.5, two. Beyond a value of 6 the mixed reverse micelle was destroyed.

Calculation of the concentration ratio of DEHPA : DNNSA in this work (Lay, 1994) indicated that the maximum value of the distribution coefficient for both metals was obtained at a ratio of 1.33, and was independent of the ionic strength used. However Figures 4 and 5 show that the distribution coefficients for both metals decrease with increasing ionic strength, more so in the case of Al which

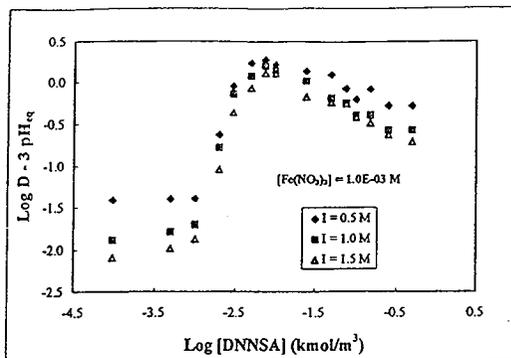


Figure 5. Mixed system: Effect of [DNNSA] and I on Fe distribution. pH 0.6

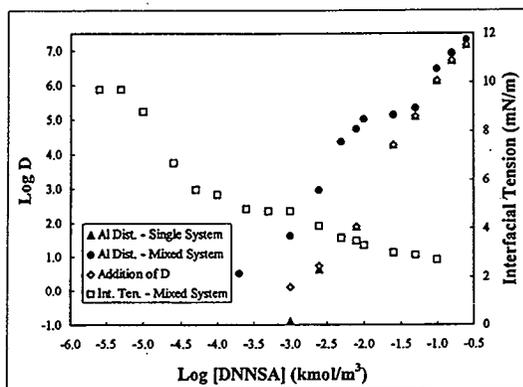


Figure 6. Dependence of aluminium distribution on [DNNSA]; pH 3.0, I = 0.5.

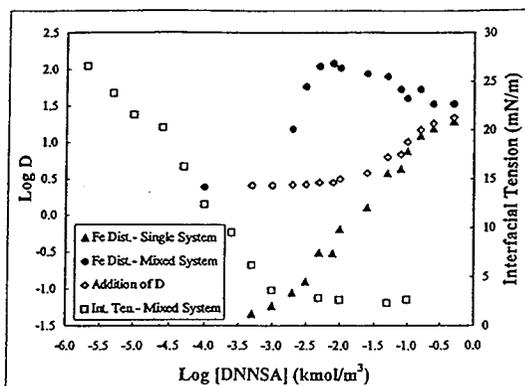


Figure 7. Dependence of iron distribution on [DNNSA]; pH 0.6, I = 0.5

is extracted at higher pH. This behaviour follows the same trend as the dependence of interfacial activity with I, i.e. interfacial tension increases with increasing ionic strength. Therefore it can be concluded that although the ratio DEHPA:DNNSA remains the same, extraction increases with interfacial activity. This seems to indicate that the concentration of complex in the interfacial mosaic is reflected in the concentration of complex attached to the micro interface. As the interfacial adsorption of the mixed system at pH 3.0 is higher than that at pH 0.6, this may also explain the higher values of D for Al.

### CONCLUSIONS

In the mixed system the value of the C.M.C. is higher than in the single DNNSA system. This is due to coverage by adsorbed DEHPA molecules leading to a reduction of the DNNSA activity at the interface.

In the single DEHPA system the interfacial tension decreases with increasing pH, thus indicating that anionic DEHPA is interfacially more active than its unionised form.

Synergism is observed in the extraction of both metals in an interval of DNNSA concentrations between the C.M.C. and a concentration at which the mixed DEHPA-DNNSA mixed reverse micelles become very diluted and the predominant extractant becomes DNNSA. At this point the distribution coefficients of the single and mixed systems overlap.

In both the single and the mixed systems metal distribution increases with DNNSA concentration and decreases with increasing I. The latter follows the trend of the variation of interfacial tension with I suggesting that the interfacial activity of the mixture plays a leading role in the extraction capacity of the system. This seems to be also the case when comparing the distribution coefficients of Al and Fe.. The distribution coefficients of Al, extracted at pH 3.0, are higher than those of Fe, extracted at pH 0.6.

### ACKNOWLEDGEMENTS

The authors wish to express their gratitude to the Brazilian Research Council-CNPq and to the Science and Engineering Research Council (grant No. GR/H39802) for their financial support.

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## SEPARATION OF METALS by Liquid-Liquid-Extraction with $\beta$ -Diketones and 4-Acyl-5-Pyrazolones from Different Complex-Forming Media

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### ABSTRACT

A series of different  $\beta$ -diketones and 4-acyl-5-pyrazolones was synthesized, similar to the commercially available product LIX 54<sup>®</sup> and enabled a study of the influence of structural parameters on the metal separation.

The solubility of the extractant and the influence of different solvents on the extraction behaviour were tested. The logD/pH functions were determined in the presence of ammonia, cyanide, chloride and tartrate.

The extraction is seriously hindered by ammonia or cyanide but is promoted by tartrate, especially at medium pH values. Generally, branched substituents are favourable as they cause a good solubility of the extractant and its metal chelates.

The tested metals were extracted in the order Cu > Zn > Ni > Cd. The composition of the extracted species is MeL<sub>2</sub>.

### INTRODUCTION

Within the group of commercially used extractants,  $\beta$ -diketones besides LIX 54<sup>®</sup> (HENKEL KGaA) only play a limited role-Logsdail and Slater (1993). The employment of 4-acylpyrazolones which have a similar ligand structure like common  $\beta$ -diketones is not known in spite of the favourable qualities such as coordination ability, stability and acid strength of these compounds- Akama and Tong (1993), Goetz-Grandmont et al. (1992).

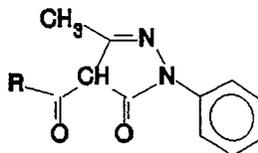
Recent work was done with acylisoxazolones which are suitable as extractants because of their stronger acid strength-Fujino et al. (1994). Other interesting extractants are bis-pyrazolones-Goetz-Grandmont et al. (1995). LIX 54 was identified as a mixture of iso-octanoyl-benzoylmethanes-Mickler et al. (1992). The aim of this paper was to clear up the influence of alkyl substituents on the extraction behaviour of similar  $\beta$ -diketones and 4-acylpyrazolones. Both groups of extractants were used to extract copper, nickel, zinc and cadmium. The influence of different organic solvents as well as competing ligand in the aqueous phase such as cyanide, tartrate, ammonia or chloride were studied.

### EXPERIMENTAL

#### Extractants

##### 1. 4-Acylpyrazol-5-ones

The extractants are characterized by the formula

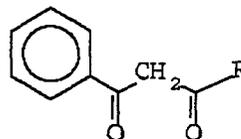


acyl group	R
stearoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>16</sub> -
palmitoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>14</sub> -
octadecenoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>7</sub> -CH=CH-(CH <sub>2</sub> ) <sub>7</sub> -
n-octanoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>6</sub> -
n-hexanoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>4</sub> -
2-ethylhexanoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>3</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-
n-butanoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>3</sub> -
cyclopentyl-propionyl-	C <sub>5</sub> H <sub>9</sub> -(CH <sub>2</sub> ) <sub>2</sub> -
cyclohexyl-acetyl-	C <sub>6</sub> H <sub>11</sub> -(CH <sub>2</sub> )-

The syntheses were performed following the method of Jensen (1959) by the reaction of 1-phenyl-3-methyl-5-pyrazolone with the corresponding acid chloride. The compounds were purified by distillation in vacuo or by recrystallization from alcohol. Some analytical data were already put together-Mickler and Uhlemann (1993).

## 2. $\beta$ -Diketones

The extractants are characterized by the formula



acyl group	R
n-octanoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>6</sub> -
2-ethylhexanoyl-	H <sub>3</sub> C-(CH <sub>2</sub> ) <sub>3</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-
cyclohexyl-acetyl-	C <sub>6</sub> H <sub>11</sub> -CH <sub>2</sub> -
cyclopentyl-propanoyl-	C <sub>5</sub> H <sub>9</sub> -(CH <sub>2</sub> ) <sub>2</sub> -
LIX 54 •	i-C <sub>7</sub> H <sub>13</sub> (mixture)

for comparison were synthesized:

p-hexylphenyl-1,3-butadione  
1-phenyl-2-hexyl-1,3-butadione

The syntheses were performed following a procedure of Man et al. (1951) by the Claisen condensation of acetophenone with the corresponding phenyl- or ethyl esters in the presence of sodium amide. The compounds were purified by distillation in vacuo. Some of their analytical data are given elsewhere.

## Extraction parameters

The experimental conditions of the liquid-liquid-extraction were the following:

$c_{Me^{II+}}$	$10^{-5} \dots 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ( $I = 0.1 \text{ mol} \cdot \text{L}^{-1} \text{ KNO}_3$ )
$c_{HL}$	$10^{-3} \dots 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ (solvent : kerosene)
phase ratio	1 + 1 ( 20 mL, separation funnels)
temperature	25° C
extraction cycle	10 minutes ( mechanical shaker)

The pH-adjustment was done by adding HNO<sub>3</sub> or NaOH respectively. For the measurements a pH-meter MV 86 (praecitronic, Germany) with glass electrode (Schott, Germany) was used. The metal concentration was determined after reextraction from the organic phase by

AAS (AAS 1100 B, Perkin Elmer). All chemicals were of p.a.-quality. The metal stock solutions were prepared by dilution of a Merck-standard solution with bidistilled water. Assuming the general equation:



the distribution coefficient  $D = c_{M^{n+}(org)} / c_{M^{n+}(aq)}$  was calculated from the metal concentration in the aqueous phase before extraction and from the organic phase after reextraction with sulfuric acid.

The extraction yield (R/%) can be calculated using the relation  $R = (D / D + 1) \cdot 100\%$ . For the extraction constant  $K_{ex}$ , the equation:  $-\log K_{ex} / n = pH_{0.5} + \log c_{HL}$  is valid. The distribution coefficient and extraction constant are connected by the relation  $\log D = n pH + \log K_{ex} + n \log c_{HL}$ . The slope  $n$  of the function  $\log D = f(pH)$  corresponds to the number of coordinated ligands. The solubility of the different compounds in kerosene was determined gravimetrically.

## RESULTS and DISCUSSION

Some results of the metal extraction are collected in table 1.

TABLE 1  
Extraction data of 4-Acylpyrazol-5-ones and  $\beta$ -Diketones

name	pH <sub>0.5</sub>				lg K <sub>ex</sub>			
	Cu	Zn	Cd	Ni	Cu	Zn	Cd	Ni
<b>PYRAZOLONES</b>								
n-octanoyl-	1.85	6.00	6.60		0.30	-6.00	-7.20	
stearoyl-	1.40	5.45	7.00	6.70	1.20	-4.90	-8.00	
2-ethylhexanoyl-	2.05	5.80	8.20		-0.10	-5.90	-10.4	-7.40
butanoyl-	2.55	*			-1.20			
octadecenoyl	1.85	5.15	6.95		0.20	-4.30	-7.90	
<b><math>\beta</math>-DIKETONES</b>								
n-octanoyl-	4.25	6.80	*		-4.50	-7.60		
2-ethylhexanoyl-	4.10	*	*		-4.20			
cyclopentylpropyl-	4.32	*	*		-4.64			
cyclohexylacyl-	3.75	7.05	*		-3.50	-8.10		
p-hexylphenyl-	3.95	6.45	*		-3.95	-6.90		
1-phenyl-2-hexyl-	4.75	*	*		-5.50			
LIX 54*	3.90	6.55	*		-3.80	-7.10		

\* Extraction rate less than 50 %

Apparently 4-acylpyrazolones are able to extract metal ions from stronger acidic solutions than the corresponding  $\beta$ -diketones. With regard to the influence of the substituents, a dependence on chain length and on the kind of branching can be seen. The nature of the substituent also accounts for the solubility of the extractant and its metal compound. This fact is demonstrated by fig. 1 for the extractants and is also found for their copper complexes. In both cases, a medium number of C-atoms of the substituent is favourable versus very lower or higher numbers. A similar experience is true for the kind of diluent. Fig. 2 shows that besides isobutyl-methylketone, n-paraffins have clear advantages in comparison with halogenated or aromatic hydrocarbons. This seems to be a result of similar alkyl chains in the extractant as well as in the solvent.

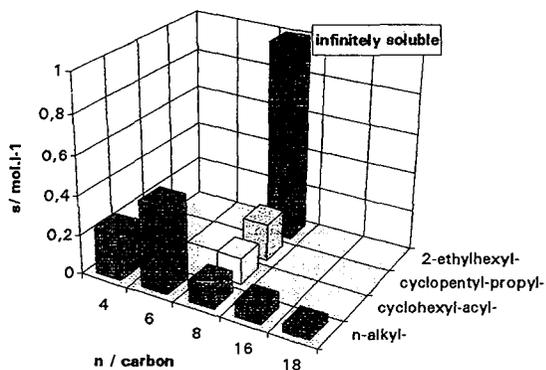


Fig. 1 Solubility of different 4-acyl-5-pyrazolones in kerosene

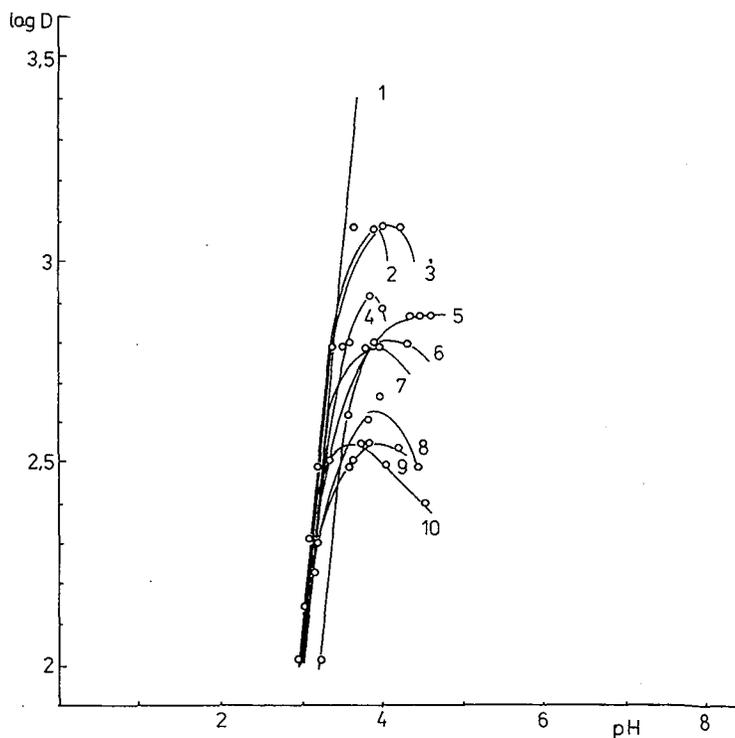


Fig. 2 Extraction of copper with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone in different solvents (1= isobutylmethylketone, 2= parex<sup>®</sup>(-n-paraffin fraction of C<sub>12</sub>-C<sub>18</sub>, PCK Schwedt), 3= cyclosol<sup>®</sup>(aromatic/aliphatic paraffins, Shell), 4= n-decane, 5= kerosene, 6= chloroform, 7= i-octane, 8= n-hexane, 9= toluene, 10= benzene)

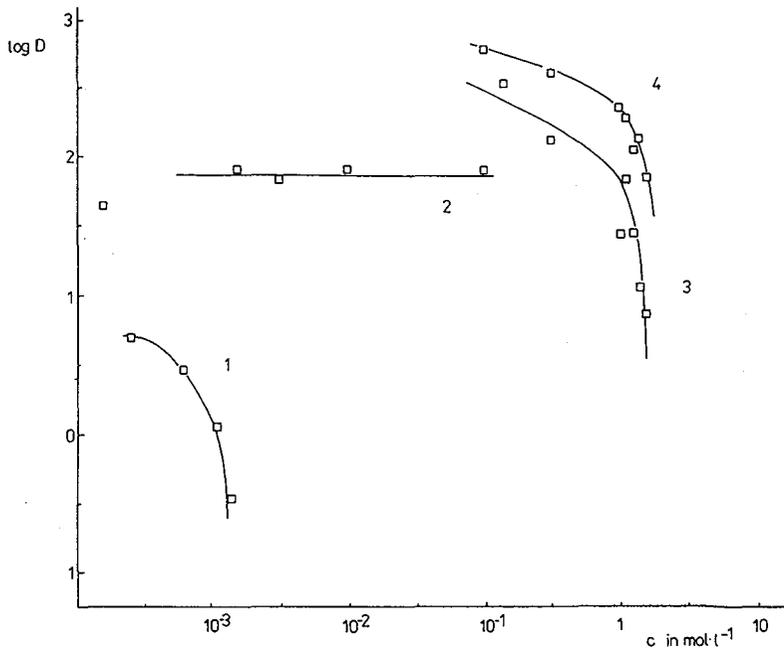


Fig. 3 Extraction of copper from different complex-forming agents in the aqueous phase  
 $\log D = f(c_i)$  1 = CN<sup>-</sup>; 2 = tartrate; 3 = NH<sub>3</sub>; 4 = Cl<sup>-</sup>

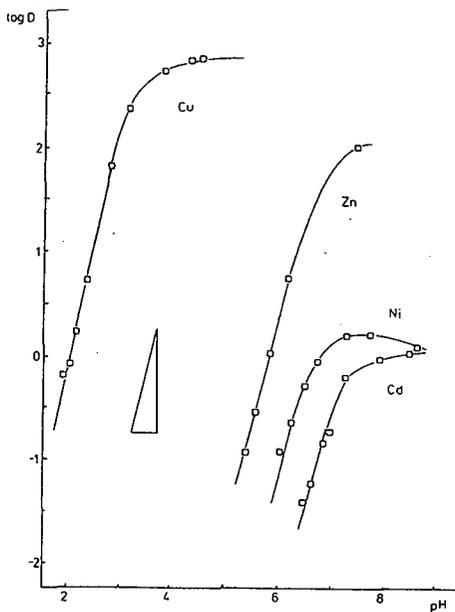


Fig. 4 Separation of metals with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone  
 $\log D = f(\text{pH})$

The dependence of the metal extraction on competing ligands in the aqueous phase is shown by fig. 3. While strong ligands such as cyanide already in small concentrations prevent the extraction, tartrate promotes the reaction because hydrolysis of the metal ions at intermediate pH-values is avoided. Ammonia and chloride hinder the extraction only at higher concentrations. The following order was found: cyanide > tartrate > ammonia > chloride which corresponds to the general complex stability.

The fig. 4 shows the possibility of a selective separation of the studied metals using 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone as extractant. All compounds are extracted as  $ML_2$  and the sequence of extraction is  $Cu > Zn > Ni > Cd$ . Good separations are found for copper and zinc from nickel and cadmium.

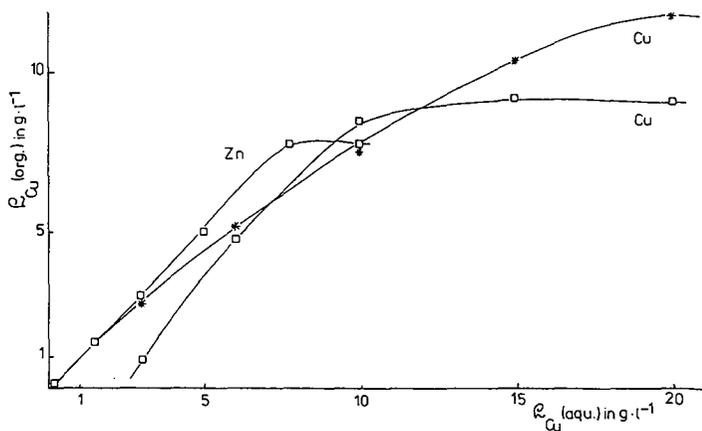


Fig. 5 Extraction isotherm of copper and zinc with 4-acyl-5-pyrazolones  
 $pH_{Cu} = 4.4$        $pH_{Zn} = 7.1$        $w_{HL} = 10\%$  \* LIX 54

The isotherms for the copper and zinc extraction are given in fig. 5. In the case of zinc the loading of the organic phase is limited to  $7.7 \text{ g} \cdot \text{L}^{-1}$  whereas the loading capacity with copper is up to  $9.2 \text{ g} \cdot \text{L}^{-1}$ . This amount is not so far from the loading capacity of  $11.85 \text{ g} \cdot \text{L}^{-1}$  found for LIX 54. The loading of the organic phase is limited by the precipitation of the metal chelates at the interface. Such problems cannot occur with the oily copper complexes of long-chain  $\beta$ -diketones. The extraction results of Zn, Ni and Cd with  $\beta$ -diketones are however unsatisfactory.

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## EXTRACTION OF NICKEL USING SAPONIFIED VERSATIC 10

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### ABSTRACT

The phase equilibria corresponding to the preneutralization stage in a metal extraction process using Versatic 10 (Shell Chemicals Co.) extractant is studied. Concentrated aqueous ammonia is used as the neutralizing agent and under such conditions the extractant forms a one-phase solution with the solvent and water, which when contacted with more water forms a microemulsion. The kinetics of nickel extraction utilizing the microemulsion has been studied in a vigorously agitated concurrent column with fast phase separation. The break up of the micellar structures is followed by measuring the decrease of water and ammonia in the outlet organic phase. The rate of extraction proved to be very fast. In most experiments, 90% of the nickel at equilibrium is extracted in less than 15 seconds. The fast rate is explained by a macroscopically homogeneous exchange between  $\text{Ni}^{2+}$  and  $\text{NH}_4^+$  in the microscopically structured media. If the stoichiometric requirements are fulfilled, the final organic phase is free from ammonia. Some water of hydration remains in the organic phase, typically the mole ratio  $\text{H}_2\text{O}:\text{Ni}$  is between 1.2 and 2.0.

### INTRODUCTION

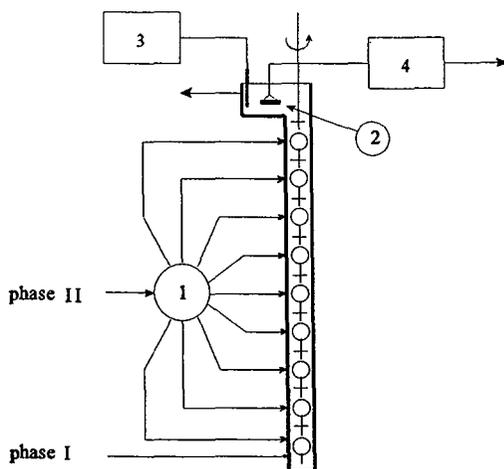
The metal extractant Versatic 10 (Shell Chemicals Co.) is a synthetic tertiary carboxylic acid. The acid is composed of a mixture with highly branched isomers of  $\text{C}_{10}$  monocarboxylic acids. It can be synthesized in large quantities and similar products have a wide field of application other than as metal extractants. It is environmentally adequate, but as an extractant, Versatic 10 is known to be used in only a few applications. The possible reason is that the extractant suffers from the drawback that it is too soluble in water in alkaline conditions (see eg. Inoue et al., 1980). As Versatic 10 extracts nickel from sulfate solutions at pH values above 6, the extractant is entrained with the raffinate if no precautions (e.g. an extra scrubbing stage) are put into practice.

When the extractant is used in the  $\text{H}^+$ -form the pH tends to decrease during the cation exchange reaction requiring neutralization. If Versatic 10 is used as its sodium or ammonium salt forms the exchange reaction will be  $2 \text{Na}^+ \rightarrow \text{Ni}^{2+}$  or  $2 \text{NH}_4^+ \rightarrow \text{Ni}^{2+}$ , respectively, and the need of pH control in the mixer can be avoided. In the saponification (or preneutralization) stage, however, the extractant forms microscopic aggregates typical of surfactant systems that is reflected in the solubilization of water into the aqueous phase. We have previously studied the phase behavior and characterized these types of aggregates in several extractant systems (Paatero and Sjöblom, 1990). The present work describes the phase behavior in the preneutralization stage of Versatic 10 using aqueous ammonia and the kinetics of the consecutive extraction of nickel is reported.

## EXPERIMENTAL

**Phase equilibria.** The components were mixed in sealed test tubes (8 or 15 mL). The location of the phase boundary (Figures 2 to 4) was determined in most cases by titrating a Versatic/isooctane mixture with aqueous ammonia and the phase transition was visually detected as clouding. Close to the water corner a two-phase system was titrated either with isooctane or Versatic and the phase transition  $2L \rightarrow L$  was recorded.

**Kinetic experiments.** The rate of nickel extraction was determined using a concurrent jacketed glass column ( $h=300$  mm,  $d_i=15$  mm) through which water at  $25.0 \pm 0.2$  °C was circulated (Fig. 1). The column consisted of 10 compartments with individual stirring blades. The rotor speed was 1500 rpm. Phase I was fed from the bottom. The location of the input for Phase II was varied enabling the change of contact time ( $\tau$ ) between 2 and 165 s. In the kinetic runs reported in this work Phase I was the aqueous phase containing 20 g Ni/L added as  $\text{NiSO}_4$ , with a pH of 4.36. Phase II consisted of 40 w-% Versatic 10 in isooctane, which was preneutralized to different degrees using 14 mol/L ammonia water. The total flow rate was between 20 and 40 mL/min. At the top of the column the organic phase was drawn through a hydrophobic filter (0.4  $\mu\text{m}$  PTFE flat membrane,  $d=25$  mm) and the nickel content in the organic phase was continuously monitored by an X-ray fluorescence analyzer (Outokumpu X-MET 880 with a  $\text{Cm}^{244}$  flow-through probe). When a steady state was obtained, samples of the aqueous and organic streams were taken. The nickel contents were determined by atomic absorption spectrometry. The water and ammonia contents in the organic phase were analyzed by gas chromatography using a 0.1 m Chromosorb 102 precolumn and a 3 m Chromosorb 103 column and a TC-detector. At low levels, ammonia was analyzed using the spectrophotometric indophenol method (VDI, 1974) and water by Karl Fischer titration.



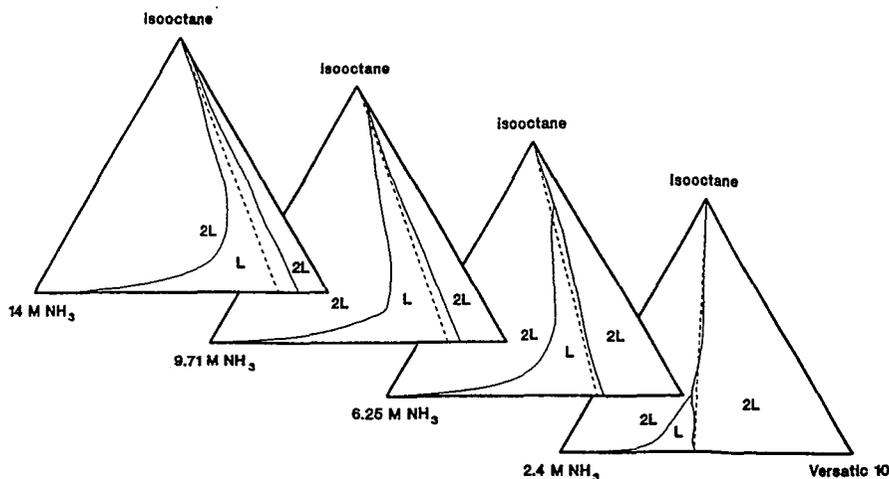
**Figure 1.** Multicompartment reactor used in the kinetic experiments. (1) 10 port valve; (2) hydrophobic filter; (3) pH meter; (4) XRF-detector.

## RESULTS

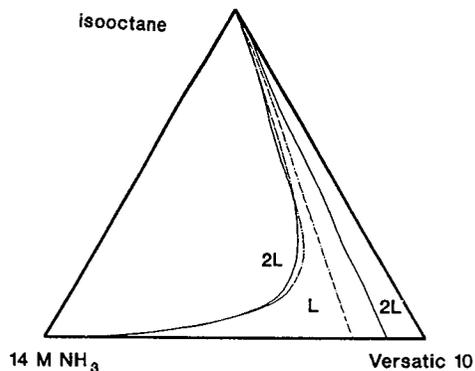
### Phase Equilibria.

Partial phase diagrams corresponding to the preneutralization of Versatic 10 with aqueous ammonia were determined at four fixed ammonia concentrations ranging from 2.4 to 14 mol  $\text{NH}_3/\text{L}$ . The latter limit corresponds to the solubility of  $\text{NH}_3$  in water at 25 °C. In the pseudo ternary phase diagrams in Figure 2, the one-phase region (L) is formed at a  $\text{NH}_3$ :Versatic ratio of 1:2, i.e., at a degree of neutralization,  $N$ , of 50%. In the system where 14 mol  $\text{NH}_3/\text{L}$  is used the solution inside the one phase region contains only little water, at  $N=50\%$  the hydration number is about 3 calculated on the ammonium carboxylate. The water is bound to the  $\text{NH}_4^+$  counter ion, but when the system is diluted with water, free water is solubilized and the solution becomes a microemulsion. The microemulsion channel is surrounded on both sides with two-phase regions. On the right hand side is a Winsor II system, i.e. a micellar organic phase is in an equilibrium with a normal aqueous phase ( $\text{O}_m/\text{W}$ ) and on the left there is a Winsor I system, i.e. a micellar water phase is in an equilibrium with a normal organic phase ( $\text{O}/\text{W}_m$ ). In the 2.4 mol  $\text{NH}_3/\text{L}$  system the one-phase region is very small. However, the phase inversion from a WII - WI is also detectable here and its position is indicated in the diagrams with a solid line extending from the top of the one-phase region to the isooctane corner. No liquid crystalline phases were observed in these systems unlike in the corresponding systems based on the organophosphorus extractants DEHPA, Ionquest 801, and Cyanex 272 reported earlier (Paatero and Sjöblom, 1990).

The effect of nickel on the phase equilibria was studied by adding solid  $\text{NiSO}_4 \cdot 5\text{H}_2\text{O}$  into the water( $\text{NH}_3$ )/Versatic10/isooctane system. The one-phase region becomes narrower (Fig. 3). The width was further mapped at a fixed extractant content (40 w-% Versatic in isooctane) but with varying degrees of neutralization (the ordinate in Fig. 4) and varying nickel contents (the abscissa in Fig. 4). The two figures show that at low metal loading the system remains as one phase. According to Figure 4 the maximum loading inside the one phase microemulsion is about 0.06 mol Ni/mol Versatic. When  $N$  is less than 100%, the upper phase remains micellar to even higher loading. If  $N > 100\%$  the extractant

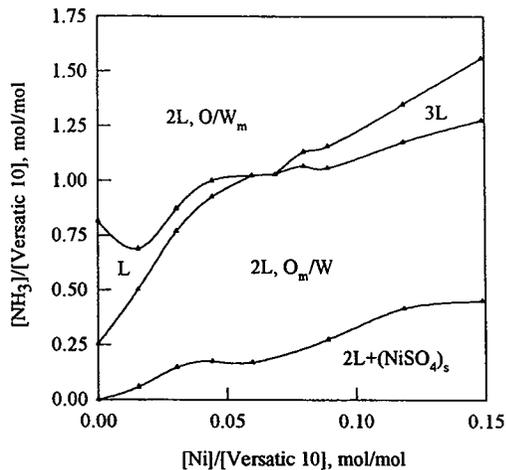


**Figure 2** Partial phase diagrams for the system water( $\text{NH}_3$ )/Versatic/isooctane at different ammonia concentrations in water at 25 °C. The dotted lines show  $\text{NH}_3$ :Versatic mole ratio 1:2.



**Figure 3** Effect of nickel on the phase behavior. The solid lines show the one phase region (L) without nickel. The dotted lines border the one phase region when the system contains 1.5 mol-% nickel calculated on the amount of Versatic.

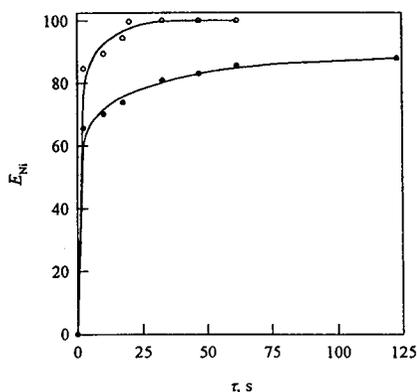
distributes into the aqueous phase as normal micelles. These equilibrium data imply that during the initial stages of the nickel extraction, the reaction must go through a macroscopically homogeneous stage. The solution is a microemulsion, where the reaction takes place at the microscopic interface on the amphiphilic aggregates. In such systems the exchange of bound water and bulk water is extremely fast (Friberg 1987). The above mechanism presumes that the mass transfer limitations are minimized as is the case in the vigorously agitated column used in this work.



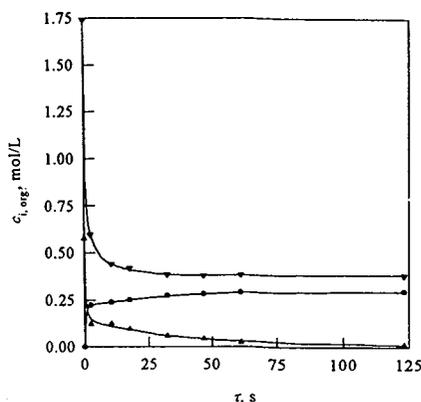
**Figure 4** The effect of nickel on phase equilibria at a fixed mass fraction of Versatic 10 ( $w=40\%$ ). An aqueous solution containing 14 mol/L  $\text{NH}_3$  is used for the neutralization.

### Nickel Extraction Kinetics

When preneutralized Versatic 10 was used to extract nickel from a sulfate solution the rate of nickel transfer into the organic phase was very fast as can be seen in Figure 5. The corresponding decrease of water and ammonia from the organic phase is plotted in Figure 6.



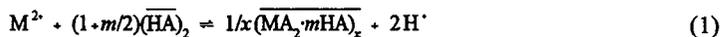
**Figure 5** Extraction of nickel using Versatic 10 neutralized to 33% (•) and 50% (◦).



**Figure 6** Extraction of nickel (•) into organic phase and the simultaneous transfer of  $\text{NH}_3$  (▲) and  $\text{H}_2\text{O}$  (▼) out of the organic phase when  $N=33\%$ .

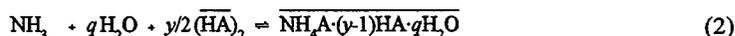
### DISCUSSION

Regardless whether the extractant is neutralized *in situ* or used as the ammonium salt, the same metal complexes are expected to be formed at equilibrium. The stoichiometries of the complexes are well characterized in the literature. The general stoichiometric relationship in the extraction of divalent metals by free carboxylic acids as reported by Fletcher and Flett (1964) is described in the general form as:

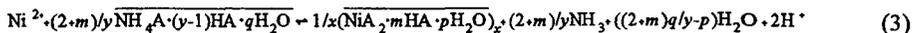


For nickel, Tanaka et al (1969) report that  $m=2$  or 4. The higher value is predominant at low metal concentrations. The lower is valid at high metal concentrations as the nickel carboxylate is dimeric ( $x=2$ ) (Wase et al. 1993). It is generally agreed that the nickel may be partially hydrolyzed or hydrated in the organic phase (van der Zeeuw (1979), Pouillon and Doyle (1988) and Preston (1985)).

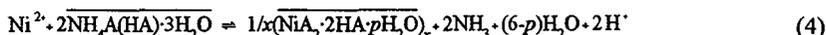
In the present case when the extractant is partially preneutralized, the stoichiometry for the neutralization is



For simplicity, ammonia is regarded to exist only as a neutral molecule in the aqueous phase. Inside the one-phase region  $N=50\%$  and consequently  $y=2$ . If concentrated aqueous ammonia (14 mol/L) is used  $q$  becomes equal to 3. When contacted with an aqueous nickel solution, the ion exchange stoichiometry becomes



In the kinetic experiment presented in Fig. 5 a stoichiometric amount of ammonia was used ( $N=50\%$ ) and the final Ni:Versatic ratio became 0.25 which corresponds to  $m=2$ .



If the stoichiometric requirements are fulfilled, the final organic phase is free from ammonia, but in all experiments in the present work some water remained in the organic phase, the mole ratio  $\text{H}_2\text{O}:\text{Ni}$  being about 1.2 to 2.0. During the initial moments of contact the microemulsion is formed and  $p$  and  $x$  increase. During the ion exchange the aggregates break up and  $x$  and  $p$  obtain their final values of  $x=1$  (or 2) and  $p < 2$ .

### SYMBOLS

$c$	concentration, (mol/L)
$E$	fraction extracted, $=100 \cdot (n_{\text{Ni}})_{\text{org}} / (n_{\text{Ni}})_{\text{aq, initial}}$
L, 2L, 3L	regions where one, two, or three liquid phases are in equilibrium
$n$	amount of substance, (mol)
$N$	degree of neutralization, $=100 \cdot n_{\text{NH}_3} / n_{\text{HA}}$
$O, O_m$	normal organic phase, micellar organic phase, respectively
$W, W_m$	normal water phase, micellar water phase, respectively
$w$	mass fraction (%)
$\tau$	contact time(s)

### ACKNOWLEDGEMENTS

A grant from the Outokumpu Research Foundation to E.J. is gratefully acknowledged.

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## CPC: Tool for Practical Separation of Metals and Fundamental Investigations of Chemical Mechanisms

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### ABSTRACT

Centrifugal Partition Chromatography (CPC) is a multistage countercurrent liquid-liquid distribution technique that is ideally suited for, not only separating closely related metal ions, but also for discerning fundamental kinetic and equilibrium problems associated with such separations. The examples of complete separations that will be presented include the trivalent lanthanides, platinum group metals (PGM) including their oxidation states and chloroanions, and the transition metals, using monodentate and polydentate ligands (8-quinolinols, acylpyrazolones, hydroxyoximes, alkylphosphonic acids, and phosphine oxides) and ion-pair extractants (tetraalkylammonium and protonated phosphine oxide systems). In addition to these separations which can be achieved under mild conditions, the CPC chromatograms also provide information on the equilibrium and kinetics of the metal complex formation and dissociation reactions. The reduced plate height characterized by the parameter CETP (channel equivalent of a theoretical plate) provides a tool in predicting the chemical mechanisms that limit the CPC efficiencies. The mechanisms of the metal complex dissociation reactions can be derived by an evaluation of the CETP as a function of the concentrations of the species in the organic and aqueous phases. These mechanisms have been correlated with those from kinetic experiments in micelles using stopped flow and in highly mixed two phase systems examined by spectrophotometry with the aid of the microporous teflon phase separator (MTPS). A linear correlation between the  $CETP_{ck}$  (reduced plate height due to slow chemical kinetics) and  $t_{1/2}$  (half-life) measured by stopped flow and MTPS were found. In addition, the interfacial areas generated and the size of the mobile phase droplets in the CPC experiments could be calculated from these correlations. The work in our laboratory to date has demonstrated the versatility of CPC as a tool for separation and for gaining fundamental understanding of metal extraction processes. CPC is also a useful technique for understanding the separation of metals by conventional liquid chromatography and solvent extraction flow injection analysis.

### INTRODUCTION

The separation of metal ions by single stage methods, especially the closely related ones such as the trivalent lanthanides poses daunting challenges even to the most selective of extractants, Freiser(1988). Thus the use of multistage methods is necessary for their separation and one such technique is centrifugal partition chromatography (CPC), which is a liquid-liquid multistage countercurrent distribution technique, Armstrong(1988). The CPC apparatus manufactured by Sanki Engineering Company, Japan, consists of a series of cartridges, with each cartridge containing 40 - 400 channels depending upon the desired internal volume. These channels serve as a stage in the separation experiment and the total number of channels is between 400 - 4800 depending upon the number of cartridges employed. These cartridges are arranged in a rotor which is rotated at a certain speed (700 - 1200 rpm) and the centrifugal force generated keeps one of the two phases

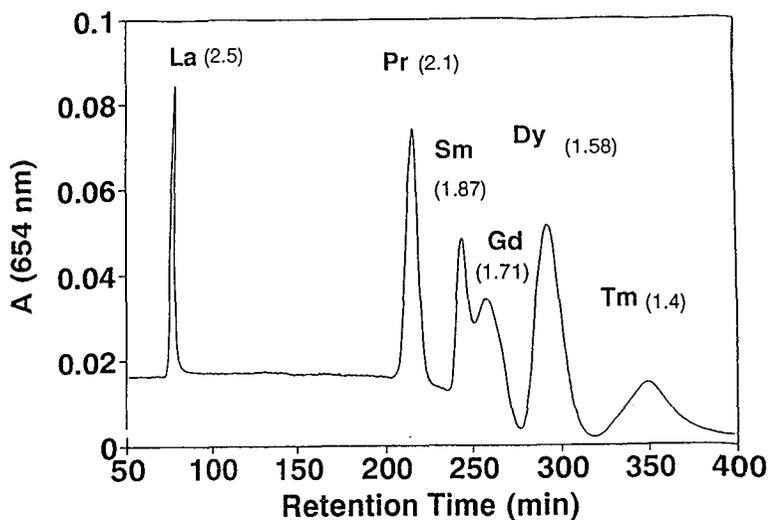
(usually the organic phase) stationary while the other phase (usually the aqueous phase) is moving through it at a constant flow rate. The injected analyte mixture is carried by the aqueous mobile phase into the cartridges where they are extracted into the organic stationary phase by simple distribution, or by complexation with a suitable ligand. The back-extraction can be conducted by isocratic or gradient elution and the eluted analytes can be detected by a suitable detection method such as uv-vis spectrophotometry. If the analytes are completely separated, they appear as discrete peaks, very much like those obtained in conventional chromatographic methods like HPLC, and hence it is called centrifugal partition chromatography. As such the traditional chromatographic methods of analysis are applicable for the CPC chromatograms. CPC is ideally suited for a complete separation of difficult to separate metal mixtures such as the lanthanides because of the following advantages: large number of stages (400 - 4800 depending upon the operational volume); high load capacity for extractants and analytes; negligible loss of extractants from the organic phase as bleeding of the stationary phase is minimal; flexible organic-aqueous phase volume ratios; and readily adaptable to pilot scale. The ratio of the volumes of the stationary and mobile phases in CPC is much bigger than in conventional LC.

Most importantly, CPC enables us to understand the factors influencing the slow chemical kinetic steps which limit the CPC efficiencies of metal separations. The quantity channel equivalent of a theoretical plate (CETP), which is a measure of the CPC inefficiency is the tool to such an understanding. The experimental CETP value of the metal ions comprises of a mass transfer and diffusion component (CETP<sub>diff</sub>), and a chemical kinetic component (CETP<sub>ck</sub>) which can be experimentally determined. The variation of CETP<sub>ck</sub> with flow rate of the mobile phase and concentrations of species in the aqueous and mobile phases identifies the slow chemical kinetic step and the location of such a step, i.e., in the bulk aqueous, or at the aqueous-organic interface or both. A direct correlation exists between CETP<sub>ck</sub> and the half-life ( $t_{1/2}$ ) of the slow kinetic step. It is also possible to determine the average size of the mobile phase droplets from such a correlation.

## SEPARATION OF METAL IONS

### Separation of Tervalent Lanthanides

The extractants that we have used in the separations of the lanthanides are an organophosphinic acid, bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and an acylpyrazolone, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP). The extractions of lanthanides were performed at pH values  $\leq 4$  to avoid the formation of hydroxide species of these metals. In this regard, Cyanex 272 ( $pK_a = 3.18$ ) and HPMBP ( $pK_a = 4.0$ ) are ideally suited for the extraction of lanthanides. The Cyanex 272 in organic solvents exists in dimeric form and the acylpyrazolone exists predominantly in its enol form due to inter/intramolecular hydrogen bonding. The separation of a mixture of light and heavy lanthanides with Cyanex 272 employing a pH gradient in the aqueous mobile phase is shown in Figure 1, Cai et. al.(1990), and the extraction equilibrium constants are given in Table 1 which also includes the values in the micellar pseudophase, Inaba et. al.(1993). The micellar pseudophase was employed to study the dissociation kinetics and to correlate CETP<sub>ck</sub> with the  $t_{1/2}$  for the dissociation reactions (vide infra). It is evident from Table 1 that the selectivity for adjacent lanthanides is better with Cyanex 272 than with HPMBP. Better extractibility was observed and poor selectivity was obtained in micelles.



**Figure 1.** Separation of light and heavy lanthanides with 0.1 M Cyanex 272 using the heptane-H<sub>2</sub>O phase pair employing a continuous aqueous pH gradient. The pH at which each lanthanide elutes is given in parenthesis.

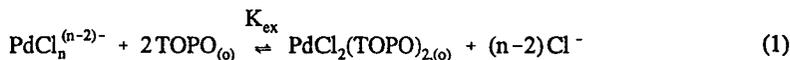
**Table 1.**  
Log K<sub>ex</sub> values for trivalent lanthanides in two phase systems and Triton X-100 micelles.

METAL	CYANEX 272		HPMBP	
	Micelles	SX*	Micelles	SX*
Pt <sup>3+</sup>	-1.72	-3.83	-0.87	-3.99
Eu <sup>3+</sup>	-0.19	-2.12	-0.61	-3.49
Tb <sup>3+</sup>	0.35	-1.22	-0.42	-2.86
Ho <sup>3+</sup>	0.79	-0.62	-0.15	-2.35
Yb <sup>3+</sup>	1.52	0.27	-0.06	-1.83

SX\* : solvent extraction. Cyanex 272 : Heptane-H<sub>2</sub>O; HPMBP : Toluene-H<sub>2</sub>O

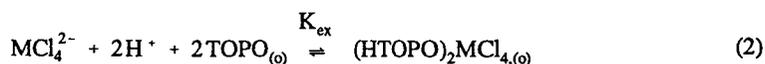
#### Separation of Platinum Group Metals (PGM)

The separation of Pd(II), Pt(II), Pt(IV), Rh(III), Ir(III) and Ir(IV) and the chloro species of Pt(II), namely PtCl<sub>2</sub>, PtCl<sub>3</sub><sup>-</sup> and PtCl<sub>4</sub><sup>2-</sup> have been achieved, Surakitbanharn et. al. (1991). A very important practical aspect of our work is that these separations were performed under relatively mild conditions in contrast to the traditional methods of the separation of PGM which involve harsh conditions such as high acidity. These separations were performed by complexation with trioctylphosphine oxide (TOPO) by ion-pairing with protonated TOPO (HTOPO<sup>+</sup>) and tetraheptyl p-toluenesulfonate (QpTS). The complex PdCl<sub>2</sub>(TOPO)<sub>2</sub> was exclusively formed irrespective of the nature of the Pd(II) chloro species in the aqueous phase, equation 1, where n = 2 - 4.



The  $K_{\text{ex}}$  values for  $\text{PdCl}_2$ ,  $\text{PdCl}_3^-$  and  $\text{PdCl}_4^{2-}$  respectively are  $794.3 \text{ dm}^6 \text{ mol}^{-2}$ ,  $2.75 \text{ dm}^3 \text{ mol}^{-1}$ , and  $0.14$ . A single peak was observed in the CPC chromatogram of Pd(II) at any concentration of Cl<sup>-</sup> as its hydrolysis equilibration is rapid. The corresponding values for the Pt(II) species are  $48 \text{ dm}^6 \text{ mol}^{-2}$ ,  $0.047 \text{ dm}^3 \text{ mol}^{-1}$  and  $0.018$  respectively, which clearly indicate the better extractibility of Pd(II) over Pt(II).

The ligand TOPO could be protonated at HCl concentrations greater than  $0.1 \text{ M}$ . The  $\text{HTOPO}^+$  extracted  $\text{PdCl}_4^{2-}$  and  $\text{PtCl}_4^{2-}$  as ion-pairs  $(\text{HTOPO})_2\text{MCl}_4$  ( $\text{M} = \text{Pt}$  or  $\text{Pd}$ ) and seen in equation 2.



The chromatogram of the separation of  $\text{RhCl}_6^{3-}$ ,  $\text{PdCl}_4^{2-}$  and  $\text{PtCl}_4^{2-}$  by  $\text{HTOPO}^+$  is shown in Figure 2. The  $K_{\text{ex}}$  values of Pd(II) and Pt(II) are  $93.3 \text{ dm}^{12} \text{ mol}^{-4}$  and  $1961 \text{ dm}^{12} \text{ mol}^{-4}$ , respectively indicating that Pd(II) elutes ahead of Pt(II) in the ion-pair separation while the opposite is true in the separation by complexation. While the chromatogram of Pt(II) is exclusively due to the formation of  $(\text{HTOPO})_2\text{PtCl}_4$ , the chromatogram of Pd(II) is due to the formation of  $(\text{HTOPO})\text{PdCl}_3$  as well. In fact, under the experimental conditions employed, this is the major Pd ion-pair species extracted. The extraction equilibrium constant for  $(\text{HTOPO})\text{PdCl}_3$  is  $18.25 \text{ dm}^3 \text{ mol}^{-1}$ . Similarly Pt(IV) and Ir(IV) could be separated by  $\text{HTOPO}^+$  by ion pair formation with their  $\text{MCl}_6^{2-}$  species. The  $K_{\text{ex}}$  values for the Pt(IV) and Ir(IV) species are  $1576 \text{ dm}^{12} \text{ mol}^{-4}$  and  $8035 \text{ dm}^{12} \text{ mol}^{-4}$  respectively.

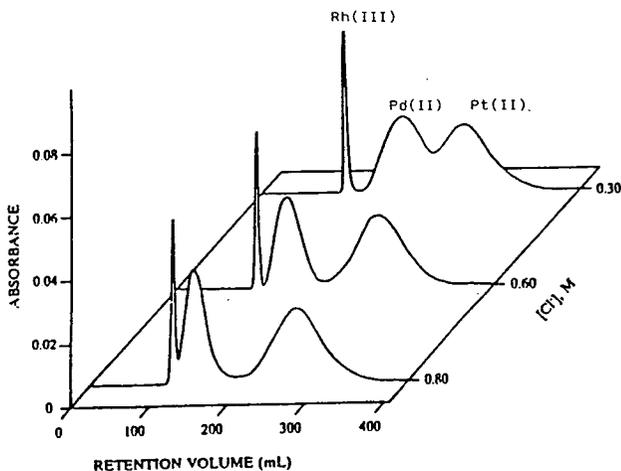
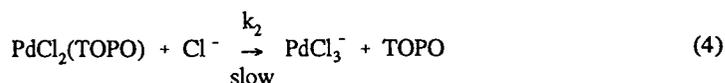
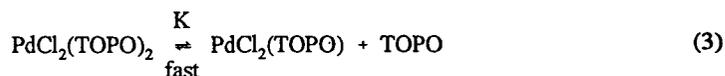


Figure 2. Separation of Rh(III), Pd(II) and Pt(II) as their chloro anions with  $\text{HTOPO}^+$ , as a function of  $[\text{Cl}^-]$ .  $[\text{TOPO}] = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ , aqueous flow =  $4 \text{ cm}^3 \text{ min}^{-1}$ .

## CHEMICAL KINETICS AND CPC EFFICIENCY

The  $CETP_{ck}$  values determined by varying the concentrations of the species in the aqueous and organic phases clearly showed that the slow back-extraction kinetics of the metal complexes was indeed responsible for the broad CPC chromatograms. The dependency of  $CETP_{ck}$  on the concentrations of species in the aqueous and organic phases could be used to derive a mechanism for the dissociation of the metal complexes. The mechanism of the dissociation of the  $PdCl_2(TOPO)_2$  is shown in equations 3 - 5, with equation 4 being the rate-limiting step, Surakitbanham et. al. (1991).



This result was independently verified by studying the dissociation of  $PdCl_2(TOPO)_2$  in Triton X-100 micelles using the stopped flow technique, as this reaction was too fast for conventional spectrophotometric kinetic measurements. The dissociation reactions with half-lives in the millisecond - second range can adversely affect the CPC efficiencies. A very significant finding of this work is that a linear relationship exists between  $CETP_{ck}$  and  $t_{1/2}$  as shown in Figure 3 for the Pd(II)-TOPO system. Since the  $CETP_{ck}$  values are a measure of the half-lives of the slow dissociation steps in the metal complex dissociation reactions, CPC is a useful tool for examining such reactions. The analysis of the band widths of the CPC chromatograms indicates that forward and back-extraction reactions that appear to be rapid in single-stage equilibrations may still be slow enough to reduce the efficiency of the multistage separation.

The  $CETP_{ck}$  vs.  $t_{1/2}$  for the trivalent lanthanides, Inaba et. al.(1994) and Ni(II) (ligand: HPMBP), Chen et. al.(1994) are also shown in Figure 3. It is clear that for the different metal-ligand systems examined, the same CPC band width represents a different  $t_{1/2}$  value for each system. In many metal-ligand systems we are forced to correlate  $CETP_{ck}$  values with  $t_{1/2}$  values from the micellar system because the dissociation reactions are too fast to be studied by conventional spectrophotometry. The  $K_{DC}$  (distribution constant of the metal complex) values are different in the two-phase system from the micellar pseudophase system. Further more, we are comparing a system with a combination of bulk and interfacial kinetics (CPC), with a system that has predominantly interfacial kinetics (micelles). Thus the slope of the  $CETP_{ck}$  versus  $t_{1/2}$  plot will vary depending on the extent of the mixed bulk and interfacial reactions in the CPC experiments, and the magnitudes of the bulk and interfacial rate constants.

The  $CETP_{ck}$  versus  $t_{1/2}$  plot for the Ni(II) system involved both the CPC and kinetic measurements in the  $CHCl_3$ - $H_2O$  system and the slope obtained for this line was +1. This

relationship enables the determination of the specific interfacial area generated and hence the size of the mobile phase droplets in the CPC experiments. The specific interfacial area obtained was  $207.7 \text{ cm}^{-1}$  which corresponds to an average mobile phase droplet radius of  $144 \text{ }\mu\text{m}$  ( $r=3/\text{specific interfacial area}$ ). This area is similar to the area generated in a highly stirred two-phase system at a stirring rate of 3500 rpm for Ni(II)-HPMBP in the  $\text{CHCl}_3\text{-H}_2\text{O}$  system. This radius is smaller than the radius of the capillary duct through which the mobile phase droplets enter the channels ( $450 \text{ }\mu\text{m}$ ), and much larger than the value obtained using Stoke's law ( $7.4 \text{ }\mu\text{m}$ ).

The studies described here clearly indicate the usefulness of CPC as a tool for the separation of metal ions and for investigation of the chemical mechanisms.

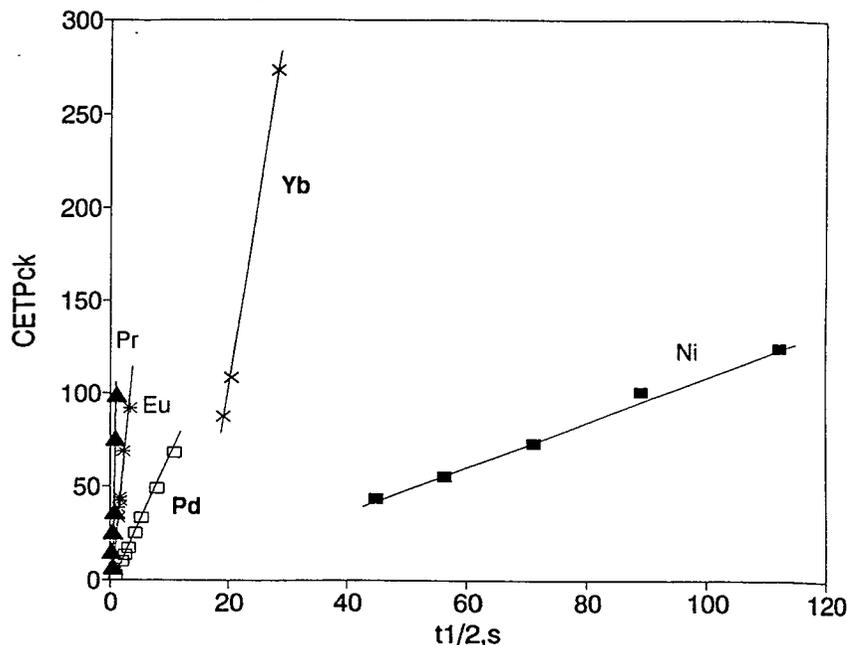


Figure 3.  $\text{CETP}_{ck}$  vs.  $t_{1/2}$  for Pd, Pr, Eu, Yb and Ni.

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## SOLVENT EXTRACTION OF RUTHENIUM BY A MONO N-SUBSTITUTED AMIDE

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### ABSTRACT

For the Platinum Group Metals (PGM) chemist ruthenium is probably the most interesting of the PGM due to its very diverse chemistry with stable compounds being known for the metal in at least nine different oxidation states. Despite this the separation of ruthenium by the various PGM refiners has generally been based on the potentially hazardous distillation as its volatile oxide.

This paper outlines the results of preliminary studies aimed at the development of a non-hazardous solvent extraction process. The extraction of ruthenium chloro and nitrosyl complexes by a novel mono N-substituted amide has been investigated. In both cases unexpected extraction behaviour has been observed and the way in which this related to the chemistry of the ruthenium species formed in aqueous solution is discussed.

### INTRODUCTION

For the PGM Chemist ruthenium is probably the most interesting of the PGM. This is due to the fact that it possesses the most diverse chemistry of all of the PGM. Not only does it manifest the widest oxidation state range of the PGM with stable complexes known in at least eleven oxidation states, but also the species formed often differ significantly. In particular it forms very stable complexes with ligands such as oxo, nitrido and nitrosyl which, with the exception of osmium, are not readily formed with the other PGM. Furthermore, it readily forms polymeric species with bridging ligands.

Despite the very extensive chemistry available for ruthenium, its separation by the various PGM refiners has generally been based on distillation of its volatile tetroxide which forms under very highly oxidising conditions. The distillation is highly selective for ruthenium and osmium and can also be highly efficient. Ruthenium tetroxide is a highly toxic and potentially unstable molecule which is also a very powerful oxidant reacting violently with organic materials. Despite these properties the distillation of ruthenium tetroxide is perfectly safe, providing the equipment is very carefully designed and correctly operated, and the process has been successfully operated by a number of companies over many years. The process is, however, fairly unforgiving and problems can occasionally occur. There has consequently always been an interest in an alternative non-hazardous route.

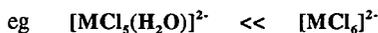
### SEPARATION OF PRECIOUS METALS BY SOLVENT EXTRACTION

Chloride is the only common media into which all the precious metals, except silver, can be efficiently brought into solution. The separation of the precious metals from both each other and the

accompanying base metals is then achieved by exploiting the differences in the chloro complexes formed. These chloro complexes are normally anionic and over the last thirty years techniques have been developed to exploit the differences in anion-exchange behaviour of the various species formed. Initially ion-exchange resins were employed. These have, however, been largely supplanted by solvent extraction using liquid anion-exchangers which offer much higher selectivity and increased efficiency. The order of extraction of the precious metal chloro complexes by anion-exchangers is



This is believed to be due to the fact that it is more difficult to pack three bulky organic cations around a  $[\text{MCl}_6]^{3-}$  anion than two for  $[\text{MCl}_4]^{2-}$  or one for  $[\text{MCl}_4]^-$ . These steric effects may also partly explain the difference in the extraction behaviour of  $[\text{MCl}_6]^{2-}$  and  $[\text{MCl}_4]^{2-}$ . The precious metals can also form aquated species in which one or more of the chloro ligands are substituted by aqua groups. Due to the hydrophobic nature of the organic phase these aquated species are very poorly extracted compared with a chloro-complex of similar size and charge.



The separation of the precious metals by solvent extraction is based on manipulating the oxidation states of the PGM in order to exploit the differences in the size and charge of the complexes formed, and hence their anion-exchange behaviour, together with differences in their kinetic behaviour (Grant,1990). In the flowsheet operated by Precious Metals Refiners, gold is extracted first followed by palladium and platinum. Ruthenium is separated by distillation as tetroxide followed by iridium extraction leaving rhodium to be separated from the remaining base metals. Other PGM refiners flowsheets exploit similar chemistry but in the case of the INCO (Barnes and Edwards,1982), Heraeus (Muller,1993) and the new Impala (Anon.,1995) flowsheets the ruthenium is distilled either at the start or immediately after the separation of gold. These flowsheets all have the obvious disadvantage that the recovery of the far more economically significant platinum (\$465 ozT<sup>-1</sup>) and palladium (\$165 ozT<sup>-1</sup>) is delayed by the earlier separation of ruthenium (\$25 ozT<sup>-1</sup>).

#### RUTHENIUM CHLORO COMPLEX CHEMISTRY

All of the PGM in their tetravalent oxidation state form hexachlorometallate(IV) anions in acid chloride media. These complexes generally have high stability constants and aquation only becomes significant at extremely low chloride concentrations. The exception is ruthenium whose mono aqua complex is unstable and undergoes polymerisation to form an oxo bridged dimer.



There have been very few reliable studies of ruthenium chloro-aqua chemistry due, not least, to the fact that for many years this dimer was thought to be  $[\text{RuCl}_5(\text{OH})]^{2-}$ . Furthermore they are often contradictory. Based on these studies we believe that the chemistry of ruthenium in acidic chloride media (>1M Cl<sup>-</sup>) may be summarised by the reaction diagram presented in Figure 1. There are some reports (eg Woodhead and Fletcher,1962) that the dimer is present in Ru(IV) solutions in 6M hydrochloric acid media. Given that the majority of these solutions derive from the distillation of ruthenium tetroxide into hydrochloric acid, however, this may not represent the true equilibrium situation.

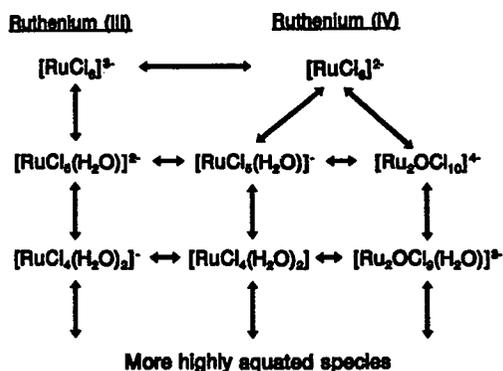
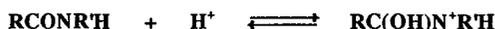


Figure 1. Reaction diagram for ruthenium in acid chloride media.

#### MONO N-SUBSTITUTED AMIDE EXTRACTANTS

As part of a programme to develop a "second generation" solvent extraction flowsheet for Precious Metal Refiners a wide range of potential extractants were synthesised and screened. This identified the novel mono N-substituted amides as being extremely effective reagents for the extraction of the PGM hexachlorometallate(IV) anions (Grant and Murrer, 1988). These amides are weak bases which undergo protonation in contact with strong acid forming an organic cation.



Consequently they are similar to conventional weak base extractants such as tributylphosphate(TBP) in that they can extract anions at high acidity whilst stripping can readily be achieved by reversing the protonation at low acidity. The variation in distribution coefficients is, however, much greater and not only are they much stronger extractants than TBP but they are also easier to strip.

The mono amides also show high selectivity for the tetravalent  $[\text{MCl}_6]^{2-}$  anions. In particular they show far higher selectivity for  $[\text{PtCl}_6]^{2-}$  over  $[\text{PdCl}_4]^{2-}$  which would allow the normal order of extraction of these two metals to be reversed which would result in a reduction in the platinum inventory. They are also highly selective over base metals such as copper and lead which also form  $[\text{MCl}_4]^{2-}$  anions as well as the trivalent PGM chloro complexes such as  $[\text{RhCl}_6]^{3-}$ . Consequently they are excellent reagents for the extraction of iridium(IV) (Grant, Burnham and Collard, 1990). Both the extractive power and the selectivity of the amides can be modified quite significantly by changing the steric bulk of both the carboxyl (R) and the N-substituent (R') and in this way the optimum extractant can be developed (Grant and Murrer, 1988). Preston and Du Preez (1993) have also confirmed our findings in their recent study of a range of amides.

#### EXTRACTION OF RUTHENIUM(IV) CHLORO COMPLEXES

During the early days of the development of the solvent extraction flowsheet for Precious Metal Refiners the extraction of ruthenium from oxidised process liquors was briefly investigated and it

was found that extraction was rather poor with less than 50% extraction being achieved. This incomplete extraction was attributed to the presence of the dimer ( $[\text{Ru}_2\text{OCl}_{10}]^{4+}$ ) which would be expected to be poorly extracted due to the high anionic charge relative to its size. Due to this complication it was therefore decided to retain the highly efficient although potentially hazardous distillation of ruthenium as the tetroxide.

Precious Metal Refiners have introduced the solvent extraction of iridium using a mono N-substituted amide into their flowsheet. It was observed rather surprisingly that the low levels of ruthenium remaining from the earlier distillation were on regular occasions very strongly extracted (>95%). As a result it was decided to re-evaluate the extraction of ruthenium in its tetravalent oxidation state.

An equilibrated Ru(IV) solution ( $10\text{g l}^{-1}$  Ru) was prepared by dissolving commercial "ruthenium trichloride" (actually a mixture of Ru(IV) complexes) in 6M HCl and then refluxing for 24 hours. Hydrogen peroxide was continually bled in to ensure that oxidation was maintained whilst the solution equilibrated. This solution was then extracted three times at 1:1 phase ratio using a 0.5M solution of the amide in Exxsol D-80 with 15% TBP added as a modifier.

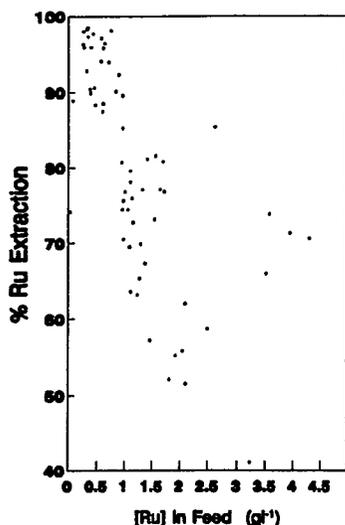


Figure 2. Effect of concentration of Ru in process feed on percentage extraction.

Analysis showed that only 38% of the ruthenium was extracted. Furthermore virtually all of this was extracted during the first contact suggesting that the majority of the ruthenium was present as a species which was not extracted. The absorption spectra were then run of both this non extractable species and the extracted species after stripping it into 0.5M acid. These were identified from comparison with literature spectra as  $[\text{Ru}_2\text{OCl}_{10}]^{4+}$  ( $\lambda_{\text{max}}$  385nm, 480nm) and  $[\text{RuCl}_6]^{2-}$  ( $\lambda_{\text{max}}$  475nm, 455nm, 415nm) respectively.

The reason for this much poorer extraction compared with that regularly observed on the plant was not initially obvious. When all the plant data was plotted graphically (Figure 2) it became evident that the level of extraction tended to decrease as the concentration of ruthenium in the feed increased.

This was investigated by preparing equilibrated Ru(IV) solutions containing varying levels of ruthenium. As can be seen from Table 1, the extraction of ruthenium from these solutions varied markedly with the concentration. A redox titration method was developed to measure the concentrations of the two species. This was based on the fact that the monomeric Ru(IV) species are readily reduced using titanium(III) chloride, as this does not involve a change in coordination, whilst reduction of the dimer involves the breaking of the oxo bridge which is slow even at elevated temperatures. Consequently it is possible to titrate the  $[\text{RuCl}_6]^{2-}$  selectively. The results (Table 1) show that the marked increase in % extraction with decreasing ruthenium concentration is the result of a considerable change in the ratio of the two species. This is believed to be due to the dimerisation reaction as this is the only equilibrium which is not independent of the ruthenium concentration. The marked change in the

ratio of the two species with concentration is undoubtedly another reason for the discrepancies in the papers published on the Ru(IV) chloro system.

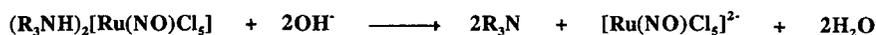
TABLE 1  
The effect of [Ru] in the feed on distribution of Ru(IV) species and % extraction

[Ru],g <sup>l</sup> <sup>-1</sup>	% Extraction	% [RuCl <sub>6</sub> ] <sup>2-</sup>	Ratio of [RuCl <sub>6</sub> ] <sup>2-</sup> : [Ru <sub>2</sub> OCl <sub>10</sub> ] <sup>4-</sup>
10	37.9	38.6	0.56 : 1
5	65.0	62.6	1.63 : 1
2	95.2	94.1	16.2 : 1

#### EXTRACTION OF RUTHENIUM NITROSYL COMPLEXES

Whilst it should be possible to achieve an efficient extraction from the Ru(IV) chloro system by operating at less than a gram per litre, this is not an attractive prospect due to the volumes involved. Consequently it was decided to look at an alternative system in which ruthenium is reputedly present as a single species. One unique property of ruthenium is that it forms exceptionally stable nitrosyl complexes containing the Ru(NO) moiety. The nitrosyl readily forms whenever ruthenium containing solutions are treated with nitric acid or any of a very wide range of compounds containing the NO group. Consequently the [Ru(NO)Cl<sub>5</sub>]<sup>2-</sup> complex is widely encountered particularly in analytical solutions where *Aqua Regia* has been employed to dissolve the sample. As a result the extraction of this complex has been widely investigated particularly by the Russians.

The extraction of this complex was also investigated and subsequently patented (Fieberg and Edwards, 1976) by the Council for Mineral Technology (MINTeK) as part of their solvent extraction flowsheet. Although high extraction efficiencies were reported with amine extractants, stripping was a problem. One option was to deprotonate the amine using an alkaline solution



but this creates problems with any base metals present hydrolysing and affecting phase separation. The other option was to displace the ruthenium using a strongly extracted anion such as perchlorate.



This has the disadvantage that the perchlorate must then itself be stripped using an alkaline strip before the extractant can be reused. The alternative is to extract with TBP which is easier to strip but is really too weak an extractant to efficiently extract the nitrosyl complex.

A solution of the nitrosyl was prepared by treating a Ru(IV) chloride solution according to the method disclosed in the MINTeK patent. This solution was then extracted three times under the same conditions as the above extraction of the Ru(IV) chloride solution. Analysis of the raffinate samples (Table 2) showed that the nitrosyl was efficiently extracted by the amide. It was observed, however, that as the extractions proceeded the colour of the aqueous changed from the bright purple of the [Ru(NO)Cl<sub>5</sub>]<sup>2-</sup> in the feed to an orange red in the third raffinate.

The feed was examined using low pressure column chromatography. This showed that there were two species present in the feed in approximately a 2:1 ratio. The first larger peak was purple and this was positively identified as [Ru(NO)Cl<sub>5</sub>]<sup>2-</sup> by collecting a fraction as it emerged from the

column and comparing its absorption spectrum. The second component was separated as a fraction using nitric acid as the eluent. It was then identified as  $[\text{Ru}(\text{NO})\text{Cl}_4(\text{H}_2\text{O})]^-$  by elemental analysis following precipitation as its silver salt. Although this species is known in the literature there are no reports of the fact that it is present at appreciable levels (*ca* 36%) in strong chloride media (6M).

The levels of the two species in the various samples were determined by chromatography and the distribution coefficients calculated (Table 2). These show that the tetra chloro complex is less strongly extracted than the penta chloro complex. Clearly the introduction of the aqua group more than cancels out the improvement in extraction which should come from the decrease in the charge from 2- to 1-. The distribution coefficients for the tetra chloro complex are, however, high enough that complete extraction could be achieved given extra contacts or a higher phase ratio.

TABLE 2  
Extraction of ruthenium nitrosyl complexes by 0.5M amide + 15%TBP in Exxsol D-80

	$[\text{Ru}]_{\text{total}}$ $\text{g l}^{-1}$	$[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$ $\text{g l}^{-1}$	$[\text{Ru}(\text{NO})\text{Cl}_4(\text{H}_2\text{O})]^-$ $\text{g l}^{-1}$	Distribution coefficients	
				$[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$	$[\text{Ru}(\text{NO})\text{Cl}_4(\text{H}_2\text{O})]^-$
Feed	10.113	6.420	3.693		
1st Raffinate	2.717	1.325	1.392	3.84	1.65
2nd Raffinate	0.572	0.150	0.377	7.85	2.69
3rd Raffinate	0.120	0.027	0.093	4.53	3.05

The loaded organics were combined and stripped using weak (0.5M) hydrochloric acid. Analysis showed that around 10% of the ruthenium remained "locked-up" in the organic after stripping. Determination of the levels of the two species in the strip showed that it was the tetra chloro complex which was "locking-up". This is believed to be due to either the amide or the TBP displacing the aqua group to give an organic soluble complex which will not then strip. Investigations are continuing into how to overcome the problem.

#### ACKNOWLEDGEMENT

The authors would like to thank Anglo American Platinum Corporation Limited for permission to publish this paper.

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## THE EXTRACTION OF RARE-EARTH ELEMENTS FROM HYDROCHLORIC ACID SOLUTIONS BY DI-(2-ETHYLHEXYL)-PHOSPHORIC ACID IN THE PRESENCE OF TRIOCTYL PHOSPHINE OXIDE OR PYRIDINE

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### ABSTRACT

The distributions of trivalent rare-earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium between hydrochloric acid solutions and solutions of di-(2-ethylhexyl)-phosphoric acid (DEHPA) + trioctyl phosphine oxide (TOPO) or pyridine (py) in kerosene have been examined under different conditions. Infrared and nuclear magnetic resonance spectra were made for the organic extracts. As a result, the addition of TOPO and py give the antagonistic and synergistic effects, respectively, on the extraction of rare-earth elements from hydrochloric acid solutions by DEHPA. For both extraction systems, however, the variation of the distribution coefficients for rare-earth elements plotted as a function of their atomic numbers reveals a tetrad effect curve similar to the extraction by DEHPA alone. It is also found that the separation factors of adjacent elements resemble each other.

### INTRODUCTION

As big progress has been made in the industrial applications of rare-earths, the separation of the rare-earth elements by solvent extraction has been extensively studied in various kinds of extraction systems. One of the present authors (Sato, 1989) has investigated the extraction system using acid organophosphorus compounds (di-(2-ethylhexyl)-phosphoric acid, DEHPA, and 2-ethylhexyl 2-ethylhexylphosphonic acid, EHEHPA). In this paper, the effect of the addition of trioctyl phosphine oxide (TOPO) or pyridine (py) on the extraction of the rare-earth elements from hydrochloric acid solutions by DEHPA has been investigated in order to obtain further information on the separation abilities of adjacent elements.

### EXPERIMENTAL

#### Chemicals

The DEHPA (Daihachi Chemical Industry Co., Ltd.) was purified by washing several times successively with 10 % sodium carbonate solution, 6 mol dm<sup>-3</sup> hydrochloric acid and water. TOPO (Hokko Chemical Industry Co., Ltd.) and pyridine (Koei Chemical Industry Co., Ltd.) were of high purity and were used without purification. These materials were used as the diluted solutions with purified kerosene (except for infrared (IR) spectrophotometry with n-hexane and for nuclear magnetic resonance (NMR) measurements with carbon tetrachloride). The stock solutions of rare-earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium were prepared by dissolving their chlorides, following the dissolution of their oxides (Shinetsu Chemical Industry Co., Ltd.) in concentrated hydrochloric acid and evaporating the hydrochloric acid to a selected concentration. Other chemicals were of analytical reagent grade.

### Extraction and Analytical Procedures

Equal volumes (15 ml each) of the organic solution and the aqueous solution of the chloride of the rare-earth element (generally  $1 \text{ g l}^{-1}$ ) were placed in  $50 \text{ cm}^3$  stoppered conical flasks and shaken for 10 min. After shaking, both phases were separated with a centrifuge and portions of them were pipetted to determine the distribution coefficient (the concentration ratio of the rare-earth element in the organic phase to that in the aqueous phase). The rare-earth element in the organic phase was stripped with  $1 \text{ mol dm}^{-3}$  hydrochloric acid in the presence of 2-ethylhexyl alcohol. The concentration of the rare-earth element was determined by EDTA titration using XO (xylenol orange) as an indicator. All experiments were carried out at  $20^\circ\text{C}$ .

### IR and NMR Spectral Measurements

IR spectra of the organic extracts were determined on a JASCO model IRA-1 using a capillary film between thallium halide plates. NMR spectra of the organic phases were obtained by a JEOL model JNM-PMX60SI NMR spectrometer using tetramethylsilane as an internal reference.

## RESULTS AND DISCUSSION

### Effect of TOPO Addition

The extraction of dysprosium(III) from hydrochloric acid solutions by DEHPA in kerosene gave the result that the distribution coefficient decreases with increasing aqueous acidity up to a concentration of hydrochloric acid of  $2 \text{ mol dm}^{-3}$ , suggesting that dysprosium(III) is taken up through a cation-exchange reaction liberating the hydrogen ion. At higher acidities, more than  $2 \text{ mol dm}^{-3}$ , the distribution coefficient is little influenced by acid concentration due to a solvating reaction (Sato, 1989).

The distribution behaviour of dysprosium(III) between DEHPA solutions in the presence of TOPO and aqueous hydrochloric acid solutions is presented in Fig. 1. This shows that the distribution coefficient in the presence of TOPO decreases remarkably with increasing TOPO concentration above  $\sim 0.025 \text{ mol dm}^{-3}$  (when the molar ratio  $[\text{TOPO}]/[\text{DEHPA}] = \sim 0.5$ ), indicating that the addition of TOPO gives an antagonistic effect for the extraction of dysprosium(III) by DEHPA at low aqueous acidity. At higher acidities, however, since the extraction is accompanied by a solvating reaction, the distribution coefficient does not depend on the addition of TOPO.

The synergistic enhancement of the extraction of uranium(VI) from aqueous solutions by a combination of acidic dialkyl phosphorus compound and nonionic phosphorylated reagent has been reported by a number of researchers (Marcus and Kertes, 1969). The antagonistic effect may be due to the specific interaction between DEHPA and TOPO or TBP which decreases the activity of DEHPA in the organic phase (Kandil et al., 1980). A similar specific interaction has been obtained in the synergistic effect of TBP for the extraction of uranium(VI) from sulfuric acid solutions by DEHPA (Sato, 1964). For the extraction of thorium(IV) from aqueous perchlorate solutions by dibutyl phosphoric acid (DBP), it has been explained that the antagonistic effect of TBP results from the decrease in the amount of free DBP available for the extraction of thorium(IV), due to the formation of a 1:1 DBP-TBP complex (Dyrssen et al., 1960). Further, since a combination of DEHPA and TBP forms the species  $(\text{HX})_2 \cdot \text{TBP}$  (Sato, 1964), where  $\text{HX} = \text{DEHPA}$ , TOPO is expected to combine with DEHPA as the species  $(\text{HX})_2 \cdot \text{TOPO}$ , because the distribution coefficient is little influenced in the presence of TOPO below a molar ratio of  $[\text{TOPO}]/[\text{DEHPA}] = \sim 0.5$ . Accordingly, it is presumed that, in the extraction of dysprosium(III), the species  $(\text{HX})_2 \cdot \text{TOPO}$  is less effective than the dimeric species  $(\text{HX})_2$ .

Furthermore, IR spectrophotometry was carried out in order to clarify the effect of the addition of TOPO in the extraction of dysprosium(III) by DEHPA. The IR spectra of the mixed solutions of DEHPA and TOPO in kerosene exhibit a shift of the  $\text{P}=\text{O}$  stretching band of DEHPA at  $1230 \text{ cm}^{-1}$  to a higher frequency at  $1245$

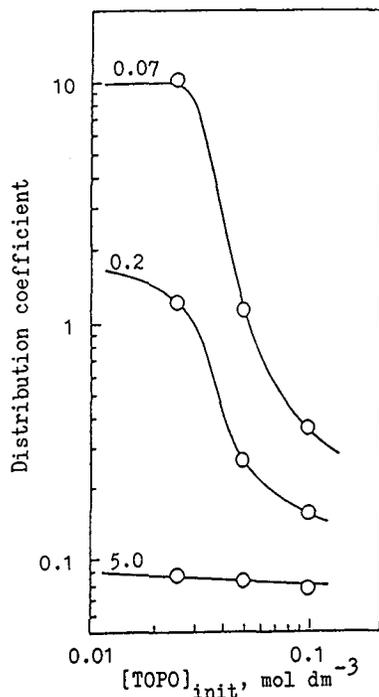


Figure 1. Variation of distribution coefficient with the amount of TOPO added to 0.05 mol dm<sup>-3</sup> DEHPA in the extraction of dysprosium(III) from hydrochloric acid solutions by DEHPA and TOPO in kerosene (numerals on curves are [HCl]<sub>init</sub> aq, mol dm<sup>-3</sup>).

cm<sup>-1</sup> and of TOPO at 1185 cm<sup>-1</sup> to a lower frequency at 1160 cm<sup>-1</sup> with an increasing molar ratio of [TOPO]/[DEHPA] of 0.5, 1 and 2. This implies that there is an interaction between the phosphoryl oxygen of DEHPA and TOPO through hydrogen bonding. Simultaneously the intensities of the OH stretching bands at 2680 and 2350 cm<sup>-1</sup> and the OH bending band at 1690 cm<sup>-1</sup> slightly decrease with increasing molar ratio. Hence the IR spectral results suggest the reduction of the available dimeric species caused by the presence of excess TOPO has some influence on the diminution in the distribution coefficient.

A similar antagonistic effect also appears in the extraction of the rare-earth elements used.

#### Effect of Pyridine Addition

In the extraction of dysprosium(III) with DEHPA in the presence of pyridine, the distribution coefficient rises with increasing pyridine at low aqueous acidity, as shown in Fig.2. However, since the solvating reaction occurs at higher acidity, the distribution coefficient is not influenced by the addition of pyridine. A similar synergistic effect is also observed in the extraction of the rare-earth elements used, as indicated in Fig.3. In this case, the results for the extraction system in the presence of pyridine reveal the same tetrad effect curve as seen for the distribution coefficient for the rare-earth elements by DEHPA alone, plotted as a function of the atomic numbers (Sato, 1989). It is thus seen that there is a depressed quartet which is divided at the atomic numbers of 60, 64 and 67. IR and NMR spectral measurements were carried out in order to clarify the effect of pyridine on the extraction of dysprosium(III) by DEHPA. The IR spectra of the mixed solutions of DEHPA and pyridine in kerosene exhibit the shift of the P=O stretching band of DEHPA at 1230 cm<sup>-1</sup> to higher frequency with increasing molar ratio of [py]/[DEHPA]: the absorptions appear at 1240, 1240 and 1245 cm<sup>-1</sup> for molar ratios of 0.5, 1 and 2, respectively. This suggests that there

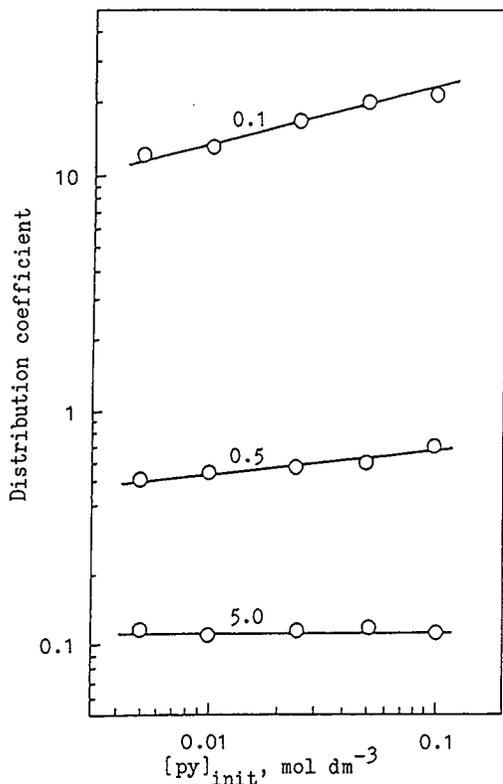


Figure 2. Variation of distribution coefficient with the amount of pyridine added to  $0.05 \text{ mol dm}^{-3}$  DEHPA in the extraction of dysprosium(III) from hydrochloric acid solutions by DEHPA and pyridine in kerosene (numerals on curves are  $[\text{HCl}]_{\text{init aq}}, \text{mol dm}^{-3}$ ).

is an interaction between the phosphoryl oxygen of DEHPA and the nitrogen of pyridine. However, since the intensity of the OH bands in the organic extracts is not influenced by the mixture of DEHPA and pyridine, it is inferred that the hydrogen bonding of dimeric DEHPA still remains. In the NMR spectra of the mixed solutions of DEHPA and pyridine, it is found that the OH proton signal of DEHPA at  $\tau = -2.15$  shifts to higher field consistent with the IR spectral results. In contrast, signals of the protons at the  $\alpha$ ,  $\beta$  and  $\gamma$  positions in pyridine do not cause significant shift, showing that the interaction between them is not so strong as to produce the pyridinium ion. From these it is deduced that although the pyridine molecule enters into a hydrogen bond, the bonding between the hydrogen of DEHPA and the nitrogen of pyridine is not so strong. Thus the species,  $(\text{HX})_2 \cdot \text{py}$  and  $(\text{HX})_2 \cdot 2\text{py}$  are formed depending on the amount of pyridine added to the DEHPA, and then give the synergistic effect on the extraction of rare-earth elements.

#### Effect on Separation Factor

A comparison of the distribution coefficients for the rare-earth elements by DEHPA in the presence of pyridine with those by DEHPA alone (Sato, 1989), it is seen that the separation factor (the ratio of the distribution coefficients for  $\text{Ln}_1$  and  $\text{Ln}_2$ ,  $E_a^0(\text{Ln}_1)/E_a^0(\text{Ln}_2)$ ) of the former is not so different from that of the latter. This arises from the fact that the variation of the distribution coefficient for the rare-earth elements plotted as a function of their atomic numbers shows a similar tetrad effect curve for both the extraction systems, as illustrated in Fig.3. Accordingly, the separation factors of adjacent

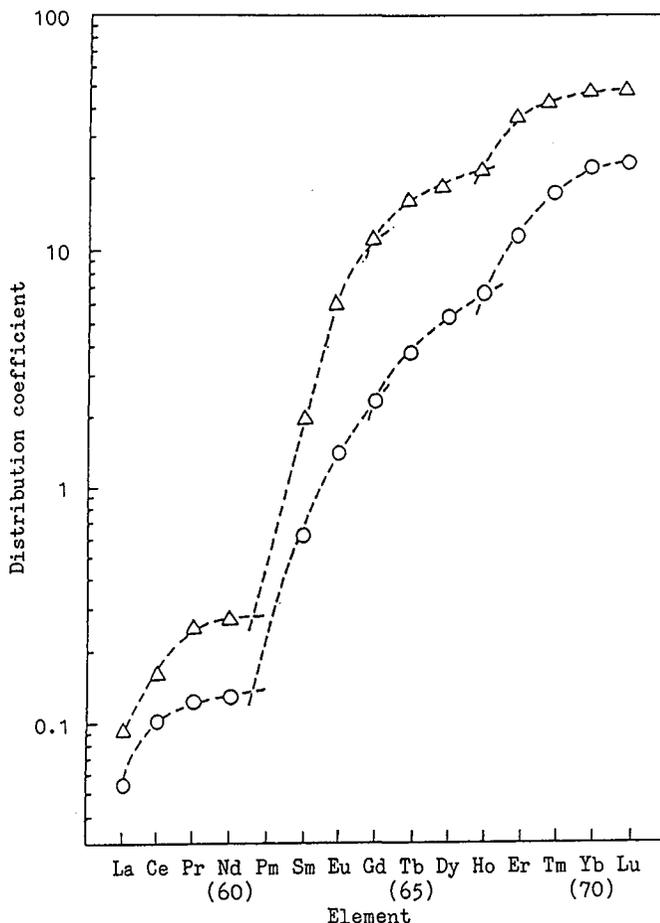


Figure 3. Dependence of the distribution coefficient on rare-elements arranged in order of their atomic numbers in the extractions from  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid solution with  $0.05 \text{ mol dm}^{-3}$  DEHPA in the presence of  $0.05 \text{ mol dm}^{-3}$  pyridine (O, DEHPA alone;  $\Delta$ , DEHPA + py; numbers in the parentheses denote atomic numbers).

elements resemble each other, and the values for the extraction by DEHPA in the presence of pyridine are analogous to those by DEHPA alone (Sato, 1989). On the other hand, the variation of distribution coefficient for the extraction of rare-earth elements by DEHPA in the presence of TOPO also indicates a tetrad effect curve similar to that by DEHPA alone. It is thus known that the separation factors of adjacent elements by DEHPA are not affected much by the addition of TOPO.

#### CONCLUSION

It is observed that the results for the extraction by DEHPA in the presence of pyridine reveal a tetrad effect curve similar to the extraction of the rare-

earth elements by DEHPA alone when plotted as a function of the atomic numbers (Fig.3). A similar curve is found in the extraction of rare-earth elements by DEHPA in the presence of TOPO, although the distribution coefficients decrease in comparison with those by DEHPA alone. However, when the separation factor of each element is determined in those extraction systems, the values obtained do not show much difference in the extraction between DEHPA alone and DEHPA in the presence of TOPO or pyridine. Accordingly, it is concluded that the addition of TOPO or pyridine to the extraction of the rare-earth elements by DEHPA gives the antagonistic and synergistic effects, respectively, on the extraction by DEHPA alone, but the separation factor of each extraction system is not so remarkably different.

#### ACKNOWLEDGEMENTS

We wish to thank the Shinetsu Chemical Industry Co., Ltd. for the gift of the oxides of rare-earth elements, and the Chemical Industry Co., Ltds. of Daihachi, Hokko and Koei for the samples of DEHPA, TOPO and pyridine, respectively.

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## KINETICS STUDIES OF SOLVENT EXTRACTION OF RARE EARTHS INTO DEHPA

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### ABSTRACT

The kinetics of rare earth solvent extraction into di(2-ethylhexyl) phosphoric acid have been studied using radiotracers (<sup>141</sup>Ce, <sup>152</sup>Eu, <sup>153</sup>Gd, <sup>160</sup>Tb and <sup>88</sup>Y) in a modified Lewis cell. The experimental procedure involved continuous monitoring of both aqueous and organic phases using an automated  $\gamma$ -counting system. Using this method, highly reproducible results were obtained without chemical analysis or disturbance of the system.

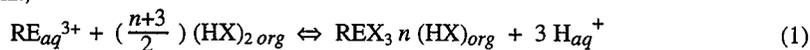
The initial rate extraction was first order with respect to individual rare earth concentration. At low acidities ( $[H^+] < 0.01 M$ ), the extraction rates of rare earths were equal and independent of pH. However, at high acidities, the extraction rate was strongly dependent on pH and varied between the rare earths. Similarly, differences in the extraction rate of individual rare earths were apparent at low DEHPA concentration. The initial extraction rate can be described by the equation :

$$R = \frac{4.2 \times 10^{-6} [M^{3+}] [(HX)_2]^{2.5}}{K_r [H^+]^3 + [(HX)_2]^{2.5}}$$

where  $R$  is in moles  $m^{-2} \text{ min}^{-1}$  and concentrations are expressed as moles  $L^{-1}$  ( $M$ ).  $K_r$  varies according to the individual rare earth element and was found to be 0.535, 0.036, 0.032, 0.019 and 0.011 for cerium, europium, gadolinium, terbium and yttrium, respectively.

### INTRODUCTION

Solvent extraction is the preferred process for purification of rare earths on an industrial scale. DEHPA, di(2-ethylhexyl) phosphoric acid, in a suitable organic diluent is the most commonly used extractant from chloride solutions. The extraction of rare earths into DEHPA is a cation-exchange reaction, viz.,



where  $(HX)$  and  $(HX)_2$  are the monomeric and dimeric species of DEHPA. Previous work has established that the value of  $n$  varies according to the degree of polymerisation which depends on the type of the diluent used. For aliphatic diluents, such as n-heptane,  $n$  was found to be 2 [Hirashima *et al.* (1975); Sato *et al.* (1973); Thomas *et al.* (1974) and Mason *et al.* (1976)], whereas it was 3 in aromatic diluents [Thomas *et al.* (1974); Mason *et al.* (1976); Brown *et al.* (1979) and Peppard *et al.* (1963)].

Although there have been many studies of the mechanism and kinetics of extraction using organophosphorus extractants [Peppard *et al.* (1958); Harada *et al.* (1970); Hirato *et al.* (1988); Li *et al.* (1987); Yue *et al.* (1990); Miyake *et al.* (1990); Minagawa *et al.* (1990) and Lim *et al.* (1993)], most have been concerned with a single element and none of these have sought to compare individual rare earth elements under the same conditions.

This paper investigates differences in the kinetics of extraction of five rare earth elements into DEHPA using radioactive tracers which facilitate continuous on-line measurement with high precision.

## EXPERIMENTAL

### Apparatus

A constant interfacial area apparatus, based on a modification of the Lewis cell, was used for all experiments [Lewis (1954) and Hanna *et al.* (1985)]. The cell consists of two identical chambers of volume 200 mL. The interfacial area could be varied by insertion of concentric teflon rings. A perspex water jacket was used to maintain a constant temperature in the cells (see Fig. 1).

Each cell was fitted with a stirrer judiciously placed to minimise disturbance of the interface. Both phases could be continuously sampled using capillary tubing connected to peristaltic pumps. Each phase passed through a glass coil wrapped around a shielded sodium iodide detector before returning to the cell. The total volume of the measuring coils plus tubing was about 2 mL.

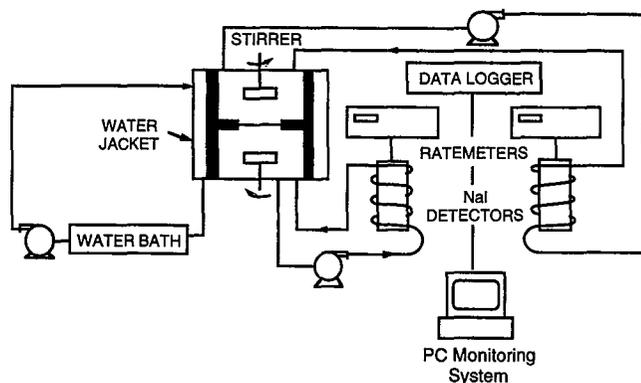


Figure 1 Overall Set-up for Kinetics Measurements

### Radiotracers and Reagents

The radionuclides,  $^{141}\text{Ce}$ ,  $^{152}\text{Eu}$ ,  $^{153}\text{Gd}$  and  $^{160}\text{Tb}$ , were prepared by irradiation of their oxides in the HIFAR reactor at ANSTO.  $^{88}\text{Y}$  was obtained as a yttrium chloride in 0.1 M HCl solution from Los Alamos, USA. These radionuclides were chosen because they are  $\gamma$ -emitters with suitable half-lives (30 days to 2 years). The oxides were converted to the chloride form through repeated evaporation with 2 M HCl. They were then dissolved in 0.1 M HCl and made up to 10 mL. The stock solutions were prepared from inactive rare earth chemicals and were spiked with the radionuclide of interest. The DEHPA was obtained from BDH Ltd and had a purity of 98.5%. The organic solution was prepared by diluting DEHPA in analytical grade n-heptane.

### Experimental Procedure

Solutions of the aqueous phase containing hydrochloric acid and of the organic phase containing DEHPA in n-heptane were carefully poured into the reaction vessel. The two phases were stirred at a constant speed by stirrers whose speed could be precisely and independently regulated. Experimental conditions were chosen to minimise pH changes. The phases were equilibrated for about 5-10 hours. The tracer solution (1 mL, prepared from aliquots of the active and inactive solutions) was then introduced into the aqueous phase. The radioactivities (and hence rare earth concentrations) in the organic and aqueous phases were measured continuously using the detectors interfaced to a PC data logging system. The experiments ran from 3 hours to 2 days as appropriate. At the end of each experiment, samples were taken from both phases and the aqueous phase pH was measured. The phases were mixed at a volume ratio of 1 and shaken for three hours. The distribution coefficient was determined from the ratio of radioactivities in the organic and aqueous phases.

## RESULTS AND DISCUSSION

### Extraction Kinetics

Fig. 2 shows the changes in rare earth concentration with time for a typical experiment. Initially, the rare earth concentration in the organic phases increases linearly with time. Under these conditions, the initial extraction rate  $R$  (moles  $m^{-2} min^{-1}$ ) can be calculated from the slope of the initial straight line according to equation (2):

$$R = \frac{V_{org}}{A} \frac{d[RE_{org}]}{dt} \quad (2)$$

where  $V_{org}$ ,  $A$  and  $RE$  are the volume of organic solution, interfacial area and the concentration of rare earth in the organic solution, respectively.

Preliminary experiments established that the rate of extraction was affected by stirrer speeds up to 80 rpm, thereafter the rate appeared to be constant until 125 rpm when the surface became disturbed. Accordingly, it was decided to standardise on a stirrer speed of 100 rpm in both phases. The extraction rate was also found to be increased linearly with interfacial area.

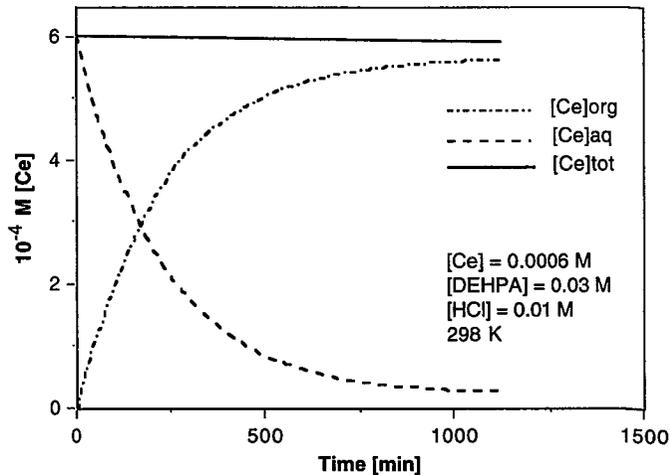


Figure 2 Relationship between rare earth concentration with time

The effect of rare earth concentration on the initial rate of extraction is shown in Fig. 3. The results show the extraction rate increases linearly with increasing initial rare earth concentration indicating a first order dependency. Moreover, no difference in rate is discernible between the individual rare earths at the high (DEHPA/RE) ratios used in these experiments.

The effect of DEHPA concentration on the rate of extraction is shown in Fig. 4. The extraction rate for individual rare earths are equal and constant at high DEHPA concentrations. However, the extraction rate decreases at lower DEHPA concentrations and differences are apparent between the rare earths.

The effect of acidity on the rate of extraction is shown in Fig. 5. In order to avoid effects due to changes in ionic strength, the total chloride concentration in the aqueous phase was kept constant at 0.4 M by adding sodium chloride. The data show that the extraction rate of individual rare earths is independent of pH at low acidities but decreases at high acidities. There is a correlation between pH values when acidity dependency occurs and the ionic radii of the rare earths. The light rare earth,

cerium, shows an acid dependency when the pH is below 2. For the more extractable rare earths, such as yttrium and terbium, the acid dependency is apparent below pH 1.3.

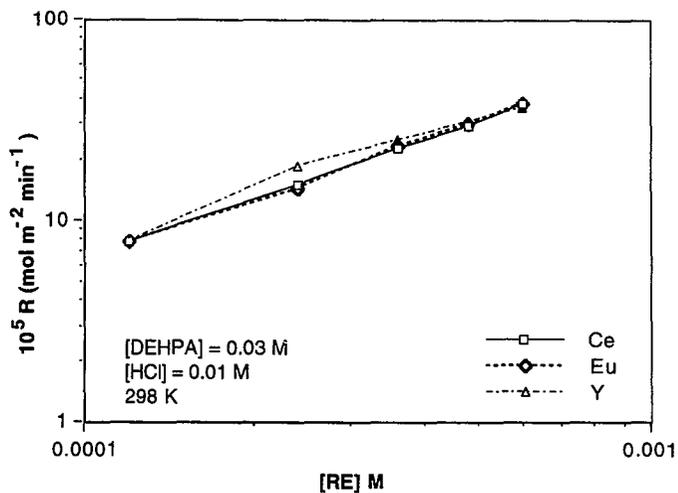


Figure 3 Effect of rare earth concentration on the rate of extraction

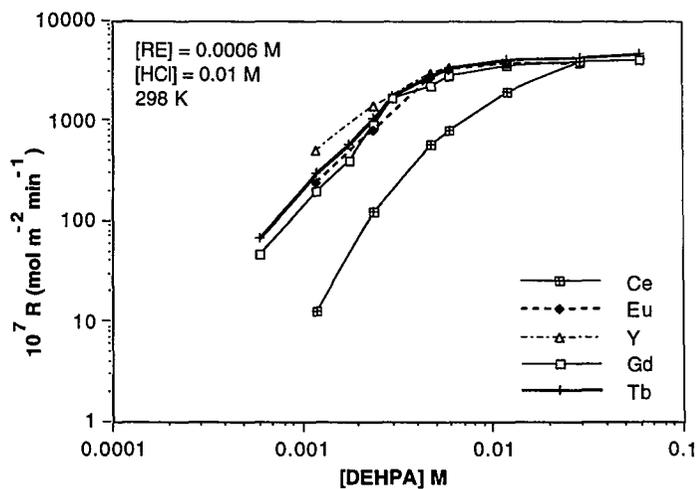


Figure 4 Effect of DEHPA concentration on the rate of extraction

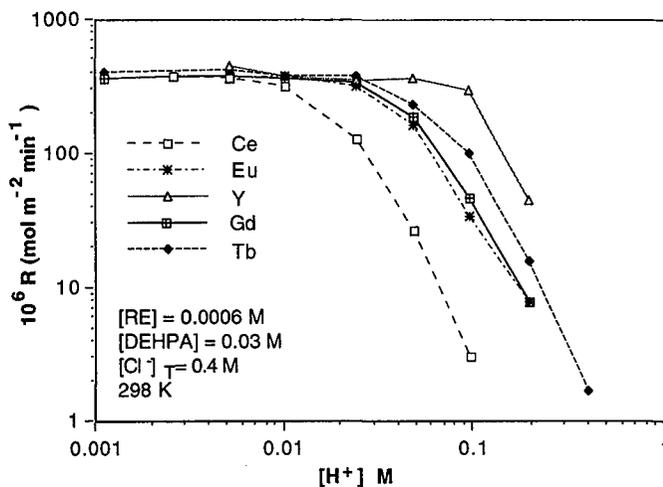


Figure 5 Effect of hydrogen ion concentration of the rate of extraction

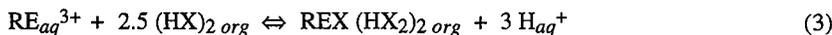
### Interpretation of Results

The experimental data in Fig. 3-5 suggest that the initial extraction rate can be correlated by an equation of the form:

$$R = \frac{K_p [M^{3+}] [(HX)_2]^q}{K_r [H^+]^p + [(HX)_2]^q} \quad (4)$$

Best fit values for  $K_p$ ,  $K_r$ ,  $q$  and  $p$  were determined for each rare earth using the "Solver" function within Microsoft Excel. The constant  $K_p$  was found to be independent of the individual rare earth elements and equal to  $4.2 \times 10^{-6}$ . The best fit exponent for  $p$  ranged from 2.4 to 3.2 (depending on particular rare earth), however, on theoretical grounds (see equation (1)) a value of 3 was chosen since it did not increase the average error significantly.

The best fit exponent for  $q$  ranged from 2.3 to 2.7 with an average value of 2.5. This exponent is consistent with the stoichiometry of equation (1) for  $n=2$  which is appropriate since an aliphatic diluent (n-heptane) was used in these experiments [Mason *et al.* (1976)]. The overall equation becomes:

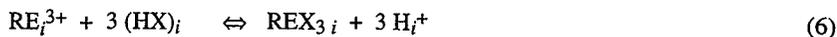


The initial extraction rate equation can then be written as:

$$R = \frac{4.2 \times 10^{-6} [M^{3+}] [(HX)_2]^{2.5}}{K_r [H^+]^3 + [(HX)_2]^{2.5}} \quad (5)$$

where  $R$  is in moles  $m^{-2} min^{-1}$  and concentrations are expressed as moles  $L^{-1}$  ( $M$ ).  $K_r$  varies according to the individual rare earth element and was found to be 0.535, 0.036, 0.032, 0.019 and 0.011 for cerium, europium, gadolinium, terbium and yttrium, respectively. The correlation of 92 experimental points using this equation gave an average error of 11.7%. This is regarded as an acceptable fit given that the rate,  $R$ , ranges over 3 orders of magnitude.

Equation (5) is consistent with a mechanism involving the following reactions [Bhattacharrya *et al.* (1985)]:



The form of this equation alone does not uniquely identified the rate determining step(s) since both reaction controlled processes and diffusion with fast chemical reaction fit equation (5) [Danesi *et al.* (1980)]. Mixed diffusion and reaction controlled processes also conform to this equation [Danesi *et al.* (1980)]. Given that the stirrer speed affects the overall reaction rate at speeds up to 80 rpm, it is highly likely that both diffusion and the above reactions ((6) and (7)) play significant roles in the overall reaction rate.

### CONCLUSIONS

- The initial extraction rate into DEHPA is, within experimental error, the same for all the rare earths provided the DEHPA concentration and pH are sufficiently high.
- At high acidities, the extraction rate was strongly dependent on pH and varied between the rare earths. Likewise, differences in the extraction rate of individual rare earths were apparent at low DEHPA concentration.
- The reaction rate can be described mathematically by equation (5). It is postulated that the rate controlling processes are mixed diffusion and chemical reaction.

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## METAL CONTENT INFLUENCE ON EXTRACTION OF CHLOROMETALLIC ACIDS BY SOLVENTS CONTAINING DIISOPROPYL ETHER

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### ABSTRACT

The behaviour of extraction systems containing diisopropyl ether (IPE) and metals forming chlorometallic acids was investigated in respect to change in metal content. The systems were of the  $\text{MeCl}_3$  -  $\text{HCl}$  -  $\text{H}_2\text{O}$  - IPE - S type. The metals (Me) were iron(III) and gallium(III) and the component of the mixed solvent (S) added to IPE were the inert solvent benzene or the active solvent pentyl alcohol.

Under defined conditions, change in metal content induced major variations in phase volumes including change in the number of coexisting phases, changes in the concentration of metal and other components in the equilibrated phases and irregular changes of the distribution ratios in the investigated systems.

### INTRODUCTION

Former investigations of over twenty extraction systems containing diisopropyl ether (IPE) show that such systems having non-ideal behaviour can improve, under specific conditions, the separation of metals forming chlorometallic acids such as iron, gold and gallium. The influence of the temperature [Maljković (1980, 1994)], the initial concentration of components in the aqueous [Maljković (1966, 1981)] and organic [Maljković (1979)] phases and the type of solvent added to IPE [Maljković (1990, 1993)] on the behaviour of extraction systems containing IPE, pure or in mixture with an other solvent, was investigated. Change in these factors may bring about enhancement of metal (acid) extraction, a synergistic effect, coextraction and alteration in the number of coexisting phases (the third phase appearance). The form and extent of influence depend on their very complex mutual relationships. Such systems, especially in the case of the third phase appearance, are very complex and exhibit a non-ideal behaviour so that a phenomenological approach in their investigation is preferable to a thermodynamic one.

Among the factors influencing the behaviour of the extraction systems the effect of metal content was investigated to a lesser extent. In this paper some of the results obtained by examination of the influence of iron(III) and gallium(III) content on the distribution ratios of components and on the system behaviour are given.

### EXPERIMENTAL

#### Materials

Diisopropyl ether Fluka or Merck, C.P. was purified by successive treatment with a saturated solution of ferrous sulphate, 0.5 per cent solution of potassium permanganate, 0.5 per cent solution of sodium hydroxide and distilled water. Purified IPE was distilled and a fraction with b.p.  $66.8 - 67.8^\circ\text{C}$  was collected. Other solvents used were of p.a. purity with a water content less than 0.1 per cent. The chemicals used were of analytical reagent grade

### Procedure

The systems were prepared by vigorous shaking of components in 15 ml separation funnels having a calibrated stem and/or in 15 ml graduated cuvettes. The prepared systems were placed in a water bath with the thermostat kept by automatic control at  $20 \pm 0.05$  °C. Shaking was repeated in the same manner at 15 minute intervals for one hour.

The initial volume ratio of the organic phase to the aqueous phase ( $r^i$ ) was always 1.0.

The volumes of the equilibrated phases were determined before sampling.

All the data were results of two or more repeated experiments depending on the degree of reproducibility.

### Methods of Analysis

The metal concentration in the samples of the aqueous phase and in the pretreated samples of the organic phase was determined by UV,V absorption spectrometry (Rhodamin B was used for gallium determination). In the case of a larger quantity of metal, complexometric titration was applied with Titriplex III and the indicators gallocyanin (for gallium) or 2-oxy-5-sulphobenzoic acid (for iron).

The concentration of chloride in the samples of aqueous and organic phases was determined by precipitation potentiometric titration. Samples of organic phases were diluted with a suitable quantity of water (approximately 1:20) without previous treatment.

## RESULTS AND DISCUSSION

The change of volumes of the equilibrated phases as a result of gallium(III) content change in the system containing pure IPE is shown in Figure 1.

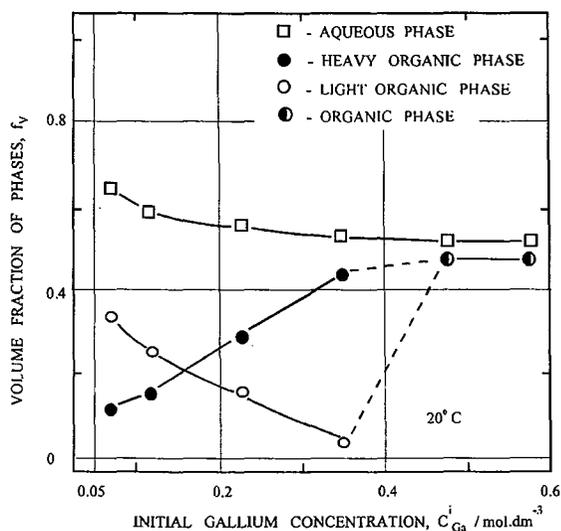


Figure 1. Volume fractions of equilibrated phases ( $f_v$ ) vs. initial gallium concentration ( $C_{Ga}^i$ ) in the system  $GaCl_3 - HCl - H_2O - IPE$  ( $r^i = 1.0$ ,  $C_{HCl}^i = 9.9$  mol.dm<sup>-3</sup>)

The effect of the change in gallium(III) concentration on variation of the volume of the phases in systems containing IPE is similar to that of iron(III). Increase in the third phase (heavy organic phase) volume following increase in initial gallium(III) concentration runs at the expense of the light organic phase, and the three-phase system finally transforms into a two-phase one. Phase volume changes are connected with the structure of extractable hydrosolvate of the chlorometallic acid  $[\text{HMeCl}_4 \cdot (\text{HCl})_x \cdot (\text{H}_2\text{O})_y \cdot (\text{IPE})_z]$  and are always the result of all factors which take action on the transfer of components among the coexisting (two or three) phases. This action may be different in extent and direction, so an increase in the initial hydrochloric acid concentration enhances the transfer of IPE into the aqueous phase [Campbell (1952)] whereas an increase in the iron(III) concentration decreases the IPE content in the aqueous phase [Maljković (1995)] in systems containing pure IPE. In addition, in systems containing diluted IPE, the possibility of IPE transfer into the aqueous phase may be limited by the quantity of IPE present in the system. The third phase is of special interest to the separation, because the metal concentration is always higher in the third phase than in the light organic one.

The formation of the third liquid phase is known to occur in IPE containing systems only at an initial hydrochloric acid concentration higher than  $7 \text{ mol} \cdot \text{dm}^{-3}$  i.e. when there is a lack of free water in the system. Therefore the effect of the initial metal concentration on its equilibrate concentration in the coexisting phases was examined at initial hydrochloric acid concentrations higher than  $7 \text{ mol} \cdot \text{dm}^{-3}$ . The effect of the initial gallium(III) concentration on equilibrate concentration of gallium(III) and chloride in the organic phases in the system containing pure IPE is shown in Fig. 2.

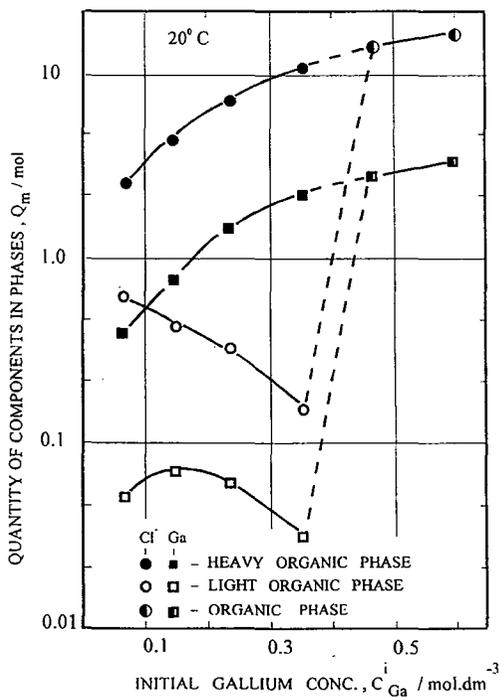


Figure 2. Effect of gallium(III) concentration on the quantity of components in equilibrated organic phases in the system  $\text{GaCl}_3 - \text{HCl} - \text{H}_2\text{O} - \text{IPE}$  ( $C_{\text{HCl}}^i = 9.9 \text{ mol} \cdot \text{dm}^{-3}$ ,  $r^i = 1.0$ )

With increase in initial metal concentration, the content of both components increases in the heavy organic phase at the expense of their content in the light organic phase.

The HCl/HGaCl<sub>4</sub> ratio in the organic phases of the three-phase region calculated from the obtained results was between 1 and 2, at an initial acid concentration of 9.9 mol.dm<sup>-3</sup>. This ratio was strongly dependent on the initial acid concentration and, for instance, in the case of iron(III), at a lower initial acid concentration (8.2 mol.dm<sup>-3</sup>) and under other congruent experimental conditions, was much smaller (between 0.2 and 0.4).

The behaviour of the system containing IPE diluted with benzene is represented by a change of iron(III) concentration in the equilibrated organic phases as a function of the initial iron(III) concentration. At a given initial acid concentration (7.6 mol.dm<sup>-3</sup>, Fig. 3) in the system with an initial IPE concentration of 3.0 mol.dm<sup>-3</sup> (three-phase system), the metal concentration in the heavy organic phase is much higher and less dependent on the initial metal concentration than in the organic phase of the system with an initial IPE concentration of 5.0 mol.dm<sup>-3</sup> (two-phase system). Changes in the distribution ratio induced by altered initial experimental conditions in the three-phase system are more complex than in the two-phase one. In the three-phase system there are three relationships (aqueous - light organic, aqueous - heavy organic and heavy organic - light organic phase) in contrast to one relationship (aqueous - organic phase) in the two-phase system; change in the solute quantity in one phase reflects itself as a change of solute quantity in the other two phases. If the solute concentration is taken into consideration instead of the solute quantity (as is required for calculation of the distribution ratio), the relationship between the changes of

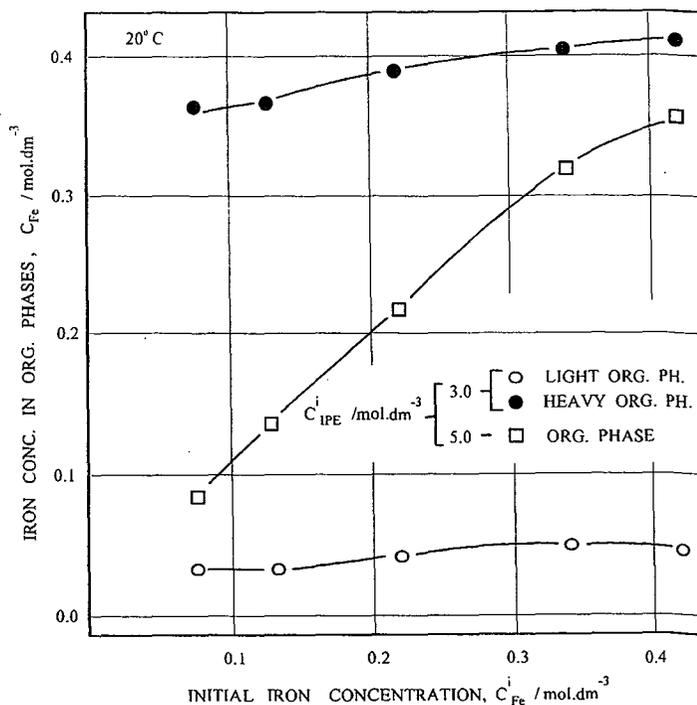


Figure 3. Effect of iron(III) concentration on the iron(III) content in equilibrated organic phase in the system FeCl<sub>3</sub> - HCl - H<sub>2</sub>O - IPE - C<sub>6</sub>H<sub>6</sub> (  $C_{HCl}^i = 7.6$  mol.dm<sup>-3</sup>,  $r^i = 1.0$  )

the concentration of the components and their distribution ratios, due to phase volume changes, become much more complex.

**TABLE 1**

Partial distribution ratio  $(D_c)^h_{aq}$  of iron(III) at different initial iron(III) concentration in the system  $FeCl_3 - HCl - H_2O - IPE - C_6H_6$   
 $(r^i=1.0, C_{HCl}^i = 7.6 \text{ mol.dm}^{-3}, C_{IPE}^i = 3.0 \text{ mol.dm}^{-3})$

$C_{Fe}^i / \text{mol.dm}^{-3}$	0.08	0.14	0.22	0.33	0.41
$(D_c)^h_{aq}$	60.3	52.9	43.6	29.1	10.0

Table 1. shows that with an increase in initial iron(III) concentration the distribution ratio decreases, although the iron(III) concentration in the heavy organic phase increases (Fig. 3). The effect of the initial iron(III) concentration was examined also in the systems containing the mixed solvent IPE - pentyl alcohol. Investigations were performed at lower initial acid concentrations because, due to the synergistic effect that appears in that system [Maljković (1993)], high distribution ratios for iron(III) and especially for gallium(III) were obtained already at a  $5.0 \text{ mol.dm}^{-3}$  initial hydrochloric acid concentration (two-phase system). With increase in the initial metal concentration in the systems containing 30% [iron(III)] or 20% [gallium(III)] for pentyl alcohol in a mixture with IPE, the distribution ratios of both metals significantly decreased (Table 2).

**TABLE 2.**

Distribution ratios of iron(III) and gallium(III) at different initial metal concentration in system  $MeCl_3 - HCl - H_2O - IPE - CH_3(CH_2)_4OH$   
 $[C_{HCl}^i = 5.0 \text{ mol.dm}^{-3}, C_{alc}^i = 30\% \text{ (Fe) and } 20\% \text{ (Ga)}]$

$C_{Ga}^i$	$(D_c)_{Ga}$	$(D_c)_{Fe}$
0.03	800	250
0.06	523	166
0.15	103	66

In the case of the extraction of metals forming chlorometallic acids with IPE containing solvents the influence of the metal on the behaviour of the system and on the distribution ratios strongly depends on the relationship between all relevant factors. There is no regularity in the behaviour especially when the system transfers from a two-phase into a three-phase one and therefore predicting the behaviour under altered conditions is practically impossible. Accumulation of data obtained at numerous different levels of each component concentration can contribute to a better knowledge of such systems.

#### ACKNOWLEDGEMENT

This work was performed with the support of the Ministry of Science and Technology of the Republic Croatia.

## NOMENCLATURE

$C_{Me}^i$	initial metal concentration in the aqueous phase
$C_{HCl}^i$	initial hydrochloric acid concentration in the aqueous phase
$C_{IPE}^i$	initial IPE concentration in the organic phase
$C_{alc}^i$	initial alcohol concentration in the organic phase
$(D_c)_{aq}^h$	partial distribution ratio between the heavy organic phase and the aqueous phase
$f_v$	phase volume fraction
$Q_m$	component quantity in the equilibrate phase
$r^i$	initial phase volume ratio of the organic to the aqueous phase

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## CENTRIFUGAL PARTITION CHROMATOGRAPHIC SEPARATION OF PLATINUM GROUP METALS BY ION-PAIR FORMATION WITH TETRAHEPTYLAMMONIUM p-TOLUENESULFONATE

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### ABSTRACT

Tetraheptylammonium p-toluenesulfonate (QpTS), a new ion-pair extractant for platinum group metals, has been characterized by both batch extraction and centrifugal partition chromatography (CPC) using the 1,2-dichloroethane (DCE)-water phase pair. It has been incorporated into a practical multistage method of separating the platinum group metals under mild conditions using CPC. Separation of Ir(IV) and Pt(IV) from Rh(III), Ir(III), Pt(II) and Pd(II) was achieved at  $[QpTS] = 0.002 \text{ mol dm}^{-3}$  in DCE,  $[NapTS] \geq 0.1 \text{ mol dm}^{-3}$  and  $pH = 2.5$  (HCl). Separation of Pt(II) and Pd(II) from Rh(III) and Ir(III) could be achieved at  $[QpTS] = 0.002 \text{ mol dm}^{-3}$  and  $[NapTS] \leq 0.01 \text{ mol dm}^{-3}$ . The mutual separation of the individual chloro species of Pt(II), namely  $PtCl_2$ ,  $PtCl_3^-$  and  $PtCl_4^{2-}$  could also be achieved under these conditions in the presence of NaCl ( $0.1 - 0.4 \text{ mol dm}^{-3}$ ). The fractions of the Pt(II)-chloro species were calculated from the CPC chromatograms and compared with values from other equilibrium measurements. The extraction equilibrium constants for the extraction of  $PtCl_3^-$  and  $PtCl_4^{2-}$  by QpTS and QCl could also be calculated from these CPC chromatograms. This is the first demonstration by CPC, of the separation of different halo species of a metal whose hydrolytic equilibria are slow.

### INTRODUCTION

Separation of groups of metal ions by chelating extractants enjoys a distinct advantage over ion-pair extractants because of significantly higher selectivity, Edward(1976). Separation of platinum group metals (PGM: Rh, Ir, Pt, Pd) by chelating extractants, however, poses a problem because of the slow kinetics of chelate formation and dissociation, Sano et. al.(1989), Gidin(1981). Earlier, we reported the successful separation by Centrifugal Partition Chromatography (CPC), a multistage liquid-liquid countercurrent distribution technique, of Pd(II) and Pt(II) from Rh(III) and Ir(III) using trioctylphosphine oxide (TOPO), a monodentate ligand, Surakitbanharan et. al.(1991). In addition, it was found that the protonated TOPO cation (HTOPO<sup>+</sup>) forms extractable ion-pair complexes with the anionic PGM chloro complexes capable of effecting the separation of Ir(IV), Pt(II) and Pd(II) from Rh(III) and Ir(III).

Multistage extraction techniques enhance separation effectiveness so that consideration of ion-pair extractions becomes practical. Success with HTOPO<sup>+</sup> has prompted us to investigate ion-pair extractants of the quaternary ammonium family towards identifying systems capable of separating the PGM from each other and their oxidation states (Pt(II) and Pt(IV), etc.). Quaternary ammonium halides have been known to rapidly extract PGM as ion-pairs of their anionic chloro complexes, Sano et. al.(1989). Usually high acidity or ammonia is needed for the back extraction of their ion-pairs for the recovery of PGM. We have identified in this work, a new family of ion-pair extractants, quaternary ammonium p-toluenesulfonates, capable of extracting and back extracting PGM under mild conditions, i.e.,  $pH = 1-3$  and  $NaCl = 0.01 - 0.1 \text{ mol dm}^{-3}$ . The extraction of PGM by one such extractant, tetraheptylammonium

p-toluenesulfonate (QpTS) has been characterized and their separation achieved using CPC. The detailed examination of the extraction equilibria of PGM chloroanions by QpTS and their separation by CPC are presented here.

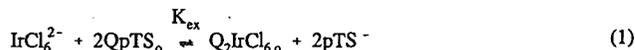
Batch solvent extraction experiments were conducted in the usual manner. The CPC experiments were conducted with a Sanki Co., Japan apparatus, consisting of a Model SPL centrifuge containing six analytical/semipreparative cartridges each having 400 channels (2400 total channels = stages; total volume = 125 cm<sup>3</sup>) operated at 800 rpm and aqueous mobile phase flow rates of 0.38 - 2 cm<sup>3</sup> min<sup>-1</sup>. The PGM were detected using their uv-vis bands with a Model 770, Schoeffel Instrument Co., detector, Surakibanham et. al.(1991).

## RESULTS AND DISCUSSION

### Extraction Equilibrium for Ir(IV)

Batch extraction experiments and slope analysis of the data were conducted to study the equilibrium of Ir(IV) extraction. At [Ir(IV)] = 4 x 10<sup>-4</sup> mol dm<sup>-3</sup>, [NapTS] = 0.2 mol dm<sup>-3</sup>, and [QBr]<sub>o,i</sub> = 4 x 10<sup>-3</sup> mol dm<sup>-3</sup> (initial concentration in DCE), log D was independent of pH in the range 0.5 - 3, and varied only slightly (linearly, slope 0.11) in the range 3-5. The slowly increasing D at pH > 3 may result from the hydrolysis of IrCl<sub>6</sub><sup>2-</sup> to IrCl<sub>4</sub>(OH)<sub>2</sub><sup>2-</sup>, Cleare et. al.(1979).

Introduction of QBr to the organic phase at concentrations from 1.5 - 5 x 10<sup>-3</sup> mol dm<sup>-3</sup> at a constant (and excess) NapTS concentration resulted in nearly quantitative transformation to QpTS. Values of log D<sub>Ir</sub> increased linearly with log [QpTS]<sub>o</sub> with a slope of 2.09 ± 0.08 and 2.14 ± 0.14 at 0.1 mol dm<sup>-3</sup> and 0.2 mol dm<sup>-3</sup> respectively. Here, [QpTS]<sub>o</sub> is the concentration of QpTS at equilibrium corrected for the consumption of Q<sup>+</sup> in the ion-pair Q<sub>2</sub>IrCl<sub>6</sub>. Similarly, the plot of log (D<sub>Ir</sub>/[QpTS]<sub>o</sub><sup>2</sup>) vs. log [NapTS] in the range [NapTS] = 0.1 - 0.5 mol dm<sup>-3</sup> exhibited a slope of about -2 at the initial QBr concentrations of 0.002 mol dm<sup>-3</sup> and 0.004 mol dm<sup>-3</sup>.



On the basis of these findings, the extraction equilibrium of Ir(IV) with QpTS can be expressed as in equation 1. The extraction equilibrium constant can be expressed as  $K_{ex} = D_{Ir}[\text{pTS}]^2[\text{QpTS}]_o^{-2}$ . The extraction equilibrium of Ir(IV) was also examined by subjecting values of D<sub>Ir</sub> obtained from CPC experiments to slope analysis. When [QpTS] (1.5 - 5 x 10<sup>-3</sup> mol dm<sup>-3</sup>) was varied in the stationary phase at constant [NapTS] = 0.2 mol dm<sup>-3</sup> in the mobile phase, log D<sub>Ir</sub> values increased linearly with log [QpTS]<sub>o</sub> with a slope of 1.95 ± 0.07. Varying [NapTS] (0.1 - 0.4 mol dm<sup>-3</sup>) in the mobile phase at constant [QpTS] = 0.002 mol dm<sup>-3</sup> in the stationary phase decreased D<sub>Ir</sub> in a manner that resulted in a linear log D<sub>Ir</sub> vs. log [NapTS] plot having a slope of -1.76 ± 0.24. There is, in general, good agreement between the D values determined by both the batch extraction and CPC experiments for the various PGM studied.

### SEPARATION OF PLATINUM METALS BY CPC

The separation of PGM by CPC was achieved using the QpTS/NapTS combination in the DCE-H<sub>2</sub>O phase pair.

### Separation of Rh(III), Pt(IV) and Ir(IV)

Base line separation of Rh(III), Pt(IV) and Ir(IV) was achieved, Figure 1, by using equal volumes (62.5 cm<sup>3</sup>) of stationary phase (0.002 mol dm<sup>-3</sup> QpTS in DCE) and mobile phase (0.15 mol dm<sup>-3</sup> NapTS/pH 2.5) and a flow rate of 0.38 cm<sup>3</sup> min<sup>-1</sup>. The log  $K_{ex}$  values for Ir(IV) and Pt(IV) from the CPC chromatograms are  $3.89 \pm 0.12$  and  $3.59 \pm 0.10$  respectively. This small difference in  $K_{ex}$  illustrates the advantage of a multistage separation technique for the separation of closely related metal ions.

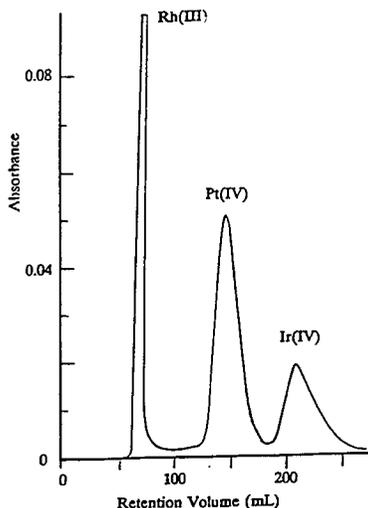


Figure 1. Separation of Rh(III), Pt(IV) and Ir(IV). [QpTS] = 0.002 mol dm<sup>-3</sup> in DCE, [NapTS] = 0.15 mol dm<sup>-3</sup> in H<sub>2</sub>O, aqueous phase flow rate = 2 cm<sup>3</sup> min<sup>-1</sup> and  $V_{DCE}/V_{aq} = 1$ .

The first peak in the chromatogram in Figure 1 is due to Rh(III), Ir(III) (some reduction of Ir(IV) to Ir(III) always occurs),  $PtCl_5(H_2O)^-$  and  $PtCl_4(H_2O)_2$ . The chromatogram of Pt(IV), examined at [NapTS] = 0.1 mol dm<sup>-3</sup> and all other conditions being same as Figure 1, exhibited two peaks at D values 0.3 and 0.9. The first peak at D = 0.3 is due to  $PtCl_5(H_2O)^-$  and  $PtCl_4(H_2O)_2$  while the second peak is due to  $PtCl_6^{2-}$ . This was further tested by heating the Pt(IV) solution with 0.1 mol dm<sup>-3</sup> NaCl at 363 K for 1 h, 4 h and 12 h. The chromatogram of the Pt(IV) sample obtained after 1 h heating clearly indicated the conversion of the hydrolyzed Pt(IV) species to  $PtCl_6^{2-}$ , and equilibrium was reached after heating for 4 h. The slow hydrolysis of  $PtCl_6^{2-}$  thus enables its separation from the hydrolyzed species and calculation of the  $K_{ex}$  from the D values even though its actual concentration is not known. These observations are also supported by the uv-vis spectrum of  $2 \times 10^{-4}$  mol dm<sup>-3</sup> Pt(IV) in 0.1 mol dm<sup>-3</sup> NaCl at pH = 2.5 where the formation of  $PtCl_6^{2-}$  upon heating could be monitored by the changes in absorbance at 260 nm, Davidson et. al.(1965). The equilibrium constant  $K_6$  for the conversion of  $PtCl_5(H_2O)^-$  to  $PtCl_6^{2-}$  can be obtained from these chromatograms and has the value 33.7 (log  $K_6 = 1.53$ )

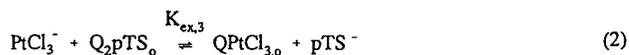
which agrees well with the value of 30.9 ( $\log K_e = 1.49$ ) determined by spectrophotometry Davidson et al.(1965).

The Pd(II), Pt(II) and Ir(III) are not extracted under these conditions and hence Pt(IV) and Ir(IV) can be separated from these and from each other.

### Separation of Pd(II) and Pt(II)

Pd(II) and Pt(II) are extracted from aqueous solutions containing lower concentration of NapTS ( $<0.01 \text{ mol dm}^{-3}$ ) and  $0.1 \text{ mol dm}^{-3}$  NaCl at pH 2.5 by DCE solutions containing  $0.002 \text{ mol dm}^{-3}$  QpTS. The D values of Pd(II) and Pt(II), however, are too close to permit their separation. Since Rh(III) and Ir(III) are not extracted under these conditions, Pt(II) and Pd(II) can be separated from Rh(III) and Ir(III). The individual CPC chromatograms of Pd(II) and Pt(II) are useful to characterize the hydrolytic equilibria of their chloro anions.

The CPC behavior of Pt(II) and Pd(II) are dependent on the concentration of  $\text{Cl}^-$  in the mobile phase. In the absence of any added NaCl ( $\text{pH} = 2.5$ ,  $[\text{HCl}] = 3.2 \times 10^{-3} \text{ mol dm}^{-3}$ ) in the mobile phase, Pt(II) exhibited two peaks and Pd(II) exhibited a very broad peak. When  $0.1 \text{ mol dm}^{-3}$  NaCl was added to the mobile phase, Pt(II) exhibited three peaks and the Pd(II) a less broad peak. These observations could be explained in terms of the hydrolytic equilibria of the chloro anions of Pt(II) and Pd(II). These equilibria are rapid for Pd(II), resulting in a broad peak due to the presence of  $\text{PdCl}^+$ ,  $\text{PdCl}_2$ ,  $\text{PdCl}_3^-$  and  $\text{PdCl}_4^{2-}$  (fraction of species,  $\alpha$ :  $\text{PdCl}^+ = 0.22$ ,  $\text{PdCl}_2 = 0.55$ ,  $\text{PdCl}_3^- = 0.22$ ,  $\text{PdCl}_4^{2-} = 0.01$ ) when no NaCl is added, Surakitbanham et al.(1991). Even though only the latter two species are extracted as their ion-pairs with  $\text{Q}^+$ , upon back-extraction the various chloroanions are rapidly formed in the concentrations indicated by their  $\alpha$ 's and the rapid equilibria between these species results in a broad chromatogram. The addition of  $0.1 \text{ mol dm}^{-3}$  NaCl favors the higher Cl complexes,  $\text{PdCl}_3^-$  and  $\text{PdCl}_4^{2-}$  ( $\alpha = 0.47$  for both) and results in a narrower chromatogram for Pd(II). Thus the Pd(II) chromatogram at  $0.1 \text{ mol dm}^{-3}$  NaCl is a composite of the ones for  $\text{PdCl}_3^-$  and  $\text{PdCl}_4^{2-}$  and the D value is the composite of the D values of the two species.



The hydrolytic equilibrium in the case of Pt(II) is much slower than Pd(II), Elding(1978). In the absence of added NaCl, the species being detected in CPC experiments are those present at  $[\text{HCl}] = 0.01 \text{ mol dm}^{-3}$  ( $\alpha$ :  $\text{PtCl}_2 = 0.07$ ,  $\text{PtCl}_3^- = 0.7$ ,  $\text{PtCl}_4^{2-} = 0.23$ ), Elding et al.(1966). Equilibrium between the chloroanions of Pt(II) is achieved very slowly at 298 K and, as a result, the back-extraction does not result in a broad peak as in the case of Pd(II). The CPC chromatogram under these conditions consists of two peaks, one due to  $\text{PtCl}_2$  at the dead volume as it is not extracted, and the other due mostly to  $\text{PtCl}_3^-$  and some  $\text{PtCl}_4^{2-}$ . When  $0.1 \text{ mol dm}^{-3}$  NaCl is added to the mobile phase, more  $\text{PtCl}_4^{2-}$  is formed leading to a third peak, Figure 2. This reasoning was tested by conducting Pt(II) experiments at  $0.1 \text{ mol dm}^{-3}$  NaCl by varying NapTS ( $3 - 8 \times 10^{-3} \text{ mol dm}^{-3}$ ) at constant QpTS ( $2 \times 10^{-3} \text{ mol dm}^{-3}$ ) and varying QpTS ( $2 - 5 \times 10^{-3} \text{ mol dm}^{-3}$ ) at constant NapTS ( $0.01 \text{ mol dm}^{-3}$ ). The plot of  $\log D$  vs  $\log [\text{QpTS}]$  yielded slopes of +1 and +2 for the  $\text{PtCl}_3^-$  and  $\text{PtCl}_4^{2-}$  respectively. The plot of  $\log D$  vs  $\log [\text{NapTS}]$  yielded slopes of -1 and -2 for the  $\text{PtCl}_3^-$  and  $\text{PtCl}_4^{2-}$  respectively, confirming the role of hydrolytic equilibria in the CPC separations. The extraction equilibrium for  $\text{PtCl}_3^-$  as an example is shown in equation 2. The CPC chromatograms of the chloro species of Pt(II) as a function of the concentration

of chloride at  $QpTS = 2 \times 10^{-3} \text{ mol dm}^{-3}$  and  $NaPTS = 0.004 \text{ mol dm}^{-3}$  are shown in Fig 2. As may be seen, increasing the  $[Cl^-]$  results in an increase in the concentration of  $PtCl_4^{2-}$  as expected. The bands due to  $PtCl_3^-$  and  $PtCl_3^-$  decrease and the  $PtCl_3^-$  can be only seen as a shoulder of the  $PtCl_4^{2-}$  band at  $0.6 \text{ mol dm}^{-3} Cl^-$ . The  $D$  value of  $PtCl_4^{2-}$  also decreases with increasing  $[Cl^-]$  as evident from its shift to lower retention volumes. These observations can be rationalized on the basis of QCl competing with QpTS for the extraction of  $PtCl_3^-$  and  $PtCl_4^{2-}$ .  $PtCl_2$  does not form an ion-pair and appears at the dead volume.

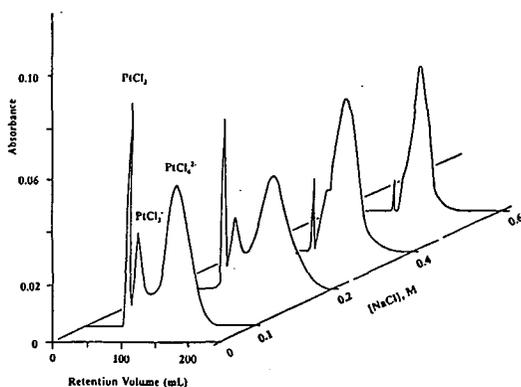


Figure 2. Separation of the chloro anions of Pt(II).  $[QpTS] = 0.002 \text{ mol dm}^{-3}$ ,  $[NapTS] = 0.004 \text{ mol dm}^{-3}$ ,  $pH = 2.5$ ,  $[NaCl] = 0.1 - 0.6 \text{ mol dm}^{-3}$ , aqueous flow rate =  $2 \text{ cm}^3 \text{ min}^{-1}$ ,  $V_{DCE}/V_{aq} = 1$ .

The fraction of  $PtCl_3^-$  and  $PtCl_4^{2-}$  can be calculated from the areas of the CPC chromatograms in Fig 2 at  $0.1 \text{ mol dm}^{-3}$  and  $0.2 \text{ mol dm}^{-3} Cl^-$ . These areas must be corrected for the different molar absorptivities of these species at  $242 \text{ nm}$ , namely  $\epsilon(PtCl_3^-) = 1.75 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and  $\epsilon(PtCl_4^{2-}) = 4.39 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . These values were determined by recording the uv spectra of  $4 \times 10^{-4} \text{ mol dm}^{-3} Pt(II)$  at  $0.01 \text{ mol dm}^{-3} Cl^-$  ( $\alpha: PtCl_3^- = 0.7, PtCl_4^{2-} = 0.23$ ) and at  $0.4 \text{ mol dm}^{-3} Cl^-$  ( $\alpha: PtCl_3^- = 0.07, PtCl_4^{2-} = 0.93$ ), Elding(1978), after the solutions had been equilibrated with these chloride concentrations for several days at room temperature and at  $363 \text{ K}$  for  $4 \text{ h}$  prior to recording their spectra. The  $\alpha$  values of  $PtCl_3^-$  and  $PtCl_4^{2-}$  determined from the CPC chromatogram are different from the equilibrium  $\alpha$  values as might be expected.

The  $K_{ex}$  values for QpTS and QCl extraction can be calculated from the chromatogram in Fig 2. The various  $K_{ex}$  values are given in Table 1. As may be seen from Table 1 the  $K_{ex}$  values for the extraction by QCl are much larger than the values for the extraction by QpTS. This illustrates the practical problem in employing QCl as an extractant in that the back-extraction of the extracted ion-pair

cannot be achieved even at very high Cl<sup>-</sup> concentrations. On the other hand the K<sub>ex</sub> values for QpTS are such that extraction and back-extraction can be achieved with relatively low concentrations of pTS<sup>-</sup>.

We can determine log of the ratio, K<sub>QpTS</sub>/K<sub>QCl</sub> from the K<sub>ex</sub> values to be 2.89 which is similar to the ratio for tetrabutylammonium, namely 2.44, Gustavii(1967).

**TABLE 1**  
Extraction Equilibrium constants

Species	K <sub>ex</sub>	
	QpTS	QCl
IrCl <sub>6</sub> <sup>2-</sup>	7.76 x 10 <sup>3</sup>	
PtCl <sub>6</sub> <sup>2-</sup>	3.89 x 10 <sup>3</sup>	
PdCl <sub>4</sub> <sup>2-</sup>	17.6	1.2 x 10 <sup>6</sup>
PtCl <sub>3</sub> <sup>-</sup>	0.63	500
PtCl <sub>4</sub> <sup>2-</sup>	2.08	1.3 x 10 <sup>6</sup>

### CONCLUSIONS

We have demonstrated that tetraheptylammonium p-toluenesulfonate is a useful ion-pair extractant for the separation by CPC of Pd(II), Pt(II), Pt(IV) and Ir(IV) from Rh(III) and Ir(III). The selectivity for Pt(II) and Pd(II) is however poor. The chloro species of Pt(II) can be separated using the ion-pair extractant due to the slow hydrolytic equilibria of these species. These chromatograms can be used to determine the fraction of each Pt(II)- chloro species which clearly are different from their equilibrium values. Further the K<sub>ex</sub> values for the extraction by tetraheptylammonium p-toluenesulfonate and tetraheptylammonium chloride can be calculated as well from these CPC chromatograms. The K<sub>ex</sub> values for the extraction by the latter species are orders of magnitude larger than the values for the extraction by the former species.

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## COMPARATIVE STUDIES OF GOLD(III) EXTRACTION USING PHOSPHOLENE DERIVATIVES FROM HYDROCHLORIC ACID SOLUTIONS

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### ABSTRACT

The extraction of hydrochloric acid and Au(III) from hydrochloric acid solutions by 1-(dodecyloxy)-3-methyl-1-oxo- $\Delta^3$ -phospholen, 1-(2-ethylhexyloxy)-3-methyl-1-oxo- $\Delta^3$ -phospholen and 1-(2,6-dimethylhept-4-yloxy)-3-methyl-1-oxo- $\Delta^3$ -phospholen dissolved in cumene, kerosene and toluene have been studied.

The distribution of gold has been determined at a constant ionic strength of 0.5, 1.0 and 1.5 as a function of the analytical concentration of extractant and chloride concentration in the aqueous phase. The experimental data have been treated by means of the program LETAGROP-DISTRB. The results indicate the formation of  $\text{HAuCl}_4\text{L}$  and  $\text{HAuCl}_4\text{L}_2$  in the organic phase.

### INTRODUCTION

Solvent extraction is an alternative method for the separation and purification of gold(III). Several types of extractants have been applied to extract  $\text{AuCl}_4^-$  from hydrochloric acid solution; such as basic extractants like amines -Alguacil 1993, Ritcey 1984, Villaescusa 1993- or solvating extractants such as cyanex 923 -Martinez 1995- or cyanex 471 -Salvado 1990-. In the present work the extraction of HCl and Au(III) from hydrochloric acid solutions by phospholene derivatives with different alkyl chains attached to the phosphorus have been studied. The compositions of the extracted species as well as their equilibrium constants have been determined. The influence of the ionic strength, and the diluent is also analyzed.

### EXPERIMENTAL

#### Reagents and Solutions

The phospholenes used, 1-(dodecyloxy)-3-methyl-1-oxo- $\Delta^3$ -phospholen (DMPL), 1-(2-ethylhexyloxy)-3-methyl-1-oxo- $\Delta^3$ -phospholen (EHMPL) and 1-(2,6-dimethylhept-4-yloxy)-3-methyl-1-oxo- $\Delta^3$ -phospholen (NMPL), were kindly donated by Bayer Leverkusen. Solutions of Au(III) were prepared by dilution with HCl from solid  $\text{HAuCl}_4$ , Johnson Mathey, of 49% purity. Cumene, kerosene and toluene (Fluka A.R) were used as solvents without purification. Tris (hydroxymethyl)-aminomethane and HCl (Merck A.R) were used. The phospholene derivatives are given in Fig. 1.

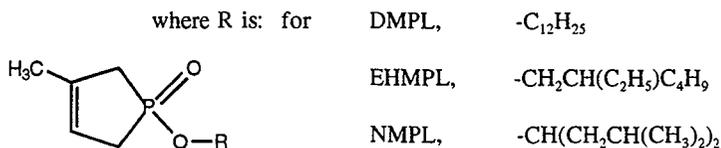


Figure 1. Structure of phospholene derivatives.

## PROCEDURE

The experiments were carried out at 25 °C. Hydrochloric acid and gold extraction were carried out by shaking mechanically organic solutions (10 ml) containing certain concentration of the phospholenes dissolved in kerosene or cumene with aqueous solutions (10 ml) for two hours; time enough to reach equilibrium. The concentration of Au(III) in the aqueous phase was varied from  $5 \times 10^{-5}$  to  $2.7 \times 10^{-4}$  mol dm<sup>-3</sup>. The ionic strength was kept constant with HCl at 0.5, 1.0 and 1.5 M. After phase separation, the equilibrium pH was measured and the metal content was determined by atomic spectrometry using a 2380 Perkin Elmer Absorption Spectrometer. In the extraction of hydrochloric acid, the acidity of the equilibrated organic phases was determined by titration with standard sodium hydroxide solutions using Bromothymol blue as indicator.

## RESULTS AND DISCUSSION

### Hydrochloric Acid Extraction

Phospholenes can extract mineral acids from aqueous solutions. To study the extraction of hydrochloric acid with the phospholenes, solutions in different diluents, and different concentrations in the diluents were shaken with 0.5, 1.0 and 1.5 mol dm<sup>-3</sup> of hydrochloric acid.

The extraction of HCl by DMPL, EHMP and NMPL can be described by using the following reaction:



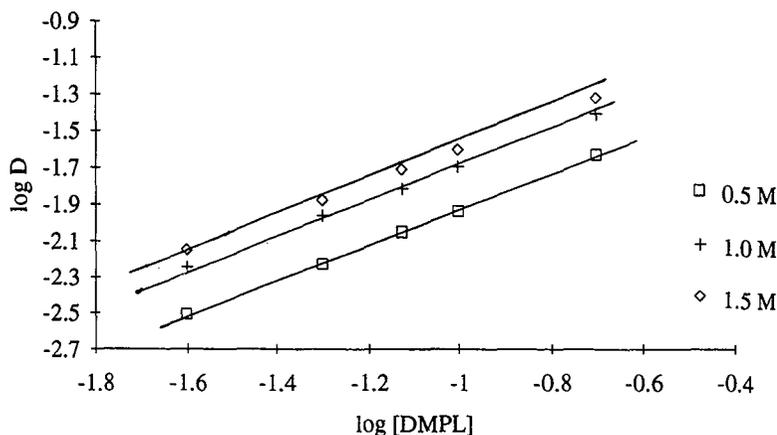
where  $\beta_n$  is the extraction constant defined as:

$$\beta_n = \frac{[\text{HClL}_n]_{\text{org}}}{[\text{HCl}] [\text{L}]^n} \quad (2)$$

Defining the HCl distribution coefficient as the relationship between the concentration of hydrochloric acid in the organic and the aqueous phase, equation (2) can be written as:

$$\log D_{\text{HCl}} = \log \beta_n + n \log [\text{L}_{\text{org}}]$$

Thus by plotting  $\log D_{\text{HCl}}$  vs  $\log [\text{L}]_{\text{org}}$  straight lines of slope  $n$  should be obtained. Examples of these plots are given in Fig. 2 where the slopes near to 1 indicate that species of stoichiometry HClL are present in organic phase.



**Figure 2.**  $\log D$  as a function of total DMPL concentration for 0.5, 1.0 and 1.5 M hydrochloric acid. The full lines have been calculated using the constants given in Table 1.

Further analysis of the experimental data has been done by the program LETAGROP-DISTRB - Liem (1971)-. In this program, for a given model, the computer searches for the best set of equilibrium constants that would minimize the error square sum defined by:

$$U = \sum (\log D_{\text{calc}} - \log D_{\text{exp}})^2$$

where  $D_{\text{exp}}$  is the experimental distribution ratio of HCl and  $D_{\text{calc}}$  is the value calculated by the program solving the mass balance equation. For a chemical system the best model is that which has the lowest U value. The results for the extraction of HCl for different phospholenes and diluents are given in Table 1.

Table 1  
Extraction constants of HCl by different phospholenes

Extractant	I	Diluent	$\log \beta_1$
DMPL	0.5	kerosene	$-0.89 \pm 0.06$
	1.0		$-0.84 \pm 0.01$
	1.5		$-0.75 \pm 0.07$
	0.5	cumene	$-0.60 \pm 0.01$
	1.0		$-0.59 \pm 0.04$
	1.5		$-0.55 \pm 0.06$
EHMPL	0.5	kerosene	$-1.17 \pm 0.02$
	1.0		$-0.92 \pm 0.06$
	1.5		$-0.56 \pm 0.06$
	0.5	cumene	$-0.37 \pm 0.03$
	1.0		$-0.37 \pm 0.05$
	1.5		$-0.34 \pm 0.12$
NMPL	0.5	kerosene	$-1.27 \pm 0.23$
	1.0		$-1.17 \pm 0.22$
	1.5		$-1.04$ Max: $-0.82$
	0.5	cumene	$-0.54 \pm 0.02$
	1.0		$-0.54 \pm 0.02$
	1.5		$-0.49 \pm 0.04$

### Gold Extraction

The distribution of gold(III) has been studied as a function of the extractant concentration in the organic phase and the gold concentration in the aqueous phase for different HCl concentrations varying from 0.5 to 1.5 mol dm<sup>-3</sup>. The distribution ratio for Au(III) is defined as:

$$D = \frac{[\text{Au(III)}]_{\text{org}}}{[\text{Au(III)}]_{\text{tot}}} \quad (3)$$

where  $[\text{Au(III)}]_{\text{tot}} = [\text{HAuCl}_4] + [\text{AuCl}_4^-]$ .

In the experimental conditions used in this work, the extraction of Au(III) by a solvating reagent L can be written as follows:



where  $K_n$  is the extraction constant defined as:

$$K_n = \frac{[\text{HAuCl}_4 \text{L}_n]_{\text{org}}}{[\text{AuCl}_4^-] [\text{H}^+] [\text{L}]_{\text{org}}^n} \quad (4)$$

By substituting equation (3) in (4) and rearranging, the following expression can be obtained:

$$\log D = \log K_n - pH + n \log [L]_{org} - \log \left( \frac{[H^+]}{K_a} + 1 \right) \quad (5)$$

where  $K_a$  is the acidity constant of  $\text{HAuCl}_4$  -Forsberg 1960-

An example of the experimental data is plotted as  $\log D$  vs  $\log [\text{DMPL}]$  for 1.0 M hydrochloric acid in Fig. 3, from which it can be observed that the slopes are near 1 and 2 at low and higher extractant concentrations, respectively. This indicates that two species,  $\text{HAuCl}_4\text{L}$  and  $\text{HAuCl}_4\text{L}_2$ , are formed in the organic phase.

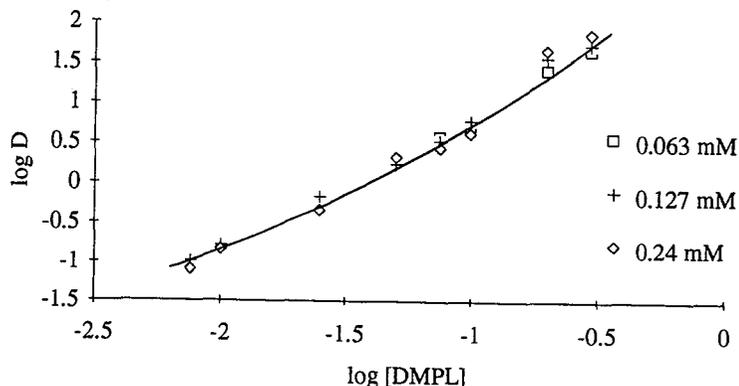


Figure 3.  $\log D$  as a function of total DMPL concentration in cumene at different initial Au(III) and 1.0 M of hydrochloric acid. The full line has been calculated from the data of Table 2.

The experimental data have been treated with the program LETAGROP-DISTRB. The model found from graphical treatment was considered as the starting point of the numerical calculations. Other species were also tried and the effect of the fit was examined.

The results of the best model and the equilibrium constant are given in Table 2.

Table 2  
Extraction constants of Au(III) for different phospholenes

Extractant	I	$\log K_1$	$\log K_2$	$\log K_1^0$	$\log K_2^0$
DMPL	0.5	$0.96 \pm 0.26$	$2.60 \pm 0.13$	$1.05 \pm 0.20$	$2.82 \pm 0.20$
	1.0	1.11 Max: 1.32	$3.06 \pm 0.11$		
	1.5	$1.37 \pm 0.15$	$2.94 \pm 0.13$		
EHMPL	0.5	$1.02 \pm 0.18$	$2.42 \pm 0.16$	$1.19 \pm 0.20$	$2.60 \pm 0.20$
	1.0	$1.28 \pm 0.11$	$2.74 \pm 0.11$		
	1.5	$1.36 \pm 0.18$	$2.77 \pm 0.23$		
NMPL	0.5	$0.68 \pm 0.26$	1.78 Max: 2.03	$0.75 \pm 0.20$	$2.14 \pm 0.20$
	1.0	$0.68 \pm 0.11$	$2.19 \pm 0.09$		
	1.5	$1.04 \pm 0.22$	$2.53 \pm 0.22$		

The results of the gold extraction at different ionic strengths I, show that the composition of the extracted species is independent of I, whereas the extraction constants vary. In order to correlate the values of the equilibrium constants with the ionic strength, the specific interaction theory developed by Guggenheim and Scatchard was used. In the approach, the acidity coefficient  $\gamma_i$  of an anion of charge  $Z_i$  in a solution of ionic strength I may be expressed as:

$$\log \gamma_i = -Z_i D(I) + \sum e_{(iK)} m_K \quad (6)$$

where  $D(I)$  is the Debye-Hückel term: 
$$D(I) = \frac{0.5109 \sqrt{I}}{1 + 1.5 \sqrt{I}} \quad (7)$$

Assuming ideal behaviour in the organic phase, the dependence of  $K_{n,1}$  on  $I$  is given by:

$$\log K_{n,1} + 2 D(I) = \log K_n^0 + [\epsilon(H^+, Cl^-) + \epsilon(AuCl_4^-, H^+)] \quad (8)$$

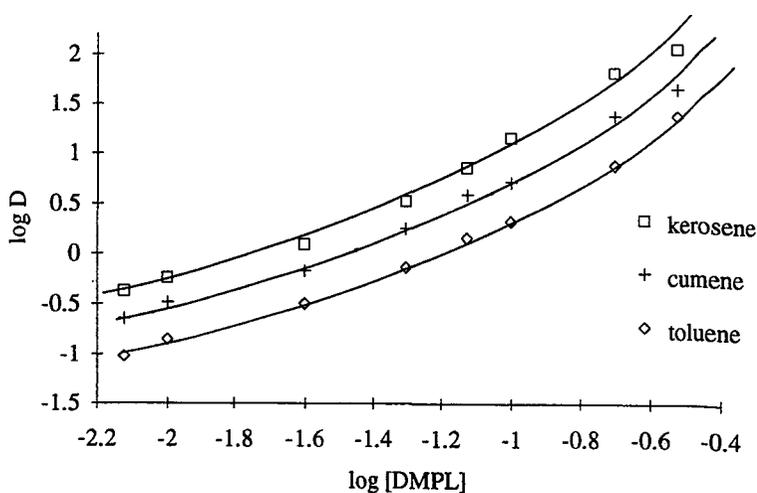


Figure 4.  $\log D$  as a function of total DMPL concentration in different diluents at initial Au(III)  $6.3 \times 10^{-5}$  and 1.0 M of hydrochloric acid concentration. The full lines have been calculated using the constant given in Table 2.

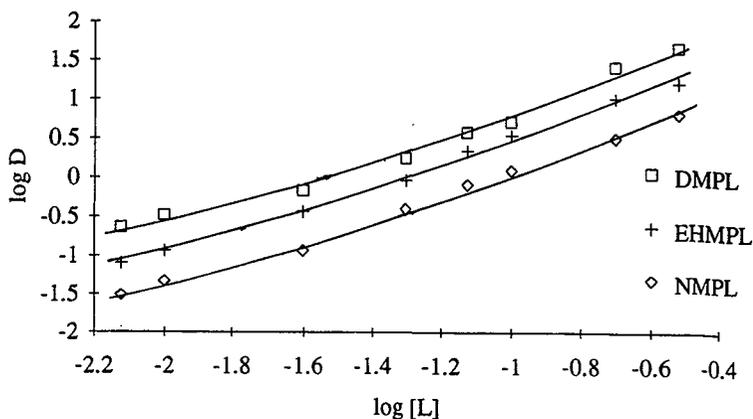


Figure 5.  $\log D$  as a function of total extractant concentration at initial Au(III) concentration  $6.3 \times 10^{-5}$  M and 1.0 M of hydrochloric acid concentration. The full lines have been calculated using the constant given in Table 2.

The term  $\epsilon$ , called interaction coefficient, is equal to zero if ions  $i$  and  $k$  are of the same charge sign and  $I$  is the ionic strength defined as  $I = \frac{1}{2} \sum Z_i^2 m_i$  and  $m_i$  is the concentration in the molality scale. By plotting  $\log K_{e,1} + 2 D(I)$  vs  $I$  the ordinate allows the calculation of the thermodynamic extraction constant  $K_1^0$  and  $K_2^0$  -Martinez 1995-. The results are given in Table 2.

Fig. 4, shows the influence of the diluents on the extraction of  $AuCl_4$ . The order is kerosene > cumene ~ toluene. The extraction of  $AuCl_4$  with phospholene derivatives follows the order DMPL > EHMPL > NMPL as seen in Fig. 5. As a general rule, extraction with neutral organophosphorus compounds improves with branching of the alkyl chain, the effect being most marked with branching near the alkoxy oxygen. This is related to the basicity of the ester, which increases with branching. Nevertheless, in this case it seems that the steric hindrance has more influence than the basicity on the extraction efficiency and the extraction ability of phosphorus towards  $AuCl_4$  decreases where there's an increase in the steric hindrance. While DMPL has a linear chain attached to the oxygen bonded to the phosphorus, EHMPL and NMPL have a branched chain with primary and secondary carbon atoms bonded to the oxygen attached to the phosphorus respectively.

#### ACKNOWLEDGEMENTS

This work has been supported by CICYT (Ministerio de Educación y Ciencia de España) Project MAT 93-6212. The authors wish to thank BAYER LEVERKUSEN for kindly donating phospholenes.

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## Options for the Recovery of Cerium by Solvent Extraction

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### ABSTRACT

This paper reports the results of an experimental program to examine the use of various commercial reagents for the extraction of cerium (IV) from sulphate solutions. Extractants tested include organophosphorus esters (TOPO, Cyanex 923 & Cyanex 925), organophosphorus acids (DEHPA, Ionquest 801 & Cyanex 272) and high molecular weight amine, Alamine 336. The suitability of reagents is assessed in terms of process relevant criteria such as extraction dependence on acidity, selectivity over other rare earths and thorium, stability of reagent towards oxidation and loading characteristics.

### INTRODUCTION

Processes for the recovery of cerium from rare earth concentrates, such as monazite and bastnasite, commonly rely on the chemical properties of cerium (IV) to effect its separation from the other rare earths. Low-grade cerium products contain different impurities, depending on the composition of the starting material. Thus roasting of bastnasite, followed by HCl leaching, produces an insoluble fraction containing up to 10% F (Kilbourn 1992). This material can be further upgraded to a medium purity product (90-98% CeO<sub>2</sub>) by dissolution and precipitation. The processing of monazite concentrate has to take into account thorium. Monazite concentrate typically contains 8% ThO<sub>2</sub> compared with < 0.5 % ThO<sub>2</sub> in bastnasite. Caustic digestion is the most common method of converting the rare earth phosphates into hydroxides which are then leached with acid. Thorium is kept in the residue by pH control. The cerium can be separated from the leach liquors by oxidative precipitation to produce a product of medium purity or by oxidation (electrolytic or chemical) and solvent extraction to produce high purity products (>99% CeO<sub>2</sub>).

Most of the literature on solvent extraction processes for cerium deal with extraction of Ce(IV) from nitrate media. Reviews by Liddell & Bautista (1984) and Ritcey & Pouskouleli (1985) indicate that the process has changed little since the early reports (Korpusov 1962) on the extraction of Ce(IV) with tributyl phosphate and back extraction by reductive stripping with hydrogen peroxide. Korpak (1971) used 40% TBP in n-heptane to extract Ce(IV) at 105 g L<sup>-1</sup> from 4.5 M HNO<sub>3</sub>. Hydrogen peroxide was used as a reducing agent. A strip liquor of purity 99.95% CeO<sub>2</sub> was reported. Hafner (1977) described the recovery of Ce(IV) from nitrate liquor (7.4 M HNO<sub>3</sub>) obtained from the leaching of bastnasite. H<sub>3</sub>BO<sub>3</sub> was used to complex fluoride. The strip solution was a mixture of 6 M HCl/H<sub>2</sub>O<sub>2</sub>/H<sub>3</sub>BO<sub>3</sub>. Saleh (1966) recovered spectrographically pure CeO<sub>2</sub> using a similar TBP process, with NaNO<sub>2</sub> as a reducing agent in the strip circuit. In this last process the starting material was monazite, but other processing steps were included to remove Th, Fe, Si and phosphate. A major variation to the TBP solvent extraction process is the use of electrolytic oxidation and reduction. Electrolytic oxidation of Ce(III) in nitrate media in the presence of a mixture of DEHPA/TBP was investigated by Zhang (1981). A method was reported for the separation of Ce from Pm (tracer concentrations) by electrolytic oxidation and extraction using reductive stripping to recover Ce. Ying-Chu Hoh (1987 & 1988) reported on both electro-oxidative extraction and electro-reductive stripping in the Ce-TBP-HNO<sub>3</sub> system.

Limited information is available for the extraction of Ce(IV) from sulphate solutions. Work at the U.S Bureau of Mines (Douglass & Bauer 1959) showed that bastnasite sulphate leach liquors required addition of 6-8 N HNO<sub>3</sub> in order to extract Ce(IV) with TBP. Sulphuric acid was used for stripping and the cerium was recovered by oxalate precipitation yielding a 99.6-99.8% CeO<sub>2</sub>

product. More recently, Rhone-Poulenc filed a patent (Horbez 1989) for a process where cerous sulphate is electrolytically oxidised and simultaneously extracted into an organophosphorus acid. The solvent was stripped with 2.5 - 5 M H<sub>2</sub>SO<sub>4</sub>.

The disadvantages of nitrate solutions are the problems associated with their disposal. In this regard, recovery of cerium from sulphate solution would be preferable. Such solutions can be obtained by dissolution of cerium concentrate from bastnasite processing, dissolution of oxidised conversion cake from monazite processing or dissolution of medium purity cerium products. This paper presents experimental data on the extraction of Ce(IV) from sulphate solutions and assesses some of the commercially available solvents.

### EXPERIMENTAL METHODS

Extraction data was obtained by contacting aqueous and organic phases in separating funnels. The temperature was controlled at 22<sup>o</sup>± 0.5 C. Aqueous Ce, Sm, Y, Th and S concentrations were determined by ICP-OES or ICP-MS. Concentrations in the organic phase were determined by two methods: i) by difference of initial and equilibrium aqueous concentrations and ii) by stripping of solvent with 6M HCl or 0.1M HCl depending on the organic reagent and element to be stripped. Organic reagents were used as supplied, with the exception of Alamine 336, Cyanex 923 and Cyanex 925 which were pre-equilibrated with Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. n-Heptane was used as diluent in all cases, except for the extraction of sulphuric acid with TOPO at 40<sup>o</sup>C. In this case, Shellsol 2037 was used.

The following procedure was used to measure solvent degradation. An aqueous cerium(IV) solution was contacted with a solvent at unit phase ratio so that the equilibrium concentration of cerium in the organic was around 2-3 g L<sup>-1</sup>. DEHPA and TOPO were not pre-equilibrated. Alamine 336 was tested both with/without pre-equilibration with Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The two phases were kept in contact with stirring, and equal volume samples were withdrawn from both phases at various time intervals. All samples were analysed for Ce<sub>total</sub> by ICP-OES and Ce(IV) by addition of ferrous sulphate and back titration with ceric sulphate.

### RESULTS & DISCUSSION

#### Acidic Extractants

The extraction of cerium over a wide range of acidities with organophosphorus acids (HR) such as DEHPA (di-2-ethylhexyl phosphoric acid), Ionquest 801 (2-ethylhexyl 2-ethylhexylphosphonic acid) and Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) is shown in Figure 1. With the organophosphorus acids studied, the order of extraction follows the pK<sub>a</sub> order, with the lower pK<sub>a</sub> acid extracting more cerium(IV) at the higher acidities. i.e.



The reverse order occurs for the extraction of sulphuric acid, with the stronger base extracting more acid as shown in Table 1. The sulphur concentration in the organic phase was taken as a measure of sulphuric acid extraction. Significant sulphuric acid extraction takes place only at aqueous concentrations > 10 N H<sub>2</sub>SO<sub>4</sub>.

**TABLE 1**  
Extraction of sulphuric acid at A:O=1 and aqueous [H<sub>2</sub>SO<sub>4</sub>]=21.6 N

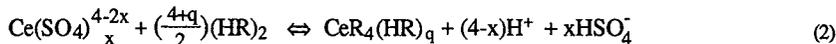
Reagent	[Reagent], M	[S] <sub>organic</sub> , g L <sup>-1</sup>
DEHPA	0.36	1.80
Ionquest 801	0.29	3.78
Cyanex 272	0.22	10.5

Extraction of cerium(III) with DEHPA decreases with increasing acidity according to the well known reaction (1) for trivalent rare earths.

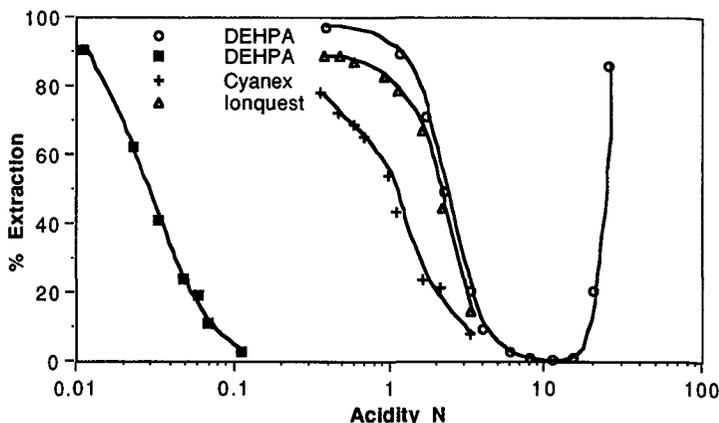


Extraction of Ce(IV) with DEHPA occurs from higher acidities, with two distinct regions of extractions; in the first region (~ 0.3-10 N H<sub>2</sub>SO<sub>4</sub>) extraction decreases with increasing acidity, and in the second region (>10 N H<sub>2</sub>SO<sub>4</sub>) extraction increases with increasing acidity (see Figure 1). At

acidities  $>10$  N  $\text{H}_2\text{SO}_4$  extraction of cerium(IV) is accompanied by extraction of significant amounts of sulphuric acid. In the first region of extraction, uptake of sulphuric acid by the extractant is not significant. However, S was detected together with Ce in the organic phase. The Ce:S ratio was dependent on both acidity and organic loading. At high solvent loading the Ce:S molar ratio was as high as 2:1. The presence of sulphur in the organic phase suggests the possibility of formation of complexes of both type  $\text{CeR}_4(\text{HR})_q$  and  $\text{CeSO}_4\text{R}_2(\text{HR})_t$ , with extraction reactions represented by general equations (2) and (3).



Of the organophosphorus acids, DEHPA is the most suitable for extraction of Ce(IV) from sulphate solutions. High extractions for cerium with Ionquest 801 and Cyanex 272 occur at less acidic regions, where hydrolysis can become a problem. At acidities 0.5-2 N  $\text{H}_2\text{SO}_4$ , extraction of sulphuric acid is not significant. It is important to minimise sulphuric acid extraction in order to prevent sulphate contamination of the strip solution. Maximum solvent loading occur with Ce:S:HR ratios of 1:0.5:3. Thus a 25 vol.% DEHPA solution will have a capacity of  $35 \text{ g L}^{-1}$  Ce and will carry up to  $8 \text{ g L}^{-1}$  S.



**Figure 1** Extraction of cerium from sulphate solution with organophosphorus acids

DEHPA (open symbol):	Organic - 0.29 M DEHPA in n-heptane, Aqueous - $2 \text{ g L}^{-1}$ Ce (IV)
DEHPA (closed symbol):	Organic - 0.1 M DEHPA in n-heptane, Aqueous - $0.34 \text{ g L}^{-1}$ Ce (III)
Ionquest:	Organic - 0.27 M Ionquest 801 in n-heptane, Aqueous - $2 \text{ g L}^{-1}$ Ce (IV)
Cyanex:	Organic - 0.27 M Cyanex 272 in n-heptane, Aqueous - $2 \text{ g L}^{-1}$ Ce (IV)

### Solvating Extractants

Extractants tested were: tributyl phosphate (TBP), dibutylbutyl phosphonate (DBBP), bis(2-ethylhexyl 2-ethylhexyl phosphonate (BEHEHP), trioctyl phosphine oxide (TOPO or Cyanex 921), Cyanex 923 (a mixture of phosphine oxides with n-octyl and n-hexyl groups) and Cyanex 925 (a mixture of phosphine oxides with n-octyl and 2,4,4-trimethylpentyl groups).

The extraction of cerium (III & IV) with TBP has previously been reported to only take place at concentrations  $> 10$  N  $\text{H}_2\text{SO}_4$  -Douglass (1959). We found no significant extraction of cerium(IV) with either TBP, DBBP or BEHEHP in the 0.5-7 N sulphuric acid range. Cerium(IV) is well extracted with TOPO. On contact with Cyanex 923 & 925, cerium(IV) was reduced to cerium(III), which was not extracted. Pre-equilibration of the reagents with sodium carbonate eliminated this problem in the case of Cyanex 923 but not in the case of Cyanex 925. Extraction of sulphuric acid by some of these reagents (Figure 2) shows that of the three phosphine oxide reagents, Cyanex 925

extracts the least amount of acid, given similar molar reagent concentrations. However, because the problem of reduction of cerium(IV), no further tests were undertaken with this reagent.

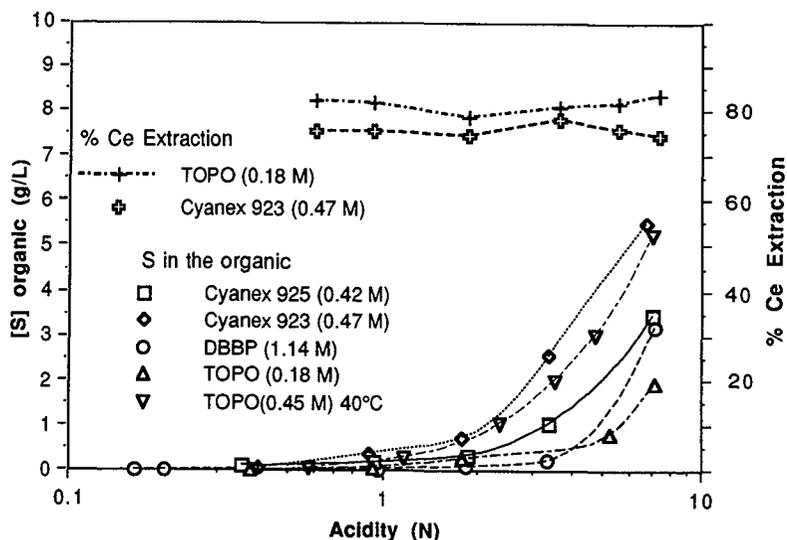


Figure 2 Extraction of sulphuric acid and cerium with solvating extractants diluted in n-heptane.

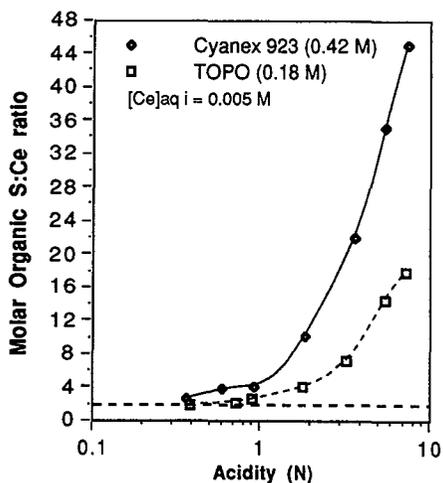


Figure 3 Molar ratio of S:Ce in the organic phase for the extraction of Ce(IV)

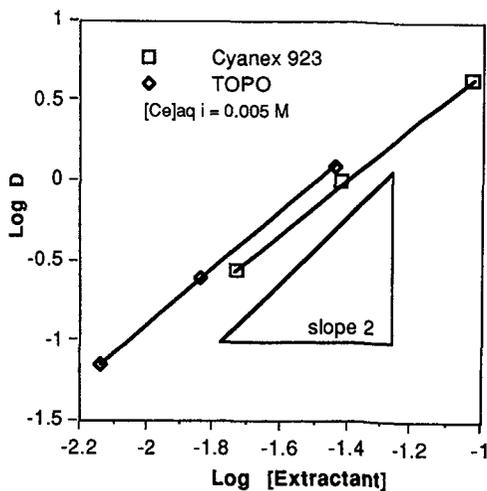
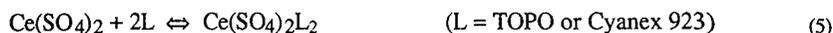


Figure 4 Logarithmic plot of the distribution coefficient versus extractant concentration at  $0.2$  M  $H_2SO_4$ .

With both TOPO and Cyanex 923, extraction of cerium(IV) was found to be independent of acidity in the 0.5-5 N sulphuric acid range (Figure 2). The minimum molar ratio of sulphur to cerium in

the organic phase is around two (Figure 3), indicating extraction of  $Ce(SO_4)_2$ . Logarithmical plots of the distribution coefficient versus the molar extractant concentration (Figure 4) yield straight lines with slopes close to two, pointing to the extraction reaction outlined in equations 5 and 6.



$$\text{Where } D = \frac{[Ce(SO_4)_2L_2]}{[Ce(SO_4)_2]} \text{ and } K = \frac{[Ce(SO_4)_2L_2]}{[L]^2[Ce(SO_4)_2]}$$

$$\text{substituting D and K into (5) } \log D = \log K + 2 \log [L] \quad (6)$$

Both TOPO and Cyanex 923 are suitable extractants for Ce(IV), but it is important to keep the acidity as low as possible to prevent sulphuric acid extraction. The solubility of TOPO in aliphatic diluents places a restriction on maximum loadings. Thus at 20°C, 100 g L<sup>-1</sup> TOPO solution will theoretically load a maximum of 17 g L<sup>-1</sup> Ce. With this reagent, Ce:S:L ratios in the organic phase at maximum loading is 1:2:2. Cyanex 923, being a liquid at room temperature, can be prepared at much higher molar concentrations and will therefore achieve higher solvent loadings.

### Selectivity

In the purification of cerium, it is important to take into account the selectivity of the reagent for Ce(IV). Table 2 shows the separation factors obtained for Ce(IV) over Th and some of the trivalent rare earths, with selected reagents. Separation factors ( $\beta_{Ln(III)}^{Ce(IV)}$ , Ln(III) = La, Gd, Yb) published by Preston (1990) for extraction from 2M NH<sub>4</sub>NO<sub>3</sub>/1M HNO<sub>3</sub> solution by TBP are of the order 10<sup>3</sup>. With the exception of DEHPA, selectivity of reagents tested compare well with that of TBP. With DEHPA, selectivity of Ce(IV) over the trivalent rare earths decreases along the series light to heavy. In addition, DEHPA extracts Th preferentially to Ce(IV). However, some opportunity exists for the selective stripping of cerium with dilute acid by reducing it to the trivalent state.

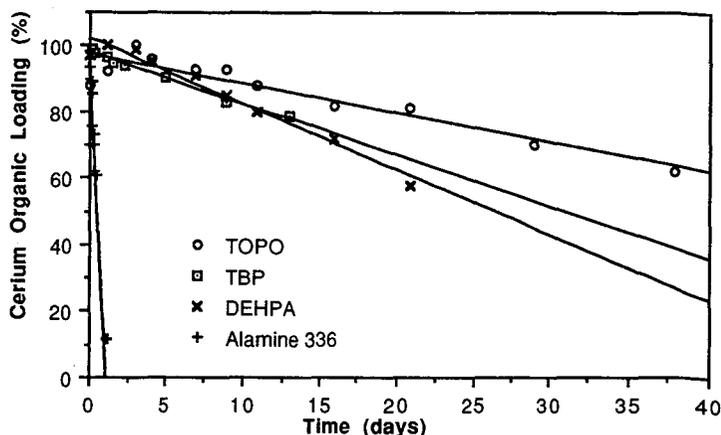
**TABLE 2**  
**Separation Factors for Extraction of Ce(IV), Ce(III), Y(III), Sm(III) and Th(IV)**

Reagent	DEHPA 5 vol. %	Alamine 336 3 vol. %	Cyanex 923	TOPO
Ce(IV)/Ce(III)	> 10 <sup>3</sup>	> 10 <sup>3</sup>	> 10 <sup>3</sup>	> 10 <sup>3</sup>
Ce(IV)/Sm(III)	275	> 10 <sup>3</sup>	> 10 <sup>3</sup>	> 10 <sup>3</sup>
Ce(IV)/Y(III)	2.3	10 <sup>3</sup>	> 10 <sup>3</sup>	> 10 <sup>3</sup>
Ce(IV)/Th(IV)	0.053	> 10 <sup>2</sup>	8.9	14.3

Initial concentrations = 1000 ppm, [H<sub>2</sub>SO<sub>4</sub>] = 1 N

### Solvent Degradation

Cerium(IV), being a strong oxidising agent, is potentially capable of degrading the extractant with prolonged contact. TOPO, DEHPA and Alamine 336 were tested for degradation using the procedure outlined in the experimental section. The degradation of the solvent was not measured directly, but the decrease in cerium organic concentration due to reduction of Ce(IV) to Ce(III) was assumed to be an indication of the rate of degradation of the solvent. The decrease in organic cerium concentration was accompanied by an increase in aqueous cerium concentration. Figure 5 plots the decrease in cerium organic loading (ie  $[Ce]_{org} / [Ce]_{org \text{ maximum}}$ ) as a function of time. Data obtained by Warf (1947) has also been included to provide a basis for comparison with TBP degradation from a nitrate system. Under the experimental conditions shown, the half-life of the solvents (50% decrease in cerium organic concentration) was 12 hours, 25 days, 32 days and 57 days for Alamine 336, DEHPA, TBP and TOPO respectively. Alamine 336 was also tested after equilibration with Na<sub>2</sub>CO<sub>3</sub> to remove possible reducing impurities, but 50% Ce(IV) reduction still occurred within 24 hours. Thus on the basis of degradation alone, Alamine 336 is not suitable for extraction of Ce(IV). The degradation rates of the other three reagents are of the same order of magnitude, with TOPO being the most resistant to oxidation.



**Figure 5 Reduction of cerium loaded onto the organic as a function of time.**

Alamine: Organic - 3 vol.% Alamine 336 in n-heptane, Aqueous - 5.5 g L<sup>-1</sup> Ce in 0.6 M H<sub>2</sub>SO<sub>4</sub>

DEHPA: Organic - 20 vol.% DEHPA in n-heptane, Aqueous - 5 g L<sup>-1</sup> Ce in 0.7 M H<sub>2</sub>SO<sub>4</sub>

TOPO: Organic - 36 g L<sup>-1</sup> TOPO in n-heptane, Aqueous - 5 g L<sup>-1</sup> Ce in 0.7 M H<sub>2</sub>SO<sub>4</sub>

TBP\*: Organic - 100% TBP (vacuum distilled), Aqueous - 1 N HNO<sub>3</sub>/0.5 N (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>

\*Note: TBP data reproduced from Warf (1947)

### CONCLUSIONS

Both neutral and acidic organophosphorus reagents (eg DEHPA & Cyanex 923) are suitable for the extraction of Ce(IV) from acidic sulphate solutions. Extraction of sulphuric acid can be minimised, but co-extraction of sulphate as part of the extraction mechanism cannot be prevented. In both instances, strip solutions will contain considerable amounts of sulphate, leading to possible contamination of solids precipitated directly from strip solutions. The selectivity of TOPO and Cyanex 923 for Ce(IV) over the trivalent rare earths and Th is better than that of DEHPA. Extraction of Ce(IV) with Alamine 336 is not recommended due to the fast rate at which Ce(IV) is reduced when in contact with the reagent.

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## KINETIC APPROACH FOR EU(III) AND AM(III) SEPARATION USING SELECTIVE THENOYLTRIFLUOROACETONE- TRIPHENYLARSINE OXIDE SYSTEMS

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### ABSTRACT

The kinetics of separation of Eu(III) and Am(III) by Thenoyltrifluoroacetone (HTTA)-Triphenylarsine oxide ( $\text{Ph}_3\text{AsO}$ ) mixture in chloroform from nitrate medium were investigated using a stirred Lewis cell. The separation factor of Am(III) and Eu(III) is evaluated in terms of time at different concentrations of HTTA,  $\text{Ph}_3\text{AsO}$ ,  $\text{H}^+$ ,  $\text{NO}_3^-$  and temperature. Optimum conditions for the enhancement of Am(III)/Eu(III) separation and the recovery of each of these nuclides on kinetic basis are discussed.

### INTRODUCTION

The exploitation of the differences in the reaction kinetics of metal ions is among the most important future trends in lanthanides/actinides separation, Nash (1994). The kinetics of extraction of trivalent lanthanides and actinides is of major importance in their extraction from irradiated nuclear fuel. In this context, the present work aims to propose a new approach for the separation of Am(III) and Eu(III) from a nitrate medium based on the difference in the kinetic behaviour of these two nuclides. In previous publications Zakareia et al (1986) and Daoud et al (1991, 1993, 1994) have studied the equilibrium and mechanism of extraction of Eu(III) and Am(III) by HTTA- $\text{Ph}_3\text{AsO}$  from perchlorate or nitrate media. The results have shown that Am(III) and Eu(III) are better extracted from a nitrate medium rather than a perchlorate medium, Daoud (1993). In addition, both nuclides are extracted at higher rates from a nitrate medium (Daoud(1994)) compared with its rate of extraction from a perchlorate medium. In the present work the effect of time on the separation factor of Am(III)/Eu(III) at different extractant concentration, pH, nitrate concentration and temperature are studied. The results are compared with those previously obtained at equilibrium and the conditions of enhancing the separation factor of these two nuclides on a kinetic basis are discussed.

### EXPERIMENTAL

#### Reagents

All chemicals used were of analytical grade (AR) and used without further purification.

The acetate buffer was prepared from sodium acetate and acetic acid adjusted to an ionic strength 0.1M with sodium perchlorate or sodium nitrate.  $^{152+154}\text{Eu}$  was prepared by neutron irradiation of the spectroscopically pure europium oxide while  $^{141}\text{Am}$  was obtained from Amersham. Both tracers were used in concentrations less than  $10^{-6}\text{M}$ .

### Procedure

The concentration of HTTA and  $\text{Ph}_3\text{AsO}$  used in the kinetic investigations were 0.032M and 0.008M for HTTA and  $\text{Ph}_3\text{AsO}$ , respectively. These concentrations were varied when studying the effect of the extractant concentration on the separation factor of Am(III) and Eu(III) in the investigated systems. The kinetics of Am(III) and Eu(III) distribution was studied using a stirred Lewis cell which is described with the measurement procedure in a previous publication, Daoud, (1991).

The separation feasibility of Am(III) from Eu(III) is evaluated in terms of the separation factor (S) between Am(III) and Eu(III) is represented by,

$$S = D_{\text{Am}} / D_{\text{Eu}} \quad (1)$$

where  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  are the distribution ratios of Am and Eu, respectively. The separation factor S was evaluated in terms of time (t) at different concentrations of HTTA,  $\text{Ph}_3\text{AsO}$ ,  $\text{NO}_3^-$ , pH and temperature.

## RESULTS AND DISCUSSION

Previous equilibrium investigations on the extraction of Am(III) and Eu(III) by a HTTA- $\text{Ph}_3\text{AsO}$  mixture in chloroform from a nitrate medium have shown that the extraction constant of Am(III) is given by,

$$K_{\text{Am}} = D[\text{H}^+]^2 / [\text{HTTA}]^3 [\text{Ph}_3\text{AsO}] \quad , \text{M}^{-2} \quad (2)$$

while the extraction constant of Eu(III) is given by

$$K_{\text{Eu}} = D[\text{H}^+] / [\text{HTTA}]^3 [\text{NO}_3^-]^2 [\text{Ph}_3\text{AsO}] \quad , \text{M}^{-5} \quad (3)$$

The mean values of  $K_{\text{Am}}$  and  $K_{\text{Eu}}$  were found to be  $(9.89 \pm 0.06) \times 10^{-2} \text{M}^{-2}$  and  $(2.32 \pm 0.02) \times 10^4 \text{M}^{-5}$ , respectively.

The separation feasibility of Am(III) from Eu(III) have shown that S is pH dependent while it is second power dependent on the reciprocal of the nitrate concentration and independent of the extractant concentration, Daoud et al (1993).

### Effect of pH

The calculated values of the distribution ratio of Am(III) and Eu(III) and their separation factors in terms of pH (3 to 4.52) are given in Table 1. The tabulated data show higher values of  $D_{\text{Eu}}$  compared with  $D_{\text{Am}}$  for all the pH values investigated. The separation factor given in the table decreases and its value is  $< 1$  and a minimum separation factor of 0.13 was reached after 120 s when the pH of the medium was 4.45. Previous separation studies on the same system under equilibrium conditions have shown that the separation factor of these nuclides increases with increase in the pH, Daoud et al (1993). Therefore, under similar experimental conditions and at the same pH, for example pH=4.0, Am(III) could be better extracted by HTTA- $\text{Ph}_3\text{AsO}$  in chloroform under equilibrium conditions ( $S=4.5$ ) while Eu(III) is better recovered kinetically from the same solution.

*Effect of nitrate concentration*

The effect of  $[\text{NO}_3^-]$  on the kinetics of Am(III)/Eu(III) separation was studied by varying its concentration in the range 0.01-0.1 M while keeping the ionic strength constant at 0.1M by adding  $\text{NaClO}_4$ . The results have shown that for all nitrate concentrations investigated Eu(III) is better extracted than Am(III) under the same experimental conditions ( $S < 1$ ), Fig.1. Previous results of Am(III)/Eu(III) separation under equilibrium conditions have shown that a maximum S value of 4.5 was reached at pH=3.5, when  $[\text{NO}_3^-]=0.054 \text{ M}$  while under these experimental conditions, and based on the variation of S with time, the separation factor is 0.48. Consequently, maximum separation in favour of Am(III) is obtained when pH=3.5 from an aqueous nitrate medium of  $[\text{NO}_3^-]=0.054 \text{ M}$  under equilibrium conditions, while the separation of Eu(III) is preferred by kinetic extraction after 30s when  $[\text{NO}_3^-]=0.06\text{M}$ .

TABLE 1

Effect of time on the separation factor of Am(III) from Eu(III) ( $S = D_{\text{Am}}/D_{\text{Eu}}$ ) by HTTA- $\text{Ph}_3\text{AsO}$  from aqueous nitrate medium at different pH's  
 $T=25^\circ\text{C}$        $[\text{HTTA}]=0.032 \text{ M}$        $[\text{Ph}_3\text{AsO}]=0.008 \text{ M}$   
 $u=0.1 \text{ M}$  stirring rate= 500 rpm

Time $\times 10^{-2}$ , s	Separation factor ( $S = D_{\text{Am}}/D_{\text{Eu}}$ )				
	pH=3.0	pH=3.50	pH=3.82	pH=4.07	pH=4.82
0.3					
0.6	0.39	0.37	0.45	0.46	0.29
0.9			0.46	0.21	0.21
1.2				0.36	0.19
1.5		0.36		0.33	0.14
1.8				0.30	0.18
2.4			0.43	0.34	0.28
3.6		0.38	0.53	0.30	
6.0	0.44	0.33	0.52	0.55	0.17
9	0.35	0.36		0.36	0.18
12	0.46	0.31	0.39	0.30	0.16
18	0.40	0.26	0.39	0.38	
27		0.39	0.41	0.39	
36		0.31			
		0.29			

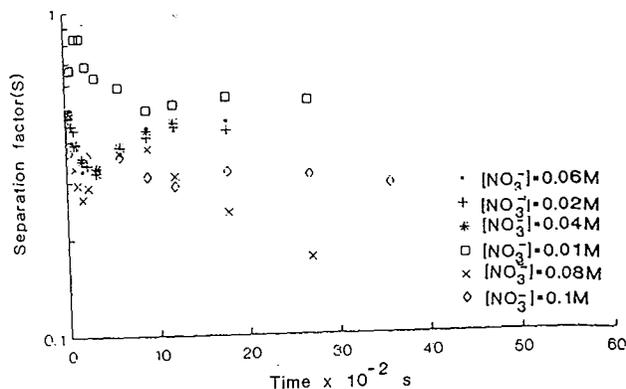


Figure 1. Effect of time on the separation factor of Am(III) and Eu(III) at different nitrate concentrations

*Effect of [HTTA]*

The effect of the HTTA concentration on the kinetics of Am(III)/Eu(III) separation was investigated by varying its concentration in the range 0.01-0.075 M, when [Ph<sub>3</sub>AsO]=0.008 M, pH=3.5 and [NO<sub>3</sub><sup>-</sup>]=0.1M. The results represented in Fig.2 show that the value of S always decreased with time. The maximum S (0.69) was reached after 30 s while its minimum value (0.15) was reached after 120 s when the HTTA concentration was 0.075 M. It has to be mentioned that under equilibrium conditions, the separation factor of Am(III)/Eu(III) did not depend either on [HTTA] or on [Ph<sub>3</sub>AsO], Daoud et al (1993). As the above results have shown that the separation of these nuclides could be kinetically controlled, therefore Am(III) is preferably separated after 30 s while Eu(III) separation is favoured after 120 s when [HTTA]= 0.075 M.

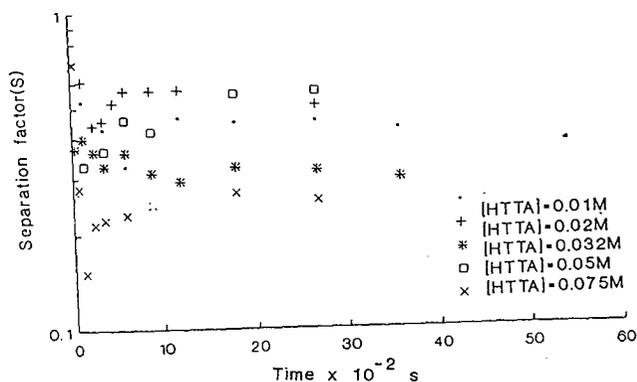


Figure 2. Effect of time on the separation factor of Am(III) and Eu(III) at different HTTA concentrations.

### Effect of $[Ph_3AsO]$

The concentration of  $[Ph_3AsO]$  in chloroform was varied in the range 0.002-0.01 M to study its effect on the kinetics of Am(III)/Eu(III) separation. The results have shown that a maximum separation factor of 1.24 was obtained after 120 s when  $[Ph_3AsO]=0.002$  M while a minimum separation value of 0.14 was reached after  $6 \times 10^2$  s when  $[Ph_3AsO]=0.006$  M, Fig.3. The above results indicate that a low  $Ph_3AsO$  concentration (0.002 M) is preferred for the separation of Am(III) while a higher concentration (0.006 M) is more suitable for the separation of Eu(III).

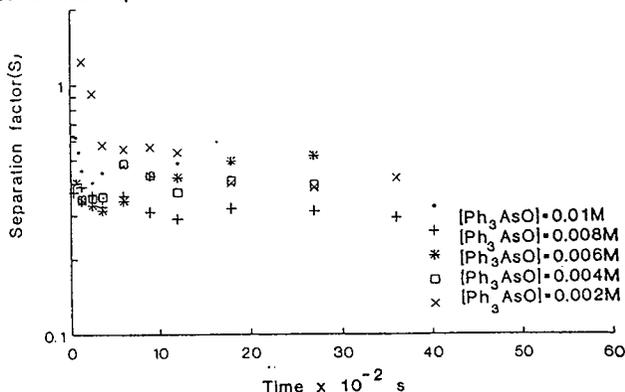


Figure 3. Effect of time on the separation factor of Am(III) and Eu(III) at different  $Ph_3AsO$  concentrations.

### Effect of temperature

The variation of temperature from 5°C to 45°C showed that a relatively high separation factor of 1.12 is reached after 60 s when the temperature is 35°C while the minimum separation value is obtained after  $12 \times 10^2$  s at 25°C, Fig.4. These results show that the increase in temperature is in favour of Am(III) extraction while the reverse is true for Eu(III). Moreover, for the same extraction experiment at 35°C we can obtain high Am(III) extraction after 60s while taking an aliquot after 1200 s gives a higher extraction of Eu(III).

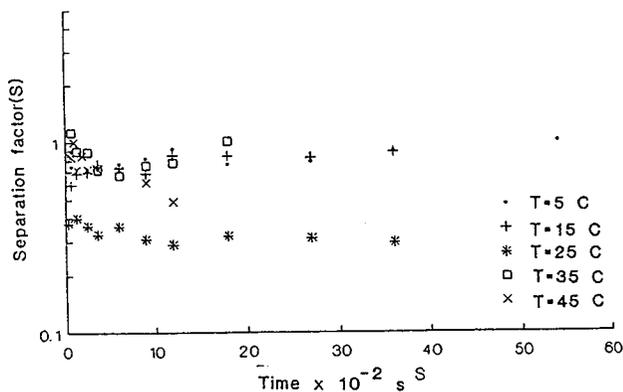


Figure 4. Effect of time on the separation factor of Am(III) and Eu(III) at different temperatures.





## LABORATORY AND BENCH-SCALE STUDIES OF HEAVY METAL ION REMOVAL FROM AQUEOUS STREAMS

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### ABSTRACT

The removal of heavy metal ions from aqueous waste streams has importance in metal ion recovery and waste stream remediation. The use of selective adsorbents to extract heavy metals is a promising alternative to classical solvent extraction. Selective adsorbents have been synthesized by covalent attachment of chelating ligands to ceramic surfaces for the selective removal of lead, cadmium, and zinc from dilute aqueous streams. The method of synthesis, evaluation of distribution coefficients, adsorbent capacity, and adsorbent stability from laboratory experiments will be discussed. Results of bench-scale studies conducted with ~ 100 g fixed beds will also be discussed. The bed stability for multiple adsorption/stripping cycles, the pH dependence of the adsorption process, and factors causing and the method to overcome adsorbate deactivation for long-term operation will be discussed.

### INTRODUCTION

The study of the removal of metal ions from dilute aqueous solution, either for pollution control or for raw material recovery, has been increasingly important in recent years. Metals or metallic compounds are used during the manufacture of a variety of products. As a result, industries generate wastes containing metals (Radha Krishnan *et al.*, 1993; Tavlarides, 1985). Various methods utilized for removal of heavy metal ions include precipitation, solvent extraction, ion exchange, adsorption, evaporation, reverse osmosis and electrolysis (Peters, 1985). However, these processes have met with various levels of limited success. For example, efficiency of adsorption is limited by the phase equilibrium properties of various solutes and the ease with which the sorbent can be regenerated (Tedder, 1994; Chen, *et al.*, 1991).

The specific objective of the present work is to develop novel adsorbents, inorganic chemically active beads (ICABs), to be used in fixed-bed adsorbers in an alternative heavy metal ion removal/recovery process. A series of ICAB materials are developed to selectively remove desired heavy metal ions from aqueous streams (Tavlarides, *et al.*, 1994). This paper discusses the method of preparation of the synthetic adsorbents, laboratory-scale studies, and bench-scale studies on the removal of lead, cadmium and zinc from aqueous streams. Uptake capacity, stability and selectivity of these materials is discussed.

## EXPERIMENTAL

Preparation of Inorganic Chemically Active Beads - Inorganic chemically active beads (ICABs) were prepared by immobilizing chelating molecules on the surface of ceramic supports based on the desired porosity, pore size, surface areas and chemical stability. Various synthesis methods used for immobilization include surface treatment, physical adsorption/volatilization and covalent bonding (Tavlarides *et al.*, 1994). The hydroxy terminal groups of the ceramic support are reacted to modify the surfaces, and these latter materials are used for immobilization of the chelating molecules on inorganic matrices by chemisorption on the hydrophobic surface and by chemical bonding.

Characterization of Inorganic Chemically Active Beads (Laboratory-scale Studies) - The synthesized materials were characterized for degree of hydrophobicity and surface coverage of chelating molecules by performing elemental analysis and potentiometric titrations. The effect of pH on the adsorption of lead, zinc and cadmium on the prepared ICABs was determined by a batch equilibration procedure. The concentrations of metal ions were determined by atomic absorption spectroscopy. The capacity of the ICABs for a given metal ion was determined by performing breakthrough studies on the packed bed. Glass columns were packed with approximately 3 g of ICABs, and flow rates to achieve about 4 minutes residence time were used. Metal ions adsorbed on the columns were desorbed with varying concentrations of different mineral acids to determine suitable stripping agents.

Bench-scale Studies - A bench-scale unit was designed for an ICAB bed of 100 g, and the manual laboratory procedure was scaled up for this unit. The scale-up criteria yielded column dimensions of 2.5 cm in diameter and 30 cm in length. The bench-scale process consists of a pump drawing from one of four solution feed tanks, pumping through the adsorption column, and discharging into one of two product tanks (Figure 1). The solenoid valves are opened or closed by the computer as required according to the sequential operating procedure during the column cycle. Also, an automatic sampler is placed below the sample valve to take effluent samples at given times during the cycle. Breakthrough curves were determined by passing 200 ppm cadmium solution at a flow rate of 3 L/hr and 6 L/hr to provide residence times of 2.9 min and 1.4 min, respectively.

## RESULTS AND DISCUSSION

Metal Ion Uptake as a Function of pH - The metal cations react with the acidic chelating agents to form complexes by releasing protons according to the reaction:

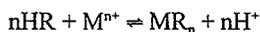


Figure 2 illustrates that cadmium is quantitatively extracted on ICAB(E) adsorbent at and above pH 5.0 where as extraction of lead and zinc is increased with pH of the aqueous solution. Thus, this pH dependency can be exploited for selective removal and separation of these metal ions.

Uptake Capacity and Regeneration of ICABs (Laboratory-scale Studies) - Breakthrough curves were obtained to determine the capacity of the materials. ICAB(E) material has shown a capacity of 80

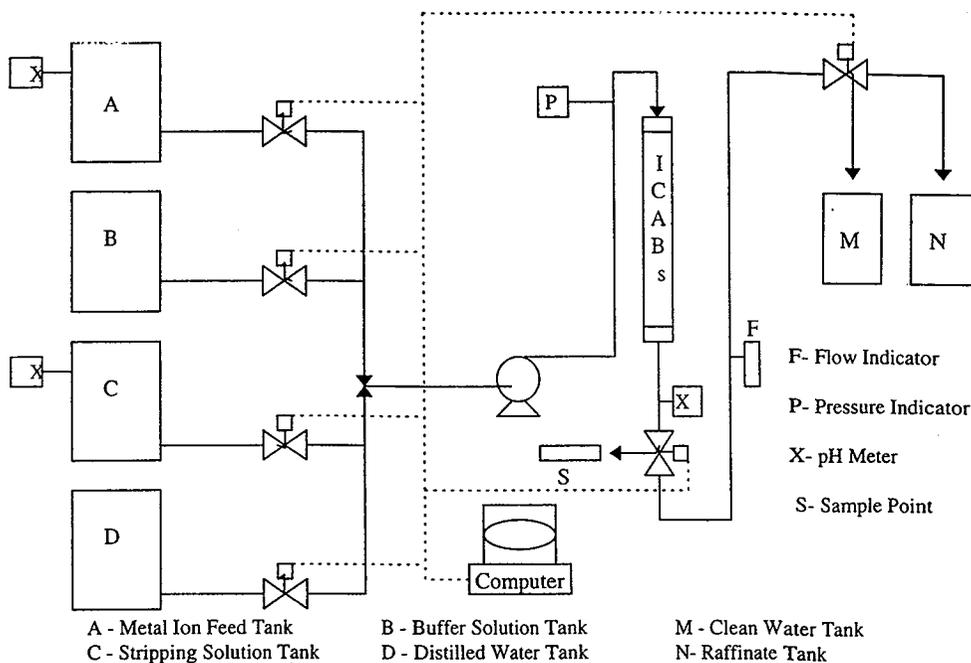


Figure 1 Schematic of the Adsorption Process Flow

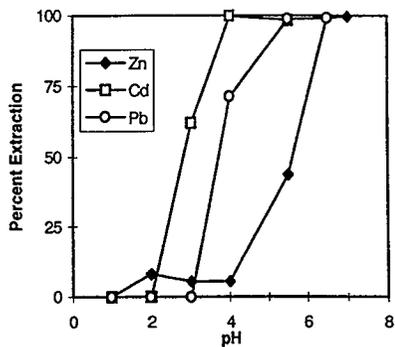


Figure 2 pH Isotherms of Pb, Cd and Zn Curves on ICAB(E)

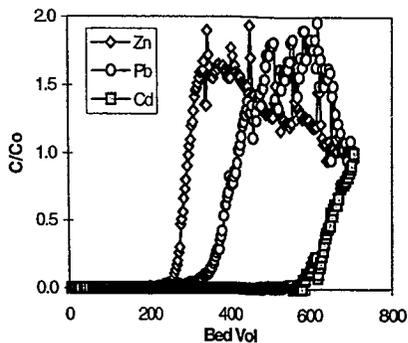


Figure 3 Multiple Metal Ion Breakthrough Curves on ICAB(E)  
 pH = 6.5, [Zn(II)] = 54.5 ppm  
 [Pb(II)] = [Cd(II)] = 50 ppm

mg/g as cadmium ions are removed to less than 1 ppm from an aqueous solution containing 200 ppm cadmium. Figure 3 is the breakthrough curve of lead, cadmium and zinc for ICAB(E) material and shows this material is capable of removing all three metal ions simultaneously from an aqueous stream containing mixtures of metal ions. ICAB(E) material has high stability as it retains a capacity of 56.5 mg/g after 20 adsorption/stripping cycles (Table 1).

**Table 1 - Uptake Capacities of ICABs**

ICABs	Metal Ion	Conc. of Feed Solution, ppm	pH of Feed Solution	Capacity mg/g
ICAB(D)				
1st cycle (lab)	Cd(II)	200.0	6.5	19.8
20th cycle (lab)	Cd(II)	200.0	6.5	5.65
ICAB(E)				
1st cycle (lab)	Cd(II)	200.0	6.5	80.03
20th cycle (lab)	Cd(II)	200.0	6.5	56.5
1st cycle (bench)	Cd(II)	184.0	6.5	67.3
3rd cycle (bench)	Cd(II)	191.5	5.8	54.0
16th cycle (bench)	Cd(II)	191.6	5.8	42.7

After the saturation of the column with metal ions, the bed can be regenerated by stripping metal ions with mineral acids. The ICAB(E) column was quantitatively regenerated with 0.1 M HCl. In another process scheme lead, cadmium and zinc were removed simultaneously at pH 6.5 and were recovered separately by first stripping zinc with 0.1 M nitric acid, then lead with 1.0 M nitric acid, and finally cadmium with 2.0 M hydrochloric acid as shown in Figure 4.

Bench-Scale Studies - A breakthrough curve of cadmium conducted at cycle 3 on the bench-scale unit is shown in Figure 5 where cadmium ions are removed to less than 1 ppm from a 200 ppm aqueous stream. Prior to this breakthrough curve, two adsorption/stripping cycles were conducted. Table 1 shows the capacity values at different cycles for bench-scale and laboratory-scale studies. A stripping curve of cadmium is shown in Figure 6. After saturation of the column, 98.3% of the loaded cadmium ions are recovered with approximately 9 bed volumes of 0.1 M HCl. Thus, cadmium ion can be recovered in a minimum volume of stripping solution, and a concentration factor of 25-30 can be achieved.

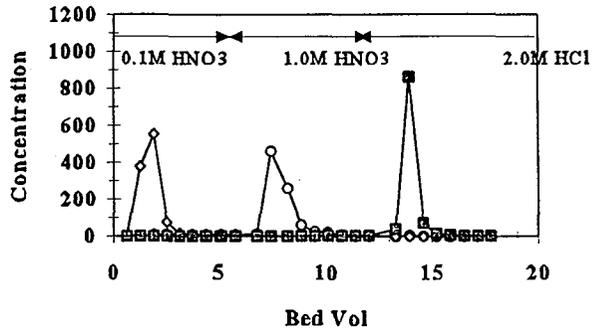


Figure 4 Separation of Zn, Pb, and Cd by selective stripping from ICAB(D)

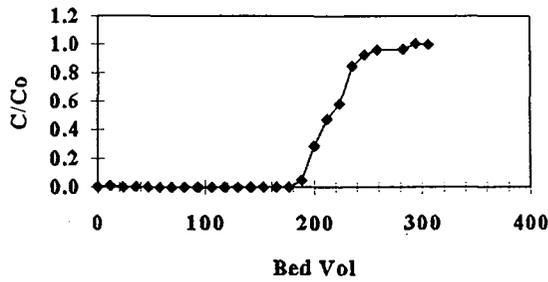


Figure 5 Breakthrough Curve of Cadmium on ICAB(E)  
 $C_o = 191.5$  ppm; pH = 5.8; Cycle Number 3 (Bench Scale)

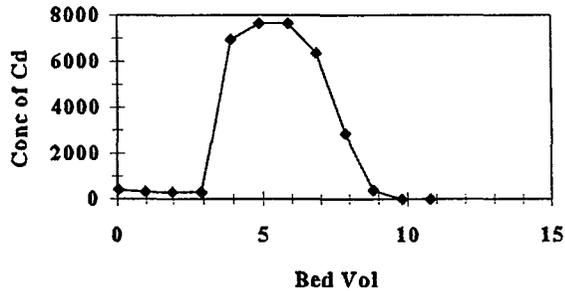


Figure 6 Stripping of Cadmium from ICAB(E) Column  
 Stripping Agent = 0.1 M HCL; Cycle Number 3 (Bench Scale)

## CONCLUSIONS AND FUTURE WORK

Selective adsorbents have been synthesized by covalent attachment of chelating ligands to ceramic surfaces. The prepared adsorbents have high capacity and stability. The materials can be regenerated by stripping adsorbed metal ions. A concentration factor of 25-30 is achieved. Also, it is possible to separate lead, cadmium and zinc by selective stripping with mineral acids. Breakthrough curves on a bench-scale unit show the feasibility of the ICAB adsorption process for heavy metal ion removal/recovery from aqueous streams.

The studies on a bench-scale unit are in progress to determine the long-term stability and interference due to other commonly associated metal ions. Also, the distribution coefficient ( $K_d$ ) of metal ion and adsorption rate data will be obtained. Models will be developed to predict adsorption/stripping cycle performance of the bed. These results will be presented as well.

## ACKNOWLEDGMENT

We acknowledge support of this research by the U.S. EPA through grant no. R818630-01-1 and by the U.S. EPA, RREL, through grant no. CR822727-0100.

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## SURFACE EXCESS ENERGIES OF HIGH PRESSURE CARBON DIOXIDE - AQUEOUS ALCOHOL SYSTEMS

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### ABSTRACT

Interfacial tensions were measured between aqueous solutions of primary and secondary alcohols and carbon dioxide at temperatures from 5 to 70 °C and pressures from 0.1 to 18 MPa. The data were analysed in terms of surface excess energy. The maximum of the surface excess energy increased with temperature. The magnitude of this maximum decreased with concentration and with alcohol carbon number. Among the mixtures and conditions examined, iso-butanol was the only alcohol which exhibited negative surface excess energies. In general, surface excess energy decreased as the temperature increased.

### INTRODUCTION

Supercritical fluids (SCF) have been known for over a century, yet they have only been studied intensely in the last decade or two as extraction solvents. Supercritical fluid extraction (SFE) is of increasing interest in the food, chemical, pharmaceutical and perfume industries. The reason for this popularity is that the solvating capacity of the SFE is higher than that of conventional extraction techniques and can be varied in the near critical state with relatively small changes in system pressure and temperature.

In a SFE process several factors determine the mass transfer rate. They include column hold-up, drop diameter, diffusion properties and column operating conditions. Among these factors drop size is particularly dependent on interfacial tension (IFT). For reliable engineering design of a SFE column it is essential to have good data on IFT between the immiscible phases. This paper analyses measured IFT data in terms of the surface excess energy.

### EXPERIMENTAL METHODS

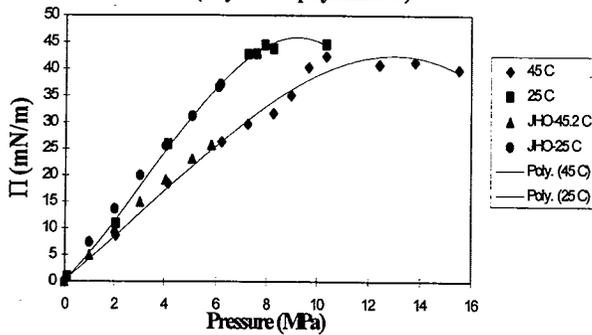
The IFT data analysed here were obtained by the capillary rise method. This technique is well established and is described in detail in Adamson (1982). The capillary rise was measured with a cathetometer to  $\pm 0.01$ mm and pressure using a precision Bourdon tube gauge, calibrated against the vapour pressure of pure carbon dioxide. Temperature was held constant to better than  $\pm 0.1$  °C and measured with a calibrated thermocouple. Two different sizes of capillary 0.605 mm and 1.400 mm i.d. were used to cover the range of IFT. The aqueous phase density was determined from IUPAC tables with no correction for dissolved solute. This approach is justified since we have established that equilibrium is quickly achieved at the interface yet diffusion of solute into the bulk is slow.

This is the situation in extraction columns for which our data are intended. This is also similar to the approach of Jho et al. (1978).

IFT was calculated from the well known equation, Adamson (1982):

$$\gamma = \frac{1}{2} r \cdot g \left( h + \frac{r}{3} \right) \Delta\rho / \cos\theta \quad (1)$$

Figure 1. Surface pressures of carbon dioxide on water.  
(Poly. - cubic polynomial fit)



In applying this equation, four corrections are required arising from the effects of 1.) chamber size, 2.) liquid contained in the curved meniscus (the  $r/3$  term), 3.) degree of departure of meniscus from sphericity and 4.) contact angle. In this work, corrections for 1.) and 3.) were found to be insignificant, 2.) was allowed for but was less than 2% and often much smaller. In the case of 4.) it is commonly assumed that contact angle is zero (if  $\theta < 8^\circ$  then  $\cos\theta \approx 1$ ). Observation indicated that

this was so and in the absence of other data, this assumption was made here.

To analyse the measured IFT data surface excess energy was employed. It is instructive to estimate this energy in binary and ternary systems of different compositions. Hiller et al. (1993) suggested a method to calculate the surface excess indirectly using the Gibbs adsorption isotherm :

$$\Gamma_i = -\frac{1}{RT} \left( \frac{d\gamma}{d \ln \alpha} \right)_{T,P} \quad (2)$$

Neglecting the small amounts of water vapour in the gas phase (Jho et al. 1978), equation (2) becomes :

$$\left( \frac{\partial \Pi}{\partial P} \right)_T = \Gamma_i \frac{z \kappa T}{P} \quad (3)$$

We calculated the surface excess of carbon dioxide by rearranging equation (3):

$$\Gamma = d. \left( \frac{\partial \Pi}{\partial P} \right)_{T,i} \quad (4)$$

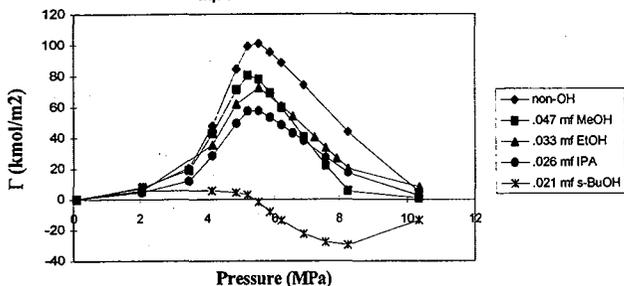
where the surface pressure,  $\Pi$ , was obtained from the following:

$$\Pi = \sigma_{H_2O} - \gamma_{CO_2/H_2O} \quad (5)$$

The surface tension of water,  $\sigma_{H_2O}$ , was obtained from the equation (6) suggested by Jasper (1972) :

$$\sigma_{H_2O} = 76.352 - 0.174 t (^{\circ}C) \quad (6)$$

Figure 2. Surface excess of carbon dioxide in water and various aqueous alcohol solutions at 15 C



The partial derivatives  $\left(\frac{\partial \Pi}{\partial P}\right)$  in equation (3) were obtained by differentiating the third order polynomial in pressure of the surface pressure. Fourth and fifth order polynomials were also examined, but proved to be inappropriate.

### Reagents

The Milli-Q water used was 'high-purity' degassed through a 0.22 $\mu$ m Millipore filter and free from surface active impurities. Its measured surface tension agreed with accepted values. The carbon dioxide was high grade (better than 99.8%), ethanol was absolute alcohol (99.9%) and other alcohols were reagent grade (99.7%) from BDH.

### RESULTS AND DISCUSSION

The ternary systems investigated here were mixtures of the water-carbon dioxide binary system with either methanol, ethanol, iso-propanol or sec-butanol. Surface pressures of the water-carbon dioxide system are presented in figure 1 and show good agreement with those of Jho et al. (1978).

Figure 2 shows the 15 °C surface excess isotherms of the water-carbon dioxide system compared with the ternary systems of 0.047 mf methanol, 0.033 mf ethanol, 0.026 mf iso-propanol and 0.021 mf sec-butanol (aqueous phase concentrations). The magnitude of the maximum excess energy of the water-carbon dioxide binary system was the greatest. This reflects the strongly non-ideal behaviour of this binary, which dominates the shape of the other ternary systems.

With the addition of the alcohols the maximum excess energy was reduced. The size of this reduction increased from the lower to the higher alcohols roughly in line with their lower solubility in water. Differences in the concentrations of the alcohols did not affect this ranking. This trend is evident in figures 3 and 4 which exhibit the surface excess energies of carbon dioxide in the aqueous ethanol and iso-propanol solutions at 15°C.

Sec-butanol exhibited very low excess energy at low pressures. This was due to the greater solubility of carbon dioxide in such solutions and reduced adsorption at the interface. This excess energy became negative from a pressure of approximately 5.5 MPa, corresponding to the minima evident in the IFT in figure 5.

Figure 3. Surface excess of carbon dioxide in the ethanol/water/carbon dioxide solutions at 15 C.

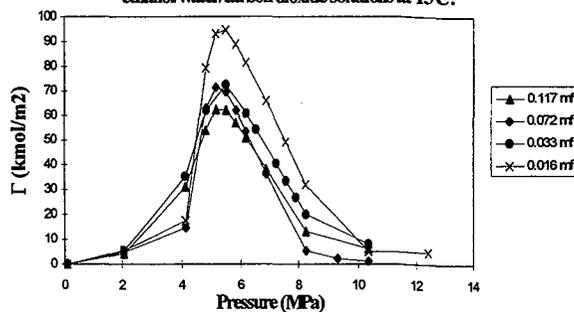
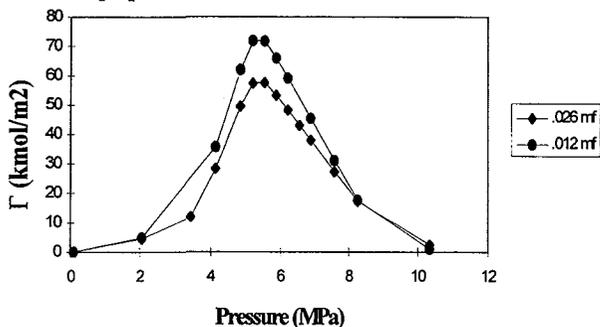


Figure 4. Surface excess of carbon dioxide in the iso-propanol/water/carbon dioxide solutions at 15 C.



of the maximum surface excess of the 0.026 mf iso-propanol-water-carbon dioxide reduced with the temperature increase from 15 to 65 °C. The maxima occurred at higher pressure with increasing temperatures. However, figure 7 shows that the aqueous sec-butanol once again behaved differently compared with lower alcohols. The occurrence of the maximum surface excess of the 0.021 mf sec-butanol-water-carbon dioxide solution obtained at the temperatures from 5 to 65 °C did not follow the same pattern as the iso-propanol one. In addition, it also displayed negative surface excess energies at all temperatures examined.

Figure 5. Interfacial tension isotherms of water/carbon dioxide and various alcohol/water/carbon dioxide solutions at 15 C.

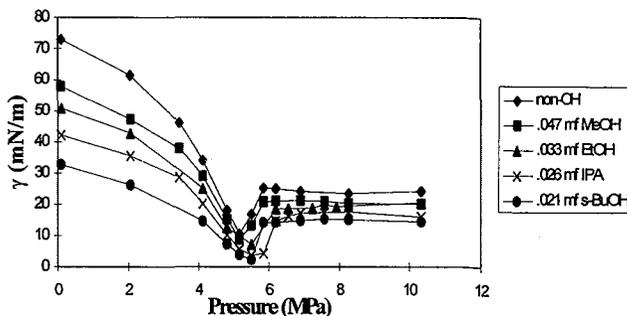
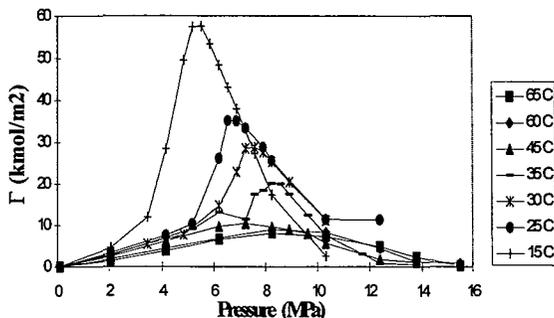


Figure 6. Surface excess isotherms of the ternary system : 0.026 mf iso-propanol/water/carbon dioxide.



The IFT of these systems exhibited a similar order of reduction as the corresponding surface excess energies and the familiar "dip" of the water-carbon dioxide binary system. They all decreased with increasing pressures until they reached a minimum when the pressure approached the carbon dioxide vapour pressure before rising with further increase in pressure. However, the IFT appeared to remain unchanged with higher pressure after a short rise.

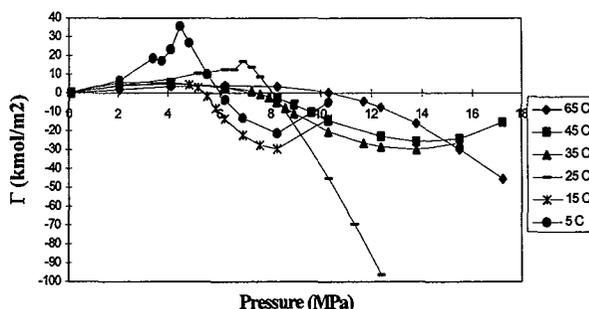
Figure 6 shows that the magnitude

## CONCLUSIONS

IFT between aqueous solutions of primary and secondary alcohols and carbon dioxide from 5 to 70 °C and from 0.1 to 18 MPa were measured. The data were analysed in terms of Gibbs adsorption and surface excess energy at the interface. The IFT data of the water-carbon dioxide binary system agreed with those of Jho et al.

The magnitude of the maximum excess energy of methanol, ethanol, iso-propanol and sec-butanol decreased from lower to higher alcohols and from lower to higher concentrations. The magnitude of the maximum excess energy was also diminished by increasing temperatures. Sec-butanol behaved differently from lower alcohols in several ways. Strongly non-ideal behaviour of the water-carbon dioxide binary system clearly dominated the behaviour of the aqueous alcohol-carbon dioxide ternary systems.

Figure 7. Surface excess of carbon dioxide in 0.021 mf sec-butanol/water/carbon dioxide as a function of pressure.



### SYMBOLS

- d = molar density ( $\text{mol.m}^{-3}$ )
- g = gravitational constant ( $9.8 \text{ m.s}^{-2}$ )
- h = height (m)
- i = components
- mf = mole fraction
- r = capillary radius (m)
- $\alpha$  = the activity of the dense gas
- $\gamma$  = interfacial tension (mN/m)
- $\Gamma$  = surface excess energy ( $\text{kmol/m}^2$ )
- $\rho$  = density ( $\text{kg.m}^{-3}$ )
- $\Delta\rho$  = density difference across interface ( $\text{kg.m}^{-3}$ )
- $\ominus$  = contact angle (degree)

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## SEPARATION OF YTTRIUM(III) FROM LANTHANOIDS(III) by SOLVENT EXTRACTION WITH SUBSTITUTED N-ALKYLCARBONYL-N-PHENYLHYDROXYLAMINES

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### ABSTRACT

A series of substituted *N*-alkylcarbonyl-*N*-phenylhydroxylamines (R-PHAs) were synthesized and utilized for the extraction of yttrium(III) and lanthanoids(III) in order to obtain effective extractants for the separation of yttrium(III) from the lanthanoids(III) and the mutual separation of the lanthanoids(III). The distribution ratio of yttrium(III) and the lanthanoids(III) between the carbon tetrachloride and the aqueous phases was measured as functions of the pH and the extractant concentration at 298 K at an ionic strength of 0.1 (NaNO<sub>3</sub>). Yttrium(III) and the lanthanoids(III) were extracted with R-PHAs(HL) as self-adducted chelates of the form, ML<sub>3</sub>(HL)<sub>x</sub>, where x is 1, 2 or 3 depending on the extraction system. The extractability of the metal ions decreased in the order of R-PHA having a primary, a secondary and a tertiary alkyl substituent attached to the carbonyl group because of the steric hindrance of the alkyl group. The separation factors for both Yb/Eu and Yb/Y pairs increased with increasing branching of the alkyl group of R-PHA. The excellent selectivity of R-PHAs having a tertiary alkyl group was attributable to a greater inductive effect of the tertiary alkyl group than those of the primary and secondary alkyl groups. The substituents at the phenyl group of R-PHAs gave no significant effect on the selectivity, while the extractability was enhanced considerably by introduction of electron withdrawing substituents at appropriate positions of the phenyl group of R-PHAs.

### INTRODUCTION

Demands for high purity yttrium and lanthanoids have increased rapidly in recent years as raw materials for advanced industries such as electronics and new ceramics. Because the chemical properties of these elements are very similar, their mutual separation is generally difficult. Solvent extraction is one of the most effective and simple separation and purification techniques. For an industrial-scale separation of the lanthanoids and yttrium, di(2-ethylhexyl)phosphoric acid (DEHPA) has mainly been employed as an extractant (Sherrington, 1983). However, there are some disadvantages which arise from the low separation abilities and the difficulty of stripping of the extracts (Owens, 1968). Therefore, the development of more selective extractants is desired in order to establish effective separation processes of the metal ions.

*N*-Benzoyl-*N*-phenylhydroxylamine (BPHA) and its analogues have been employed as gravimetric, spectrophotometric and extracting reagents (Majumdar, 1972). They are bidentate ligands; their complexation occurs through the carbonyl and hydroxyl oxygens. Thus, they are likely to react with "hard" metal ions including the lanthanoids(III). In fact, BPHA (Sekine, 1964) and its derivatives (Inoue, 1985) (Ceconie, 1987) are capable of extracting lanthanoids(III) from aqueous media.

In hydrometallurgical separation, chelating extractants having long-chain alkyl substituents have

received a great deal of attention. They have high solubility in non polar solvents and low solubility in water. The former is related to the loading capacity of the extractants; the latter prevents their loss during multicyclic extractions. In this respect, we have reported that several alkyl carbonyl derivatives of *N*-phenylhydroxylamine(R-PHAs) are promising extractants for some divalent metal ions (Haraguchi, 1989) and lanthanoid(III) ions(Haraguchi, 1990 ).

Despite many reports in the literature concerning the elucidation of structural factors of chelating extractants which affect complexation with metal ions, very little attention has been devoted to factors regarding substituted alkyl groups which affect the selectivity of the chelating extractants. Since R-PHAs are fairly easily synthesized(Haraguchi, 1989), they are interesting extractants. This is not only because they can provide the basic information required for hydrometallurgical separation, but that comparisons of their mutual properties might well shed light on useful structural factors affecting their extractability and selectivity for the extraction of metal ions. The present study was thus concerned with the extraction of yttrium(III) and the lanthanoids(III) in order to evaluate structural factors concerning the alkylcarbonyl group of the extractants, which may introduce some differences in the extractability and selectivity of the extractant. Furthermore, the role of the substituents at the phenyl group on the extractability and selectivity of R-PHAs will be discussed.

## EXPERIMENTAL

### Reagents

R-PHAs were synthesized from the corresponding acid chlorides and *N*-phenylhydroxylamine or some of its derivatives in a similar fashion to the described procedures(Agrawal, 1971)(Haraguchi, 1989). Confirmation of the white crystalline products was carried out by melting-point measurements, elemental analyses, as well as measurements of their H-NMR, IR and MS. Stock solutions of the metal ions ( $1 \times 10^{-2} \text{ mol dm}^{-3}$ ) were prepared by dissolving the metal nitrate(>99.99%, Raremetallic Inc.) in  $10^{-3} \text{ mol dm}^{-3}$  nitric acid. All other chemicals were of analytical grade. Distilled-deionized water was used throughout the experiments.

### Apparatus

R-PHAs extracted into the organic phase were determined with a Hitachi 320 double-beam spectrophotometer. The concentration of the metal ions in the aqueous phase was measured with a Shimadzu GVM-1000P ICP atomic emission spectrometer. A Toa HM-15A pH meter was employed for measuring the pH of the aqueous phase. A Yamato SA-31 mechanical shaker was utilized for mixing the two phases. A Kokusan H-200 centrifuge was also used for rapid and complete separation of the two phases.

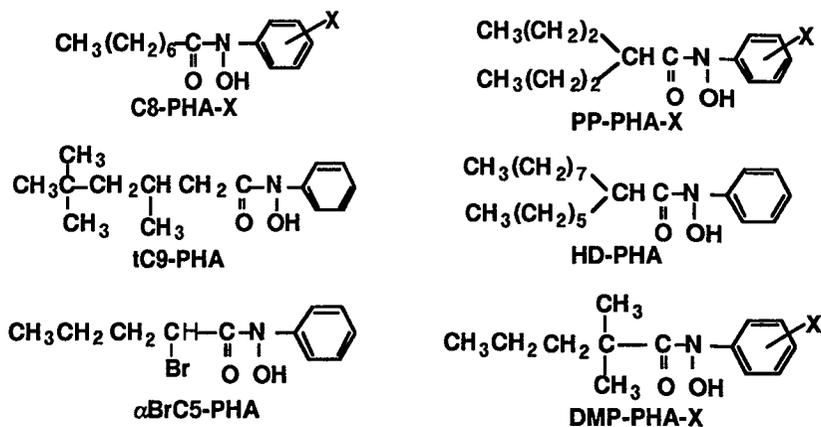
### Procedure

A  $30.0\text{-cm}^3$  aliquot of an aqueous solution containing a specified metal ion( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ), sodium tartrate( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ), sodium nitrate( $0.1 \text{ mol dm}^{-3}$ ) and an appropriate buffer component( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) was shaken with a  $5.0\text{-cm}^3$  aliquot of a carbon tetrachloride solution of a specified R-PHA, in which the R-PHA concentration was in the range from  $1.60 \times 10^{-3}$  to  $1.60 \times 10^{-2} \text{ mol dm}^{-3}$ , for 1 h equilibration at 298 K. Sodium tartrate was employed in order to prevent the hydrolysis of the metal ions. After centrifuging for 10 min at 1500 rpm, the pH as well as the metal concentration in the aqueous phase were determined. The metal concentration in the organic phase was calculated by using a material-balance.

## RESULTS AND DISCUSSION

### Preparation of R-PHAs

R-PHAs were synthesized by the addition of appropriate acid chlorides to *N*-phenylhydroxylamine or its derivatives in an ether solution in the presence of sodium hydrogen carbonate at a temperature below 273 K. The products were purified by recrystallization from an ether-hexane or an ethyl acetate-hexane solution. The acid chlorides were prepared by refluxing the corresponding carboxylic acid with thionyl chloride and distilling out the acid chlorides. The R-PHAs thus obtained are shown



X	-	-pCl	-Cl <sub>2</sub>	-mCF <sub>3</sub>	-pEt	-oEt
X <sub>(o)</sub>	-H	-H	-H	-H	-H	-C <sub>2</sub> H <sub>5</sub>
X <sub>(m)</sub>	-H	-H	-Cl	-CF <sub>3</sub>	-H	-H
X <sub>(p)</sub>	-H	-Cl	-Cl	-H	-C <sub>2</sub> H <sub>5</sub>	-H

Figure 1. Structure of R-PHAs

TABLE 1  
pK<sub>a</sub> and log K<sub>d</sub> of R-PHAs

R-PHA	pK <sub>a</sub>	log K <sub>d</sub>	R-PHA	pK <sub>a</sub>	log K <sub>d</sub>
C8-PHA	9.16	2.88	PP-PHA	9.26	2.46
C8-PHA-pCl	9.06	3.45	PP-PHA-pCl	9.21	3.08
C8-PHA-Cl <sub>2</sub>	8.67	4.20	HD-PHA	9.74	4.00
C8-PHA-mCF <sub>3</sub>	8.64	3.82	DMP-PHA	10.05	1.96
C8-PHA-oEt	10.85	3.26	DMP-PHA-pCl	9.21	3.08
C8-PHA-pEt	9.49	3.73	DMP-PHA-Cl <sub>2</sub>	9.65	3.20
tC9-PHA	9.90	2.00	DMP-PHA-mCF <sub>3</sub>	9.76	2.91
$\alpha$ -BrC5-PHA	5.15	2.36			

in Figure 1. Acid dissociation constants,  $K_a$ , and distribution constants,  $K_d$ , of the R-PHAs between the aqueous and the carbon tetrachloride phases were determined spectrophotometrically at 298 K and ionic strength 0.1 (NaNO<sub>3</sub>). These values are summarized in Table 1.

### Extraction of Metal Ions

When a free metal ion is predominant in the aqueous phase, the extraction of a ktrivalent metal ion ( $M^{3+}$ ) with a R-PHA(HL) can be generally described according to



where the subscript, (o), refers to the species in the organic phase. The extraction constant,  $K_{ex}$ , is thus defined by

$$K_{ex} = \frac{[ML_n(HL)_m]_{(o)}[H^+]^n}{[M^{3+}][HL]_{(o)}}. \quad (2)$$

The distribution ratio,  $D_M$ , of a metal ion between the two phases can be written as

$$D_M = \frac{[ML_n(HL)_m]_{(o)}}{[M^{3+}]}. \quad (3)$$

Since the present extraction system involves tartrate, the formation of tartrate complexes must be taken into account for the expression of  $D_M$ .

$$D_M = \frac{[ML_n(HL)_m]_{(o)}}{[M^{3+}]} \alpha_M. \quad (4)$$

where  $\alpha_M$  is the side reaction coefficient of a metal ion with tartrate in the aqueous phase. Therefore, Eq. (4) becomes

$$D_M = K_{ex} \alpha_M [HL]_{(o)}^{(n+m)} / [H^+]^n. \quad (5)$$

Under the present experimental conditions the value of  $\alpha_M$  can be regarded as constant (Haraguchi, 1990), the conditional extraction constant,  $K'_{ex}$ , a combination of  $\alpha_M$  with  $K_{ex}$ , can be defined, so that, Eq. (5) reduces to a logarithmic form as Eq. (6):

$$\log D_M = \log K'_{ex} + (n+m) \log [HL]_{(o)} + npH. \quad (6)$$

The stoichiometry of the extracted species and the conditional extraction constants,  $K'_{ex}$ , were obtained from the linear relationships between  $\log D_M$  and pH at constant R-PHA concentration and between  $\log D_M$  and  $\log [HL]_{(o)}$  at constant pH according to the Eq. (6). The results thus obtained are summarized in Table 2.

As shown in Table 2, the metal ions were extracted as self-adducted chelates of the type  $ML_3(HL)_x$ , where x is 1, 2 or 3 depending on the extraction system. The  $\log K'_{ex}$  values decrease in the order C8-PHA > PP-PHA, HD-PHA > DMP-PHA. The most likely reason for this observation is a steric effect of the substituent, because PP-PHA, HD-PHA and DMP-PHA have one or two additional alkyl substituents neighboring to the chelating group of R-PHAs. The values of  $\log K'_{ex}$  of the C8-PHA series for the metal ions increase in the order C8-PHA-oEt < C8-PHA-pEt < C8-PHA < C8-PHA-mCF<sub>3</sub> < C8-PHA-pCl < C8-PHA-Cl<sub>2</sub>. This order is in agreement with the order of the inductive effect of the substituents. A similar tendency was observed for the PP-PHA and DMP-PHA derivatives. The  $\log K'_{ex}$  value of C8-PHA-oEt is considerably smaller than that of C8-PHA-pEt for a specified metal ion. This probably reflects the steric hindrance of the ethyl substituent. We can thus enhance the extractability of R-PHAs by introducing electron withdrawing substituents at the appropriate position of phenyl group of R-PHAs. Whereas we can reduce the extractability by introducing electron releasing substituents at the phenyl group of the R-PHA.

### Separation Factors

When the extracted species are the same composition for a pair of metal ions,  $M_{(I)}$  and  $M_{(II)}$ , the separation factor (SF) is defined as the ratio of the conditional extraction constants for the metal pair,

$$(SF) = \frac{K'_{ex(I)}}{K'_{ex(II)}}, \quad (7)$$

where the subscripts (I) and (II) refer to the individual metal ions. The log (SF) values calculated for Eu/Pr, Yb/Eu and Yb/Y pairs are presented in Table 3.

As is evident from Table 3, the separation factor of DMP-PHA for pairs of Yb/Eu and Yb/Y are much greater than those of C8-PHA, PP-PHA and HD-PHA. The log (SF) values of DEHPA, which is currently employed for the mutual separation of the lanthanoids(III) on an industrial-scale, for Eu/Pr, Yb/Eu and Yb/Y pairs have been reported as 1.26, 2.70 and 1.02, respectively(Pierce, 1963).

**TABLE 2**  
Extracted species and logarithmic values of conditional extraction constants

Extractant	Extracted Species	log K'ex			
		Pr	Eu	Y	Yb
C8-PHA	ML <sub>3</sub> (HL) <sub>2</sub>	-12.19	-10.96	-9.85	-9.34
C8-PHA-pCl	ML <sub>3</sub> (HL) <sub>2</sub>	-10.32	-9.33	-8.44	-7.93
C8-PHA-Cl <sub>2</sub>	ML <sub>3</sub> (HL) <sub>2</sub>	-9.38	-8.66		
	ML <sub>3</sub> (HL)			-9.94	-9.12
C8-PHA-mCF <sub>3</sub>	ML <sub>3</sub> (HL) <sub>2</sub>	-10.58	-9.61	-8.73	-7.95
C8-PHA-pEt	ML <sub>3</sub> (HL) <sub>2</sub>	-12.76	-11.66	-10.66	-9.79
C8-PHA-oEt	ML <sub>3</sub> (HL) <sub>2</sub>	-20.03	-19.32		
	ML <sub>3</sub> (HL)			-20.21	-19.70
tC9-PHA	ML <sub>3</sub> (HL) <sub>2</sub>	-12.70	-11.50		-9.94
PP-PHA	ML <sub>3</sub> (HL) <sub>2</sub>	-14.44	-13.30	-12.09	-10.62
PP-PHA-pCl	ML <sub>3</sub> (HL) <sub>2</sub>	-12.58	-14.38	-10.42	-11.74
HD-PHA	ML <sub>3</sub> (HL) <sub>2</sub>	-15.40	-14.38	-13.06	-11.53
DMP-PHA	ML <sub>3</sub> (HL) <sub>3</sub>	-15.86	-14.78	-13.52	-11.69
DMP-PHA-pCl	ML <sub>3</sub> (HL) <sub>3</sub>	-14.09	-12.99	-11.74	-9.95
DMP-PHA-Cl <sub>2</sub>	ML <sub>3</sub> (HL) <sub>2</sub>	-15.75	-14.66	-13.20	-11.47
DMP-PHA-mCF <sub>3</sub>	ML <sub>3</sub> (HL) <sub>2</sub>	-16.69	-15.54	-13.67	-11.74

**TABLE 3**  
Logarithmic values of separation factors

R-PHA	Eu/Pr	Yb/Eu	Yb/Y	R-PHA	Eu/Pr	Yb/Eu	Yb/Y
C8-PHA	1.23	1.62	0.51	PP-PHA	1.14	2.68	1.50
C8-PHA-pCl	0.99	1.40	0.51	PP-PHA-pCl	0.77	2.80	1.41
C8-PHA-Cl <sub>2</sub>		0.72	0.82	HD-PHA	1.14	2.68	1.50
C8-PHA-mCF <sub>3</sub>	0.97	1.66	0.78	DMP-PHA	0.90	3.09	1.83
C8-PHA-pEt	1.10	1.87	0.87	DMP-PHA-pCl	1.10	3.04	1.79
C8-PHA-oEt	0.71		0.51	DMP-PHA-Cl <sub>2</sub>	1.09	3.19	1.73
tC9-PHA		1.56		DMP-PHA-mCF <sub>3</sub>	1.15	3.80	1.93

The log (SF) values for Yb/Eu and Yb/Y pairs for DEHPA are considerably smaller than those of DMP-PHA, so that DMP-PHA is a promising extractant for the mutual separation of heavy lanthanoids(III) and the separation of yttrium(III) from the heavy lanthanoids(III). On the other hand, the log (SF) of C8-PHA for Eu/Pr(1.23) is almost the same as that of DEHPA. Therefore, C8-PHA is a suitable extractant for the mutual separation of lighter lanthanoids(III).

The separation factor for both Yb/Eu and Yb/Y pairs increased with increased branching of the alkyl group of the R-PHAs, i.e., primary < secondary < tertiary. This result suggests that the inductive effect of the substituent attached to the carbonyl group of the R-PHA plays an important role in the selectivity. A fairly good inverse correlation has been obtained between log (SF) and the Taft polar substituent constant (Taft  $\sigma^*$ ) of the alkyl substituent for both Yb/Eu and Yb/Y pairs. This provides good evidence for the inductive effect of the alkyl substituents in the extraction of the heavy lanthanoids(III) with R-PHAs. The Taft  $\sigma^*$  should thus be useful for the molecular design of chelating extractants with long-chain alkyl groups for the separation of the heavy lanthanoids(III).

As seen in Table 3, the separation factors for Yb/Eu and Yb/Y pairs for R-PHAs having substituents on the phenyl group are almost the same as those of their parent R-PHAs which have the same alkyl structure but no substituent on the phenyl group. It is thus concluded that the substituents on the phenyl group give no significant effect on the selectivity.

Then we examined the effect of a halogen substituent on the acyl group of the R-PHA on the extraction and separation of the lanthanoids(III) and yttrium(III). The  $pK_a$  value of  $\alpha$ BrC5-PHA was 5.15, while that of C8-PHA was 9.16 (Table 1). This suggests the possibility of lowering the extraction pH of the lanthanoids(III) by using  $\alpha$ BrC5-PHA. However, the log (SF) value for  $\alpha$ BrC5-PHA for Yb/Y was 0.45, which is considerably smaller than that of DMP-PHA (1.83). Therefore, the bromo substitution on the acyl group of the R-PHAs is unsatisfactory to improve the selectivity.

The role of the substituents of the R-PHAs on the extractability and selectivity of the lanthanoids(III) and yttrium(III) found in this study will be useful in the molecular design of effective extractants for the lanthanoids(III) and yttrium(III).

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## EFFECT OF MICROEMULSIONS AND HYDRODYNAMIC CONDITIONS ON THE EXTRACTION OF IRON(III) WITH A SUPPORTED LIQUID MEMBRANE

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### ABSTRACT

In this work, the rates of extraction of zinc by a supported liquid membrane containing 0.2 M di(2-ethylhexyl)phosphoric acid (DEHPA) in dodecane and a supported microemulsion liquid membrane containing the same extractant are compared. The microemulsion membrane was obtained by addition of a mixture of Na lauryl sulphate (NaLS) and n-pentanol to the DEHPA solution. A single microporous polypropylene hollow fibre served as the membrane support. Enhancements factors of the order of four were observed in the presence of the microemulsion over a wide range of concentrations and flow rates. The extraction flux across the two types of liquid membrane increased with feed flow rate and iron concentration, as well as with a decrease in the pH of the stripping solution. Results indicate that the predominant rate controlling mechanism changes as the balance between diffusion and chemical resistances is altered by changes in concentrations and the hydrodynamic parameters.

### INTRODUCTION

The extraction of metal ions with supported and emulsion liquid membranes has been studied over a number of years. For some extraction systems research has reached the stage of testing design equations based on the mechanisms of interfacial transfer and contactor hydrodynamics. Despite the possibly high operating costs of supported liquid membrane modules (Wicksramasinghe et al, 1992) the process remains an option when concentrated stripping solutions are required from dilute feeds. A limitation for the prospective use of supported liquid membranes in processes involving chemical reactions is the potentially low extraction flux. This arises from the fact that the flow in the hollow fibre is laminar. At the highest possible rate of mass transfer in the feed, the process rate controlling step may be transport across the membrane, the rate of chemical reaction, or a combination of both, (Ortiz Uribe et al, 1988). Therefore attention is focused on searching for liquid membrane formulations that may enhance the rate determining step of transfer in order to improve the overall rate of extraction. In the case of slow reactions, such as the extraction of aluminium and iron with di(2-ethylhexyl) phosphoric acid (DEHPA), the main objective is to increase the rate of reaction. Substantial enhancement in the extraction rate of trivalent metal ions have been achieved upon formation of reverse micelles in the organic phase of a metal extraction system (Bauer, D. and Komornicki, J., 1983, Brejza, E. V. and Ortiz, E. S. P. de, 1993), One such case is the extraction of iron with DEHPA (Bauer, D. and Komornicki, J., 1983) in which the formation of a water in oil (W/O) microemulsion obtained by adding a mixture of sodium lauryl sulphate (NaLS) and n-pentanol to the organic phase, resulted in increases of about one order of magnitude in the rate of metal

extraction. In this work the same micellar organic phase was used as a supported liquid membrane in a one fibre laboratory contactor. The performance of the micellar membrane is compared with that of the non-micellar one at different feed flow rates, feed metal concentrations and stripping solution pH.

## EXPERIMENTAL

### Reagents

$\text{Na}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$  and acetone were of Analar grade. NaLS (BDH, 99%), pentanol (Sigma Chemical Co, 99%), n-dodecane (Aldrich Chemical Co., 99%) and ferric sulphate (Eatsman Kodak, 73%) were used as received. DEHPA was purchased from BDH and purified according to the procedure recommended by Union Carbide (1972). The water used was double distilled.

The aqueous feed solution was prepared by dissolving calculated amounts of iron sulphate and sodium sulphate to obtain the required iron concentration and an ionic strength of 1.0. The reference organic membrane was a 0.2 M solution of purified DEHPA in n-dodecane. The microemulsion membrane was obtained by adding a mixture of NaLS and n-pentanol to the reference organic solution. The concentrations of NaLS and n-pentanol in the organic solution were 0.07 M and 3.18 M respectively. The stripping solution was also of ionic strength 1 obtained with sodium sulphate; its pH was adjusted with sulphuric acid.

All experiments were conducted in a hollow fibre module which consists of a single microporous fibre of 0.0018 m internal diameter and 0.0004 m thickness (ENKA Accurel, A. G. S6/2) fixed inside a glass cylinder. The module has a jacket through which water at 25 °C was circulated. The volume ratio of feed solution to stripping solution in the module was 1:2.

After the module was cleaned, the membrane phase was circulated inside the fibre for 30 minutes to impregnate it, and then it was rinsed by pumping distilled water. During a run the feed was pumped into the lumen of the fibre and the stripping phase into the module shell. All experiments were conducted in the continuous mode. Iron concentrations were determined using a Perkin Elmer atomic absorption spectrophotometer, model 1100B at the wavelength of 248.3 nm.

## RESULTS AND DISCUSSION

### Comparison between the reference membrane and the microemulsion extraction fluxes

Figure 1 shows the effect of recycling the raffinate and the stripping phases on raffinate concentration and percentage extraction for the reference and the microemulsion liquid membrane. On these experiments the raffinate and the strippate collected from one run were used as feed and stripping phase in the next experiment. The feed and the stripping flow rates were 1.6 ml/min and 3.2 ml/min respectively and the initial pH of the stripping phase was 0.8. Results indicate that the presence of the microemulsion increases the extraction flux by a factor between four and five over the whole range of feed concentrations used. This is in agreement with results reported by Bauer and Komornicki (1983) for conventional solvent extraction of iron with the same microemulsion and extractant. In their case, the increase of up to one order of magnitude was reported which suggests that in the supported liquid membrane configuration the resistance to mass transfer may play an important role. This can be investigated by studying the effect of iron concentration and flow rate on the extraction flux.

### Effect of iron concentration on extraction flux.

Results plotted in Figure 2 show the effect of iron concentration on the extraction flux at two different feed flow rates. In both cases the increase in flux with concentration is linear. The increase in flux with concentration may be simply due to the increase in the concentration driving force in the feed phase. This would indicate some degree of rate control exerted by the diffusional resistance in

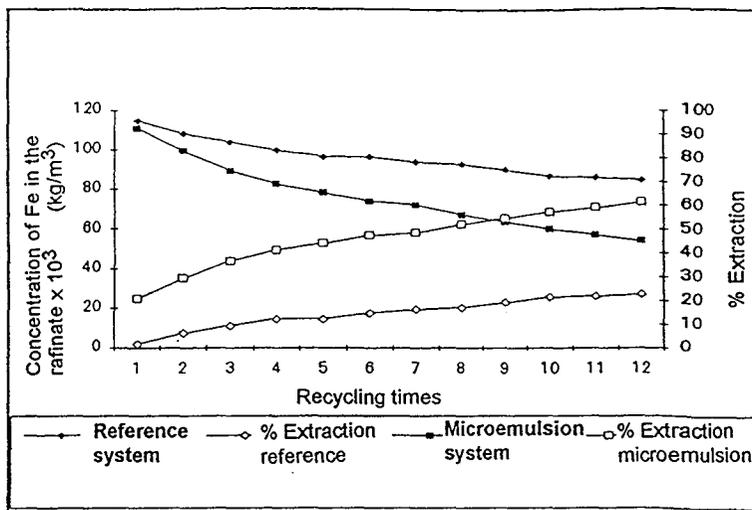


Figure 1. Comparison of the extraction behaviour of the reference system and the microemulsion.

the feed phase, showing that transfer across the membrane is not rate controlling. This is confirmed by the increase in extraction flux with flow rate, i. e. with an increase in mass transfer coefficient. However as the interfacial transfer takes place via a chemical reaction which is of first order with respect to Fe (Matsuyama et al, 1989), the possibility of some degree of chemical control cannot be disregarded. This seems to be confirmed by the extraction rate enhancement produced by the microemulsion (Figure 1). As the presence of the microemulsion can affect the interfacial rate of reaction, the rate of transport across the membrane, or both, these results suggest that the diffusional control in the feed is not totally rate controlling.

**Effect of feed flow rate**

Figure 3 shows the effect of feed flow rate on the rate of membrane extraction at different concentrations of iron in the feed. At low flow rates the slopes of these curves increase with feed concentration. In the curves, at the low concentration range, as the flow rate is increased the extraction flux seems to reach a plateau which starts at higher flow rates as the concentration of iron is increased. At the top concentration range used in this work there is no evidence of such plateau. As the Reynolds number in these experiments varies between 10 and 20, at an estimated value of the Schmidt number of 1000 the mass transfer entry region would be of the order of 1m, i.e. much longer than the length of the fibre. Consequently the mass transfer coefficient inside the fibre should increase with flow rate and the flux increases would reflect its dependence on the resistances to mass transfer in the feed. According to Leveque's solution for transfer in the entrance region, at constant values of the Schmidt number the mass transfer coefficient varies with  $Re^{1/3}$  (Leveque, 1931). The influence of feed concentration on the effect of flow rate on flux can be explained by the interrelation between the reaction rate and the diffusional resistance. At low feed concentration the rate

of reaction is low and the process seems to be controlled by the chemical reaction. This is supported by the fact that at the lowest iron concentration the flux is practically insensitive to flow rate.

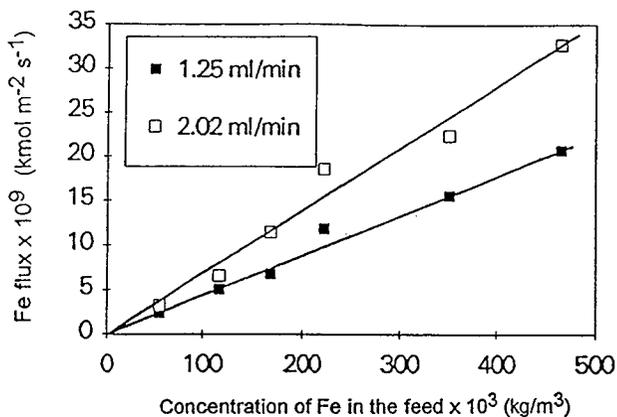


Figure 2. Effect of Fe concentration on extraction flux.

As the concentration of iron is increased, the reaction becomes faster and the diffusional resistance in the feed begins to affect the potential rate of extraction. The rate controlling mechanism thus switches from chemical to diffusional with feed concentration.

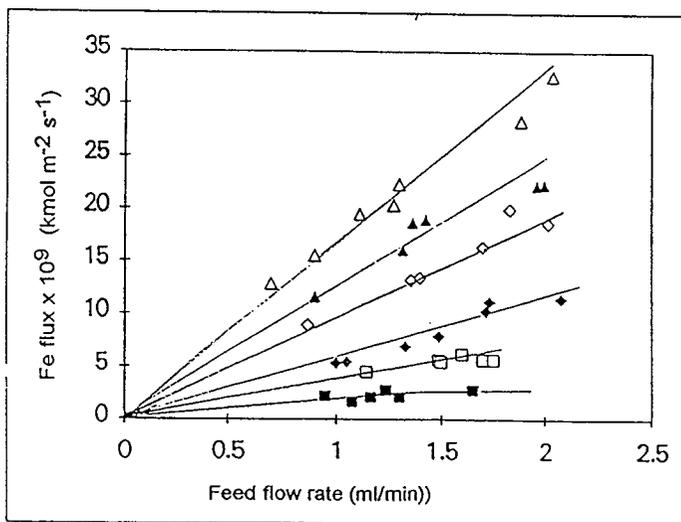


Figure 3. Combined effect of feed concentration and flow rate on Fe extraction flux. Concentrations in  $\text{kg}/\text{m}^3 \times 10^3$ : ■ 55, □ 116, ◆ 167, ◇ 223, ▲ 350, and △ 466.

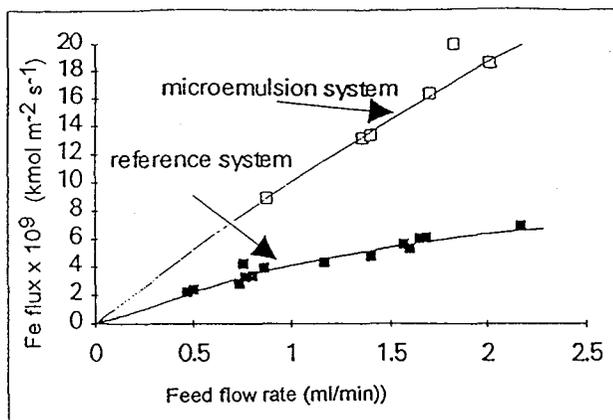


Figure 4. Effect of feed flow rate on the extraction flux in the reference system and the microemulsion membrane.

### CONCLUSIONS

By comparing the results of the supported microemulsion liquid membrane system with the supported liquid membrane, the following conclusions can be drawn:

- 1) The rate of extraction of iron with the microemulsion liquid membrane is substantially faster than that with the reference non-micellar liquid membrane under the same experimental conditions. However the enhancement factor obtained with the microemulsion in the supported liquid membrane module was of the order of 4 to 5, which is lower than that reported in the literature for the same system in a stirred contactor. This can be attributed to the diffusional resistances at the hydrodynamic conditions of the membrane module.
- 2) For both the microemulsion and the reference liquid membranes the extraction rate increased with both the concentration of iron in the feed and the feed flow rate. The increase in extraction rate with flow rate was steeper at higher iron concentrations, i.e. in the region of high extraction rates. Consequently the influence of flow rate was greater in the emulsion liquid membrane than in the reference membrane. At lower concentrations the effect of flow rate reached a plateau. These results are explained by the interaction between the rate of chemical reaction and the diffusional resistances in the rate controlling mechanism. At low iron concentrations the extraction becomes controlled by the low rate of reaction and the increase in mass transfer coefficient produced by the higher flow rate ceases to have an effect in extraction on rate increase.

### ACKNOWLEDGEMENTS

Financial support by the Science and Engineering Research Council (grant No GR/F28502) and The British Council is gratefully acknowledged.

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# SOLVENT EXTRACTION AND SEPARATION OF COBALT, NICKEL AND MAGNESIUM FROM A GREEK LATERITE LEACH LIQUOR

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## ABSTRACT

The extraction and separation of cobalt and nickel from a leach liquor derived from a sulphuric acid leach of a Greek lateritic ore using commercial organophosphorus extractants in Escaid 100 diluent are presented. The extractants used include alkyl phosphoric, alkyl phosphonic and alkyl phosphinic acids and extraction was performed both at room temperature and 50C. The results obtained are largely in agreement with published data. The feasibility of recovering magnesium by solvent extraction from the cobalt/nickel raffinate is discussed and alternative process flowsheets presented.

## INTRODUCTION

Heap leaching of a low-grade serpentinitic Greek nickel laterite with sulphuric acid produces a leach liquor containing about 7 g/l nickel; 0.4 g/l cobalt and 13 g/l magnesium together with varying amounts of iron, aluminium and chromium. Removal of the iron, aluminium and chromium impurities results in a liquor which can be treated by solvent extraction to recover cobalt, nickel and magnesium. Comparative testwork with a suite of commercial reagents has been carried out to permit selection of the most appropriate extractants for cobalt and nickel. The reagents examined for cobalt/nickel separation are alkyl phosphoric, alkyl phosphonic and alkyl phosphinic acids. This paper presents the results of comparative testwork with these reagents both at room temperature and at 50C. The solvent extraction of magnesium is discussed in terms of information available in the literature and from Cytec Canada Inc. The development of an outline workable flowsheet is given.

## REAGENTS AND MATERIALS

Samples of the solvent extraction reagents were obtained from the manufacturers and were used without further purification. Their brand names, chemical compositions and suppliers are given in Table 1.

**TABLE 1**  
Reagents and Suppliers

Reagent	Chemical Composition	Supplier
DEHPA	di(2-ethylhexyl)phosphoric acid	Albright & Wilson
Ionquest 801	2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester	Albright & Wilson
PC88-A	2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester	Daihachi Chemical Co
PIA-8	di(2-ethylhexyl)phosphinic acid	Daihachi Chemical Co
Cyanex 272	bis(2,4,4-trimethylpentyl)phosphinic acid	Cytec Inc
Cyanex 302	bis(2,4,4-trimethylpentyl)monothiophosphinic acid	Cytec Inc

The diluent employed for the solvent extraction work was Escaid 100 kindly supplied by Esso Chemicals UK Ltd. All inorganic salts were of AR grade. Stock solutions of cobalt and nickel sulphates (0.001 M) were prepared in 1 M sodium sulphate.

## EXPERIMENTAL

The  $pK_a$  values and purities of the organophosphoric acids used in this study were determined by potentiometric titration of 1 ml samples dissolved in propanol (50 ml) against 0.1 M aqueous sodium hydroxide at room temperature. The pH value at half neutralisation was recorded as the  $pK_a$  value of the organophosphorus acid.

For the room temperature solvent extraction studies, aliquots of the cobalt or nickel stock solutions were placed in a beaker and an aliquot of the required stock organic solution was added. The phases were then mixed by stirring at 300 rpm for 10 mins which had been shown in preliminary work to be more than adequate to achieve equilibrium. The phases were then separated, the equilibrium pH measured and the metal content of the aqueous phase determined by atomic absorption spectrophotometry. Selected organic phases were stripped with an equal volume 2 M sulphuric acid and also analysed to check the mass balance. In other cases the amount of metal extracted was determined by difference.

For the studies at 50C a reflux system was employed as preliminary experiments had showed that aqueous phase evaporation was a potential problem with regard to reproducibility of experimental results. After phase contact the phases were again separated and cooled prior to pH measurement and chemical analyses.

## RESULTS AND DISCUSSION

The purities and  $pH_{0.5}$  values of the organophosphorus acids are given in table 2 where they are compared with values from the literature where available.

TABLE 2  
Reagent purity and  $pK_a$  values

Reagent	Purity %	$pK_a$ values		
		Experimental	Literature	
DEHPA	97.98	3.50	3.51 3.57	(Preston et al (1988))+ (Cox et al (1983))+
PC88-A	100	5.00	4.77 4.10	(Preston et al (1988))+ (Cox et al (1983))+
Ionquest 801		4.90		
Cyanex 272	89.47 (85)#	6.25	6.37 6.02 6.00	(Sole & Hiskey (1992))* (Preston et al (1988))+ (Danesi et al (1985))+
PIA-8	98.86	6.10		
Cyanex 302	89.34 (84)#	5.90	5.63	(Sole and Hiskey (1992))*
	# Manufacturers values		* in H <sub>2</sub> O	+ 75% ethanol, 25% water

Both Cytec reagents seemed significantly purer than stated in the Cytec brochure while the  $pK_a$  values of Cyanex 272 and 302 were different to that reported by Sole and Hiskey (1992). As the current results were recorded in propanol (water added in titration) lower values would be expected in water. This is true for Cyanex 302 but not for Cyanex 272.

From log D versus pH plots for the extraction of cobalt and nickel with the above reagents at room temperature and at 50C individual slopes for both cobalt and nickel extraction at room temperature and 50C were all approximately 2.0. The  $pH_{0.5}$  values and the difference between them (a reflection on the separation factor) are shown in Table 3. Examination of this table shows that at room temperature as expected DEHPA has the smallest difference in the  $pH_{0.5}$  values which increase steadily in the series phosphoric < phosphonic < phosphinic reflecting the degree of conversion of the cobalt complex from the hydrated octahedral form to the anhydrous tetrahedral form. At 50C the values were all greater except for Ionquest 801 and

Cyanex 302. This is because, for Ionquest 801, the decrease in the  $pH_{0.5}$  value for cobalt extraction at 50C was much smaller and the fall in the  $pH_{0.5}$  for nickel was much larger than for PC88-A. Cyanex 302 exhibited the largest decrease in  $pH_{0.5}$  for nickel (1.24 pH units) of all the reagents tested (other reagents  $\sim 0.2$  pH units). The reason for this is unknown at present. No truly discernable trend in the differences in  $pH_{0.5}$  values however is apparent but the values are in fair agreement with those of Preston and du Preez (1988).

TABLE 3

Reagent	$pH_{0.5}$ values					
	Co		Ni		$pH_{Co,0.5} - pH_{Ni,0.5}$	
	RT	50	RT	50	RT	50
DEHPA	4.71	4.22	5.20	4.96	-0.49	-0.74
PC88-A	4.90	4.42	6.24	6.08	-1.34	-1.66
Ionquest 801	4.69	4.49	6.34	6.11	-1.65	-1.62
Cyanex 272	5.23	4.95	7.35	7.25	-2.12	-2.30
PIA-8	5.10	4.85	7.39	7.14	-2.29	-2.29
Cyanex 302	5.33	4.14	7.48	6.24	-2.15	-2.10

Comparison with results from other workers is difficult because of the use of different reagent concentrations, diluents and aqueous phase concentrations. However Preston and du Preez (1988) report  $pH_{0.5}$  values of 3.99, 4.29 and 4.71 for cobalt and 4.52, 5.72 and 6.55 for nickel at 20C for synthetic analogues of DEHPA, PC88-A and Cyanex 272 respectively for 0.2M acid solutions in toluene. The aqueous phases were 0.02M as nitrates in 0.4M sodium nitrate. The corresponding values at 50C were 3.61, 3.89 and 4.36 for cobalt and 4.48, 5.55 and 6.52 for nickel corresponding to  $pH_{Co,0.5} - pH_{Ni,0.5}$  values of -0.53, -1.43 and -1.84 for the phosphoric, phosphonic and phosphinic acids respectively at 20C compared with -0.87, -1.66 and -2.16 at 50C. Sole and Hiskey (1992) report values of  $pH_{0.5}$  of 5.2 and 7.05 for 0.001M cobalt and nickel respectively in 0.5M sodium sulphate for 0.1M Cyanex 272 in xylene at 25C and 4.0 and 5.8 for Cyanex 302, a difference in the  $pH_{0.5}$  values of -1.85 and -1.8. Lower  $pH_{0.5}$  values but higher differences have been measured in the present study. Tait (1993) records  $pH_{0.5}$  values of 4.0 and 5.3 for cobalt from Cyanex 302 and 272 respectively at 25C for 0.25M reagent solutions in toluene with a  $pH_{0.5}$  difference ( $pH_{Co,0.5} - pH_{Ni,0.5}$ ) of -2.6 for Cyanex 302 compared to -1.7 for Cyanex 272 from metal ion solutions 0.02M in 1.0M ammonium sulphate. Again these results differ from those obtained in this study.

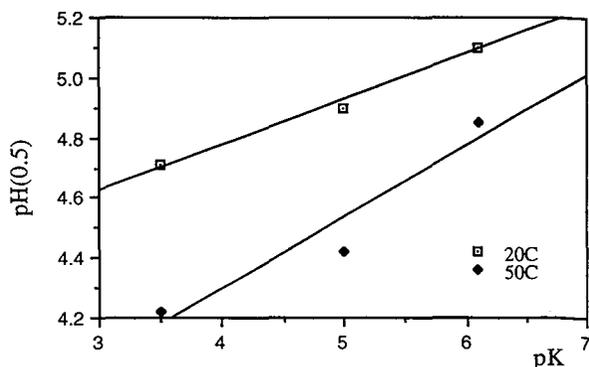


Figure 1 Plot of pKa of extractant versus  $pH(0.5)$  for cobalt extraction

The relationship between the  $pH_{0.5}$  values and the  $pK_a$  for DEHPA, PC88-A and PIA-8 is shown in Fig 1 for cobalt and Fig 2 for nickel. The figures show straight lines at room temperature of slope 0.15 for cobalt and 0.83 for nickel compared with 0.24 and 0.83 respectively for 50C. A similar comparison for the 2-ethylhexyl series given by Preston and du Preez (1988) showed straight lines for both cobalt and nickel of slopes 0.26 and 0.82 respectively which appears to be in reasonable agreement considering the current results are with unpurified reagents while those of Preston and du Preez were with synthesised and purified compounds.

The extraction of magnesium (Rickelton (1987)) at 50C with 200 g/l Cyanex 272 in Exxsol D-89 modified with 10% TBP from a chloride solution containing 177 g/l nickel and 4 g/l magnesium at a pH of 3.5 controlled with ammonia gave an magnesium/nickel separation factor of 370. Elevated temperature is necessary to minimise organic phase viscosity. Stripping is

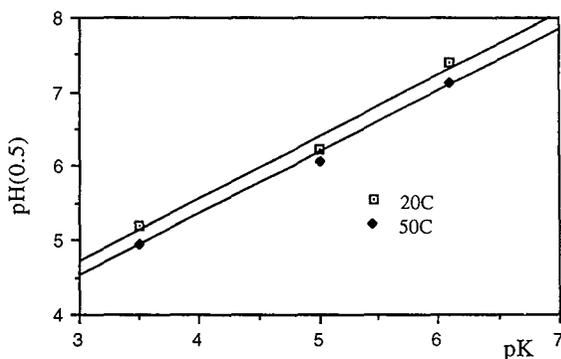


Figure 2  $pK_a$  of extractant versus  $pH(0.5)$  for nickel extraction

easy with 100 g/l sulphuric acid. Earlier data published by Preston and du Preez (1988) gave  $pH_{0.5}$  values of 4.05, 4.95, 5.60 and 5.59 for the synthesised equivalents of DEHPA, PC88A, Cyanex 272 and PIA-8 respectively. Further published information (Nyman et al (1992)) reveals that both Cyanex 272 and Ionquest 801 are suitable for magnesium removal from impure nickel solutions and the inference is that Cyanex 272 has been used commercially by Kokkola Chemicals to remove magnesium from impure nickel sulphate solutions. This gives confidence that the use of solvent extraction is a practical option for recovery of magnesium from nickel laterite leach liquors.

### OUTLINE PROCESS FLOWSHEET

Based on available knowledge of the performance of the organophosphorus acids for cobalt/nickel separation and the information in the literature on magnesium solvent extraction two possible flowsheets have been drawn up, Figures 3 and 4. The removal of iron, aluminium and chromium impurities is carried out conventionally by hydrolytic precipitation. Figure 3 shows a fairly conventional approach with two stages of hydrolytic precipitation, recycle of the second stage precipitate to pH adjust prior to the first stage precipitation, magnesium carbonate precipitation, cobalt recovery by solvent extraction using Cyanex 302 (or Cyanex 272), pH adjust with ammonia and ammonium carbonate followed by nickel recovery by solvent extraction with LIX 54 and finally recovery of ammonia via a lime boil. Prior to nickel solvent extraction all pH adjusts are made with magnesia.

The second flowsheet employs a novel approach suggested from the work of Inoue and Zhang (1993) wherein both cobalt and nickel can be removed selectively in a bulk solvent extraction step with a mixed reagent system, comprising LIX 63 and Cyanex 272, carried out directly on the leach liquor after iron removal. Cobalt can be selectively stripped from the loaded organic phase and further processed. Nickel is finally stripped with stronger acid and further processed

to produce the desired nickel product. Aluminium and chromium impurities are hydrolytically removed from the raffinate from the first bulk solvent extraction step using magnesia for pH adjust. Magnesium carbonate is then precipitated and recovered. No work has yet been done on this approach and questions remain regarding the kinetics of extraction of nickel and cobalt with the mixed extractant; selectivity with respect to chromium, not included in the Inoue report; and the efficiency of the stripping steps. These and other aspects are currently receiving further attention.

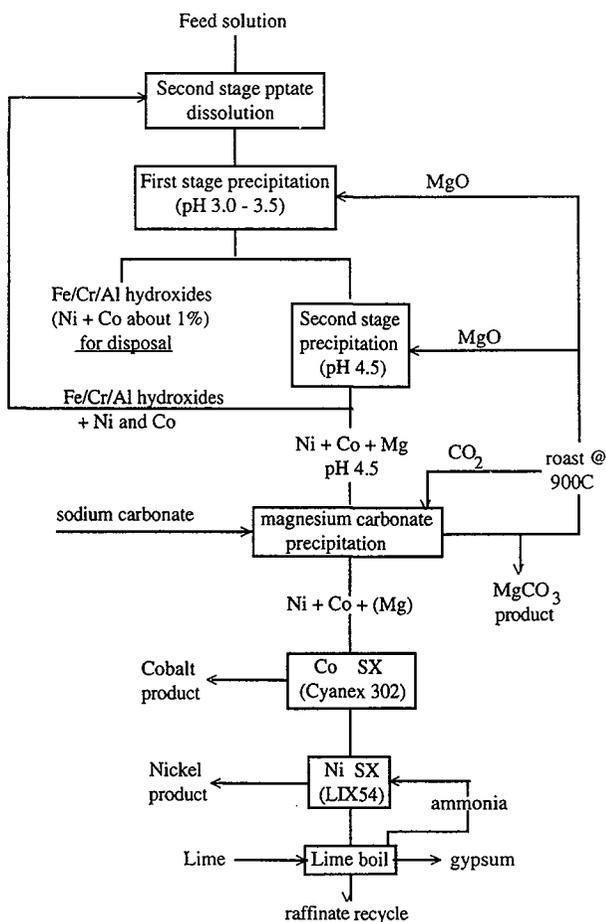


Figure 3 Process flowsheet incorporating hydrolytic removal of Fe, Al and Cr before solvent extraction

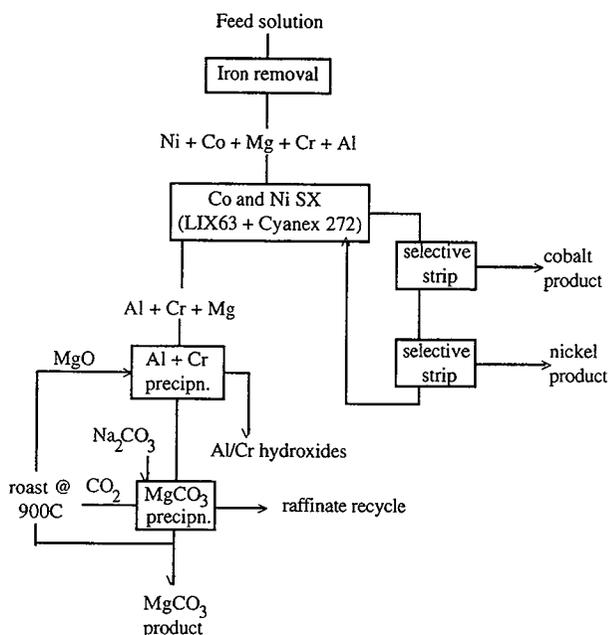


Figure 4 Process flowsheet incorporating synergistic extraction of cobalt and nickel (as Inoue 1993)

### ACKNOWLEDGEMENTS

This work was carried out as part of project number BE-8188 under contract BRE2-CT94-1020 of the European Commission Brite-EuRam programme and financial assistance from the Commission is gratefully acknowledged. Albright and Wilson, Cytec Inc., Daihachi Chemical Co., and Esso Chemicals UK Ltd. are also thanked for the supply of chemicals.

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## THE SEPARATION OF COBALT FROM NICKEL AMMONIUM SULPHATE SOLUTION BY SOLVENT EXTRACTION

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### ABSTRACT

A solvent-extraction process for the extraction of cobalt from nickel ammonium sulphate solution was evaluated. The feed solution, containing 70 g/L nickel, 1 g/L cobalt, 35 g/L ammonium sulphate and minor amounts of other base metals, originated from a base metal refinery. Cobalt can be selectively extracted from this solution using 15 vol.% Cyanex 272 or Cyanex 302 dissolved in Shellsol AB to yield a raffinate with a cobalt concentration of below 20 mg/L.

After scrubbing the loaded organic phase with a portion of the loaded strip liquor to remove co-extracted nickel, cobalt is stripped from the organic phase with sulphuric acid (150 g/L) to produce a cobalt sulphate solution of at least 90 g/L cobalt, at a Co:Ni ratio of 500 to 4000:1.

### INTRODUCTION

Organophosphorus-acid extractants are used commercially for the separation of cobalt from nickel in sulphate media -Clemente *et al.* (1980), Kasai *et al.* (1980), Preston (1982) and Rickelton *et al.* (1984). The monothio phosphinic acid, Cyanex 302, has been tested for this application on batch laboratory scale at Mintek -Tait (1993).

Selected organophosphorus-acid extractants were evaluated to determine process conditions for the extraction of cobalt from nickel ammonium sulphate solution at a Southern African base metal refinery.

### LABORATORY TESTWORK

The feed solution was taken from the refinery after jarosite precipitation, and was therefore essentially free of iron. The solution contained 70 g/L nickel, 1000 mg/L cobalt, <3 mg/L iron, 35 mg/L manganese and 35 g/L ammonium sulphate. The feed solution was maintained at 50 °C to prevent crystallization of nickel salts.

The extractants tested in the laboratory evaluation were Ionquest 801 (2-ethyl 2-ethylhexylphosphonic acid) and Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid), supplied by Albright and Wilson and Cytec, respectively. The extractants were made up to 15 vol.% in the aromatic diluent Shellsol AB, supplied by Shell. All laboratory extraction tests were carried out at 50 °C.

#### Effect of pH on Extraction

Figure 1 shows the extraction of cobalt and nickel by Ionquest 801 and Cyanex 272. Better separation is possible with Cyanex 272. At pH 5.5, close to 100% of the cobalt is extracted, with only 2% of the nickel being co-extracted.

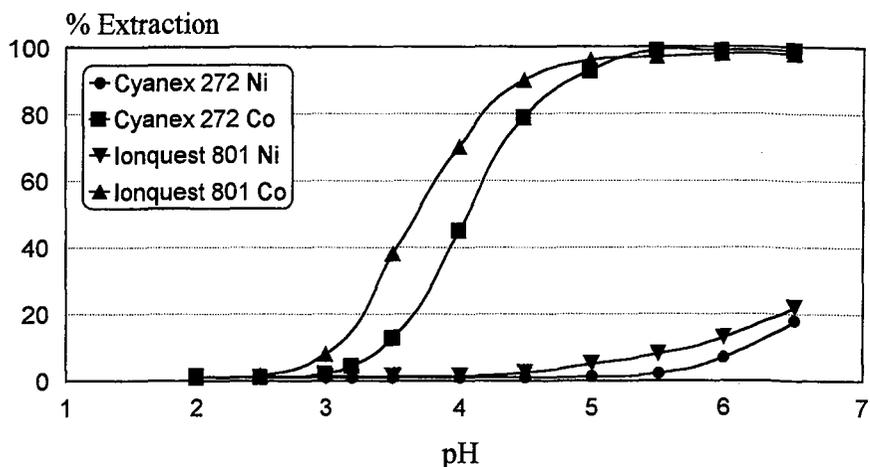


Figure 1. Extraction as a function of pH, 15 vol.% extractant in Shellsol AB

#### Extractant Choice

In batch counter-current tests simulating four extraction stages, high cobalt extractions were achieved with both extractants tested (Ionquest 801: 4.8 g/L and Cyanex 272: 4.34 g/L). Slightly lower loadings of cobalt were obtained with Cyanex 272 than with Ionquest 801 at the same pH value. The batch testwork indicated that the use of Cyanex 272 would require three stages to achieve a raffinate with a cobalt concentration of <20 mg/L, while Ionquest 801 would require four stages. In both cases, however, large amounts of nickel were co-extracted, particularly with Ionquest 801 (Ionquest 801: 2.68 g/L and Cyanex 272: 1.08 g/L). Should high purity of the cobalt product be a stringent requirement, a scrubbing circuit to remove co-extracted nickel from the organic phase would be required, regardless of which extractant was chosen. In view of the high cobalt extractions and better cobalt/nickel separation achieved with Cyanex 272, it was decided to continue the test programme with this extractant. Although Cyanex 272 is the more expensive reagent, fewer extraction stages would be required to achieve a similar cobalt/nickel separation. This would allow a capital cost saving, and would decrease the total organic inventory required. At the extractant concentration chosen (15 vol.%), no phase separation problems were encountered. The use of practical phase ratios was also possible.

#### Diluent Choice

Experience at the Rustenburg Refinery has shown that cobalt is responsible for the slow oxidative degradation of components of the diluent -Flett and West (1986). The plant has recently introduced an aliphatic, South African-manufactured diluent, Kerosol 200, supplied by Sasol Chemicals, and this problem has been reduced considerably. Because of the elevated temperature of extraction in the present system, with the possibility of diluent degradation, the preferred choice of diluent would be Kerosol 200. A large enough sample was not available at short notice for the mini-plant operation, and Shellsol AB was used instead. Isotherms prepared to compare extraction with the two diluents showed that the Kerosol 200 system is marginally more favourable than that of Shellsol AB.

## MINI-PLANT TESTWORK WITH CYANEX 272

A mini-plant counter-current trial was conducted over a period of 26 days.

### Mini-plant Configuration

A conventional mixer-settler system made of polypropylene was used. Each mixer-settler unit had a mixer volume of 500 mL and a settling area of 256 cm<sup>2</sup>. To assist in the maintenance of a temperature above 50 °C in the extraction bank, the cells were insulated and hot water was pumped through stainless-steel elements in each of the extraction settlers. All solutions were pumped into the plant using peristaltic pumps with appropriate tubing. Scrubbing and stripping units were operated with internal recycle of aqueous solution to maintain a phase ratio of close to one in the mixing compartments. The flowsheet of the mini-plant is shown in Figure 2.

Three scrubbing stages were included, rather than the two as proposed by Rickelton -Rickelton *et al.* (1984). Although McCabe-Thiele analysis on a stripping equilibrium isotherm indicated that two stripping stages would be sufficient, a third stage was included, in which any acid remaining in the loaded strip liquor would partially strip cobalt from the scrubbed organic phase.

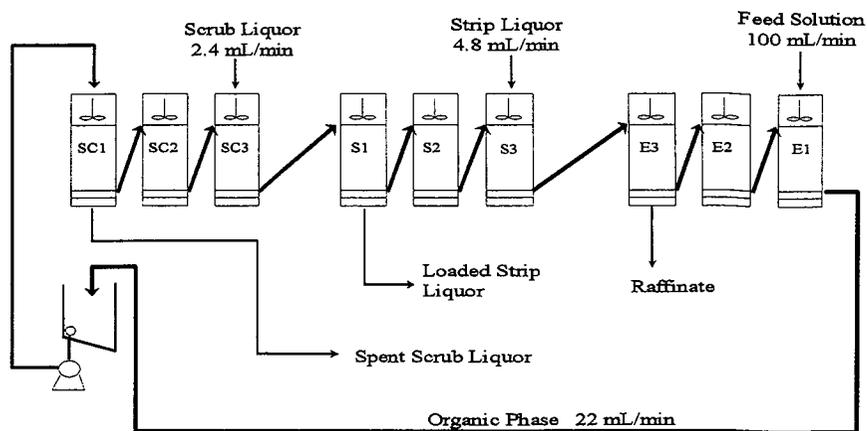


Figure 2. Configuration of mini-plant.

### Extraction

With three stages, cobalt extractions greater than 97% were consistently achieved, producing a nickel solution with a cobalt concentration of below 15 mg/L. Towards the end of the campaign, cobalt extraction was reduced slightly in an attempt to 'squeeze' as much nickel as possible from the loaded organic phase. This 'squeezing' effect reduced the cobalt extraction to approximately 90%, with a Co:Ni ratio of 20:1 being achieved.

Control of the pH in the extraction bank was essential for the production of a loaded organic phase with an acceptably high Co:Ni ratio. The pH of extraction had to be controlled at 5.2 - 5.5 in order to achieve acceptably high cobalt extractions and a Co:Ni ratio of 20:1 in the loaded organic phase. The pH of the feed solution was adjusted to 5.5 before being used in the plant. The need for neutralization in the extraction bank to maintain pH at the desired level was minimal, because of the strong buffering effect of the ammonium sulphate.

### Scrubbing

Synthetic cobalt sulphate solution was used for start-up of the scrubbing section. Once loaded strip liquor became available, a portion of it was diluted with water to 60 g/L Co for scrubbing. The Co:Ni ratio in the loaded organic phase largely determined the Co:Ni ratio achieved in the scrubbing section. The pH of scrubbing was monitored and, as expected, was found to have some effect on the selective scrubbing of nickel from the loaded organic phase. Once equilibrium was reached, Ni scrubbing of above 90% was consistently achieved, producing scrubbed organic with a Co:Ni ratio of approximately 500:1.

Towards the end of the campaign, a fourth stage was added to the scrubbing circuit in an attempt to improve scrubbing results. This resulted in only a marginal improvement in the Co:Ni ratio in the scrubbed organic phase.

### Stripping

At the start of the campaign, the scrubbed organic phase was stripped using 60 g/L H<sub>2</sub>SO<sub>4</sub> at an O:A ratio of 7.3:1 to produce a loaded strip liquor containing 40 g/L cobalt. Because of the slow aqueous flowrate in the stripping section, equilibrium was only reached after a few days of operation. Thereafter, the phase ratio in the stripping section was gradually increased, while also increasing the sulphuric acid concentration of the strip liquor. In this fashion, the cobalt concentration in the loaded strip liquor was raised to 100 g/L using 150 g/L H<sub>2</sub>SO<sub>4</sub>, to strip at an O:A ratio of 14:1.

Table 1 shows the composition of the loaded strip liquor. Manganese was the major impurity extracted along with copper and zinc. If the downstream processing of cobalt requires a recycle of solution to the solvent extraction plant (e.g., cobalt electrowinning), the removal of these impurities would have to be considered.

TABLE 1  
Composition of loaded strip liquor

Component	Concentration, g/L	Component	Concentration g/L
Co	105.6	Ca	<0.010
Ni	0.424	Cu	0.008
Zn	0.002	Fe	<0.004
Mg	<0.010	Mn	0.428
Na	0.044	SO <sub>4</sub>	174.0
Si	<0.004		

Under these conditions, most of the cobalt was stripped in the second and third stripping stages. It was clear that effective stripping was accomplished using only two stages, as cobalt stripping in the first stage was minimal. The first stage did, however, ensure that the loaded strip liquor was at the highest possible pH, thus minimising the need for neutralisation prior to downstream cobalt purification or processing.

From analyses of plant streams, it was evident that Cu, Mn, and Zn were being stripped into the aqueous phase in the third stripping stage (S3), and then re-extracted into the organic phase in S1. Thus, a small circulating load of Mn, Cu, and Zn was established within the stripping section. For this reason, a separate selective stripping section for cobalt, or an impurity removal process may, be necessary. The Co:Ni ratio

in the loaded strip liquor was approximately 250. The Co:Ni ratio in the scrubbed organic phase for a few days prior to this analysis was, however, consistently above 500. The reason for this discrepancy was the extremely slow aqueous flowrate in the stripping section.

### Organic Losses

Towards the end of the campaign, samples of loaded strip liquor and raffinate were analysed for Cyanex 272 and Shellsol AB content. The concentration of extractant in the nickel and cobalt streams was 4.5 and 7.2 mg/L, respectively. The concentration of diluent in both plant streams was <2 mg/L.

### MINI-PLANT TESTWORK WITH CYANEX 302

In view of the good cobalt/nickel separation achieved with Cyanex 302 at Mintek on a batch laboratory scale -Tait (1993)-, it was decided to test this extractant on the same mini-plant used for the Cyanex 272 testwork. At the end of the campaign with Cyanex 272, the organic phase was removed from the plant. In order to minimise the time taken to reach equilibrium conditions, the aqueous phase in each stage was retained, and the plant recommissioned using 15 vol.% Cyanex 302 in Shellsol AB. The plant was then operated for a further 12 days.

It was found that Cyanex 302 behaved in a manner very similar to Cyanex 272 in terms of cobalt extraction, although a small change to the phase ratio was required because of the lower loading capacity of Cyanex 302. A cobalt loading of 4.6 g/L was achieved with Cyanex 302, compared to 5.1 g/L with Cyanex 272 during the mini-plant campaign.

Table 2 shows a typical circuit profile with the mini-plant operating under the optimised conditions: feed solution flowrate - 100 mL/min, organic - 17 mL/min, scrub solution - 0.4 mL/min and stripping H<sub>2</sub>SO<sub>4</sub> - 0.9 mL/min. The temperature in the extraction section was maintained at 50 °C. The scrub solution was CoSO<sub>4</sub> made up to 60 g/L Co. At this stage the mini-plant configuration included four scrubbing stages operating at a pH of 4.0 to 4.2. The overall accountabilities are within acceptable limits; those stages with poor accountabilities are those with low concentrations of Co or Ni.

TABLE 2  
Typical circuit profile and accountabilities

Section/stage number	Aqueous phase, g/L		Organic phase, g/L		Accountability, %	
	Co	Ni	Co	Ni	Co	Ni
Extraction section					97.9	98.6
Feed solution	0.994	69.8				
E1	0.250	69.0	6.15	0.180	96.8	99.1
E2	0.051	68.8	1.50	0.269	93.6	99.6
E3	0.017	68.6	0.20	0.641	99.8	99.9
Scrubbing section					94.3	73.6
SC1	30.1	6.9	6.21	0.171	97.8	113.2
SC2	41.9	4.5	6.25	0.080	100.8	82.6
SC3	41.0	1.3	6.32	0.012	98.8	42.6
SC4	50.2	0.11	6.27	0.009	96.9	91.5
Stripping section					86.6	93.5
S1	102.5	0.14	5.12	0.004	94.2	80.3
S2	93.0	0.10	0.85	0.002	97.5	108.5
S3	14.9	0.05	0.01	0.001	94.7	182.4

The improvement of scrubbing was investigated while using Cyanex 302 as this cobalt extractant is reportedly more difficult to scrub than Cyanex 272 -Tait (1993). Scrubbing was improved by stepwise lowering of the pH of the scrub section until cobalt stripping began. The scrubbed organic phase was monitored on a daily basis for cobalt and nickel concentration. Although this resulted in lower cobalt loadings (2.36 g/L) in the scrubbed organic phase, the nickel concentration was reduced to below 1 mg/L in the organic phase in all the scrubbing stages. By the end of this second campaign, a Co:Ni ratio of 4069:1 in the loaded organic phase was achieved (2.36 g/L cobalt and 0.58 mg/L nickel). This indicated that high Co:Ni ratios are possible by a solvent extraction process with Cyanex 302, albeit at lower cobalt recoveries.

### CONCLUSIONS

Either Cyanex 272 or 302 can be used to selectively remove cobalt to <20 mg/L from a feed solution containing 70 g/L nickel, 1000 mg/L cobalt and 35 g/L ammonium sulphate. This can be achieved in three extraction stages. By scrubbing of the loaded organic phase with dilute cobalt sulphate solution at a suitable pH, it is possible to achieve Co:Ni ratios of 500 to 4000:1 in the scrubbed organic phase in three to four stages. The cobalt can be stripped in three stages to produce a solution containing >100 g/L cobalt and minor amounts of nickel. Copper, iron, manganese and zinc impurities will report to the cobalt stream. The H<sub>2</sub>SO<sub>4</sub> used for stripping of the organic phase is close to the stoichiometric requirement in both Cyanex 272 and Cyanex 302 systems.

### ACKNOWLEDGEMENT

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## EXTRACTION OF COPPER(II) FROM CHLORIDE SOLUTIONS BY PYRIDINEDICARBOXYLATES

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### ABSTRACT

Copper(II) extraction from solutions of various chloride ion concentrations with individual dipentyl pyridinedicarboxylates was studied. The extraction ability decreases in the following order: pyridine-2,6-dicarboxylate = pyridine-2,4-dicarboxylate > pyridine-3,5-dicarboxylate >> pyridine-2,5-dicarboxylate >> pyridine-2,3-dicarboxylate. The addition of decanol as a modifier slightly increases the efficiency of copper(II) extraction by pyridine-3,5-dicarboxylate.

### INTRODUCTION

Complex sulfide ores, which are intimate associations of chalcopyrite ( $\text{CuFeS}_2$ ), sphalerite ( $\text{ZnS}$ ) and galena ( $\text{PbS}$ ) freely disseminated in the dominant pyrite ( $\text{Fe}_2\text{S}$ ) or pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) attract ever-increasing interest because of their obvious importance as a reserve of non-ferrous metals. Such ores typically contain 0.3-3% Cu, 0.3-3% Pb, 0.2-10% Zn, 30-100 g/t Ag, and 0.1 g/t Au (Dalton, 1984). Among various process options, the production of bulk concentrates is attractive in economic terms. Copper contained in such concentrates can be leached with various chloride-based systems. Ferric chloride, cupric chloride and their mixtures are favoured leachants because of their high leaching efficiency, the rapid rate of the process and the fact that sulfur is liberated in the elemental form (Haver, 1971, 1975). Corrosion problems connected with the corrosive nature of chloride media have been overcome by the use of new polymeric construction materials, and chloride hydrometallurgy can now be seen as a logical alternative for the treatment of unconventional concentrates that smelters cannot handle.

Because of the very high efficiency of chloride leaching systems, many minor metals present in complex sulphide concentrates such as arsenic, antimony, bismuth, mercury, cadmium, selenium, manganese, etc., are also leached very effectively. Frequently, they appear in the copper product, causing the necessity of expensive refining stages to produce a marketable copper. The problem of purity of copper has been overcome by solvent extraction.

A few years ago, ICI developed and patented a new commercial reagent ACORGA CLX-50 and associated process (the CUPREX Metal Extraction Process) for extraction of copper(II) from chloride solutions obtained during the leaching of sulphide concentrates with chloride-based systems (Dalton, 1987, 1988, 1991). The active ingredient of ACORGA CLX-50 is an ester of pyridine-3,5-dicarboxylic acid and the ICI patents indicate that this type of pyridine compounds is particularly suitable for the extraction of copper(II) from chloride systems through a solvation mechanism (Dalton, 1982, 1983; Soldenhoff, 1987). ACORGA CLX-50 is capable of transferring large amounts of copper with no need for pH adjustment or control and with very high selectivity over a wide range of metals and metalloids (Dalton, 1984).

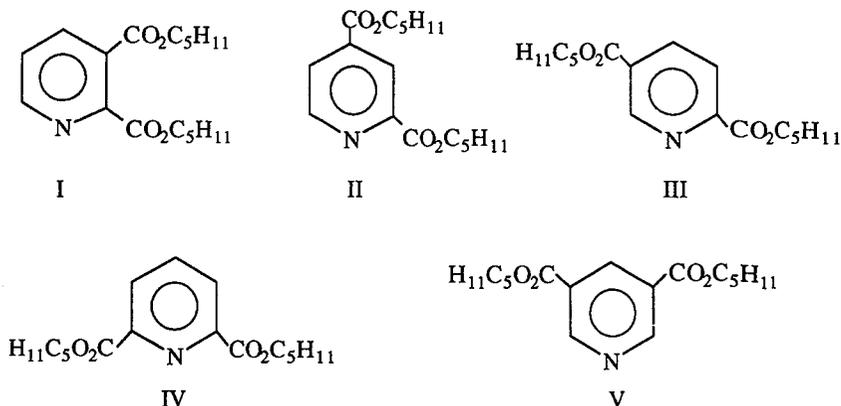
In previous works, we have investigated copper(II) extraction by model pyridine monocarboxylates and compared the results with that obtained for ACORGA CLX-50. We have also modelled the extraction equilibrium under the conditions of constant water activity and constant total concentration of ionic or molecular species dissolved in the aqueous solution. The influence of the position of the ester group in the pyridine ring on the extraction ability of pyridine monocarboxylates was also discussed. Pyridine monocarboxylates form more stable copper(II) complexes than

ACORGA CLX-50 and can therefore efficiently extract this metal even at low chloride ion concentrations; however their selectivity over iron is much lower than that of the commercial extractant and copper stripping cannot be achieved as easily as with ACORGA CLX-50 (Szymanowski, 1993, 1994; Cote, 1994).

The objective of the present work includes an investigation of the ability of various model pyridine dicarboxylates to extract copper(II) from concentrated chloride solutions and a study of the influence of the long chain alcohol content in the organic phase upon copper(II) extraction.

### EXPERIMENTAL

The following five compounds have been synthesized according to the methods described previously (Szymanowski, 1993):



The resulting products were purified by vacuum distillation. The extractants were dissolved in toluene and an approximately twenty-fold excess of extractant to metal concentration was used. Aqueous solutions of copper(II) were prepared from CuCl<sub>2</sub>·2H<sub>2</sub>O and various amounts of LiCl. In all cases, the pH of the aqueous phase was close to 3 and thus protonation of the extractants did not occur. Equal volumes of organic and aqueous phases were shaken at room temperature until equilibrium was reached (i.e., 15 min although equilibrium was obtained within a few minutes). After that, the two phases were allowed to separate and copper(II) was completely stripped from the organic phase by pure water. The copper(II) concentration in the aqueous phases was determined by titration with EDTA with murexide as indicator. To investigate the influence of the long chain alcohol content in the organic phase, mixtures of toluene and decanol (in the range 0-100% vol/vol of alcohol) were prepared.

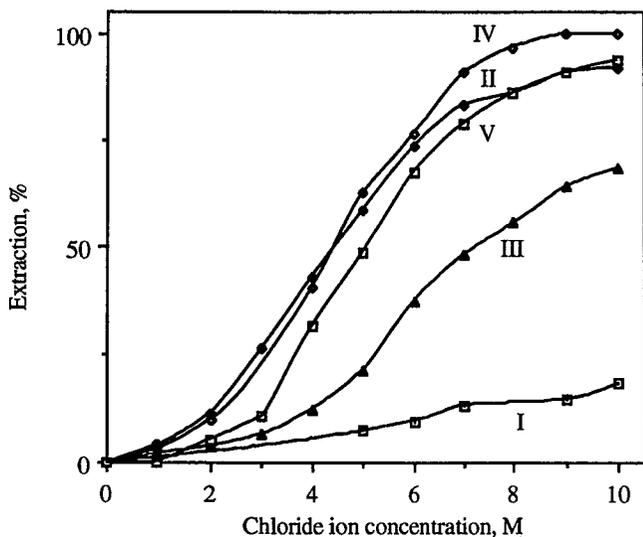
### RESULTS AND DISCUSSION

A suitable extractant for copper(II) extraction from chloride media ideally should extract this metal from solutions containing about 4-6 M chloride ions with a good yield, but not extract copper at chloride ion concentrations lower than 2 M. Only in such a case can the stripping of copper be easily carried out and high amounts of copper(II) can be transferred from the leaching solutions to the final electrolyte via the extraction-stripping cycle. Figure 1 indicates that the extraction behaviour of pyridinedicarboxylates depends significantly upon the positions of the two ester groups. The extraction ability of the studied dipentyl esters decreases in the following order: pyridine-2,6-dicarboxylate (compound IV) = pyridine-2,4-dicarboxylate (compound II) > pyridine-3,5-

dicarboxylate (compound V) >> pyridine-2,5-dicarboxylate (compound III) >> pyridine-2,3-dicarboxylate (compound I).

The chloride ion concentrations for which the yield of copper(II) extraction reached 50% are equal to 4.4, 4.4, 5.0 and 7.2 M for compounds II, IV, V and III, respectively. Pyridine-2,3-dicarboxylate (compound I) has a poor affinity for copper(II) and the extraction yield does not exceed 20%, even at 10 M  $\text{Cl}^-$ . Pyridine-2,6-dicarboxylate (compound IV) and pyridine-2,4-dicarboxylate (compound II) are the two strongest copper(II) extractants. However, the copper complex of compound IV precipitates as soon as  $[\text{Cl}^-] = 4 \text{ M}$ . Thus, the system is not directly suitable for copper(II) extraction. The high affinity of pyridine-2,6-dicarboxylate (compound IV) for copper(II) was not expected due to the potential for significant steric hindrance from the two ester groups near the pyridine nitrogen. Finally, the best compromise is obtained for pyridine-3,5-dicarboxylate (compound V). The extraction of copper is negligible at low chloride ion concentrations (i.e., below 2 M), but sharply rises with the chloride ion concentration above 2 M. Thus, the behaviour of compound V is similar to that previously reported for ACORGA CLX-50 (Cote, 1994).

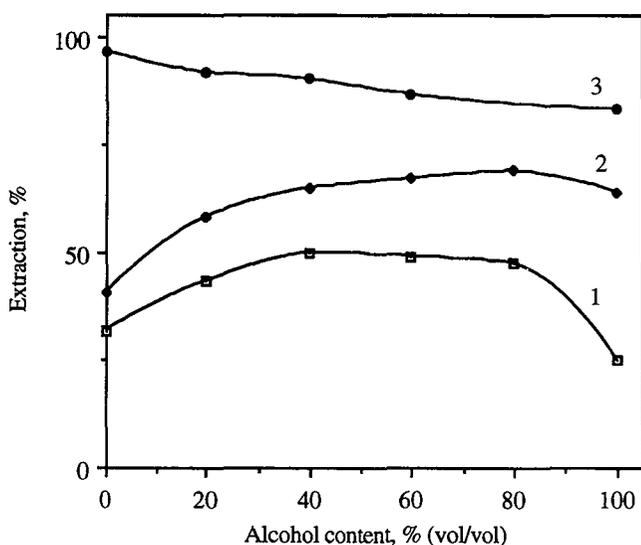
The ESR spectra of the various organic phases previously loaded with copper(II) have been recorded at the temperature of liquid nitrogen. Examination of these spectra suggests that the feature of copper complexation is similar for all the considered pyridine dicarboxylates, except perhaps for pyridine-2,6-dicarboxylate (compound IV). Indeed, in the latter case the spectrum of the organic phase exhibits a hyperfine structure which does not appear on the other spectra.



**Figure 1.** Extraction of copper(II) (initially  $10^{-2} \text{ M}$ ) by 0.2 M pyridine dicarboxylates in toluene from aqueous LiCl solutions. (I) 2,3-dicarboxylate; (II) 2,4-dicarboxylate; (III) 2,5-dicarboxylate; (IV) 2,6-dicarboxylate; (V) 3,5-dicarboxylate.

In order to avoid the precipitation of the copper complex of pyridine-2,6-dicarboxylate (compound IV), decanol was used as a modifier (Figures 2 and 3). It was assumed that the addition of a long chain alcohol can improve the copper complex solubility in the organic phase. Indeed, decanol having a hydroxyl group can form hydrogen bonds with the oxygen atoms present in the ester substituents of the studied compounds, regardless whether these compounds are free or participating

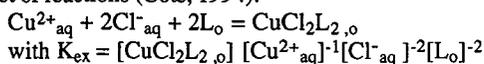
in the formation of the copper complexes. The latter situation is obviously favourable for the extraction of copper(II). On the other hand, decanol, and more generally, alcohols can also form associates with the various esters via their pyridine nitrogen, which is a phenomenon having a negative effect on the complexing power of these esters and finally on the efficiency of copper extraction. The experimental results are presented in Figure 2. At a chloride ion concentration equal to 4 M, addition of decanol enhances copper(II) extraction with pyridine-3,5-carboxylate (compound V) and pyridine-2,6-dicarboxylate (compound IV) up to a content of alcohol of 40% and 80% (vol/vol), respectively. This means that improvement of the solvating properties of the diluent and/or decanol association with the copper complex have a stronger effect than the alcohol association with the extractant molecules. The latter effect seems to be dominant in the domain of very high alcohol content where the efficiency of copper extraction decreases. The precipitation of the copper complex of pyridine-2,6-dicarboxylate no longer occurs at 4 M Cl<sup>-</sup> in the presence of decanol, but cannot be avoided at 8 M Cl<sup>-</sup>. Thus, it should be concluded that pyridine-2,6-dicarboxylate (compound IV) is not suitable for obtaining an organic phase having a high capacity in copper, but this could possibly be changed by replacing the two pentyl groups in the ester substituents of compound IV by two longer alkyl chains, such as decyl or dodecyl.



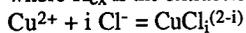
**Figure 2.** Effect of the addition of decanol upon the extraction of copper(II) (initially  $10^{-2}$  M) by 0.2 M pyridine dicarboxylates in toluene. (1) 3,5-dicarboxylate from 4 M LiCl; (2) 2,6-dicarboxylate from 4 M LiCl; (3) 2,6-dicarboxylate from 8 M LiCl.

The positive effect of 20% (vol/vol) alcohol addition upon copper(II) extraction with pyridine-3,5-carboxylate (compound V) is observed in the whole region of chloride ion concentration (i.e., 0-10 M) (Figure 3).

The effect of the position of the ester groups upon extraction of copper(II) can be quantitatively described by the apparent extraction equilibrium constants (i.e., involving concentration of species). The process of extraction with the pyridine carboxylates studied can be described by the following set of reactions (Cote, 1994):

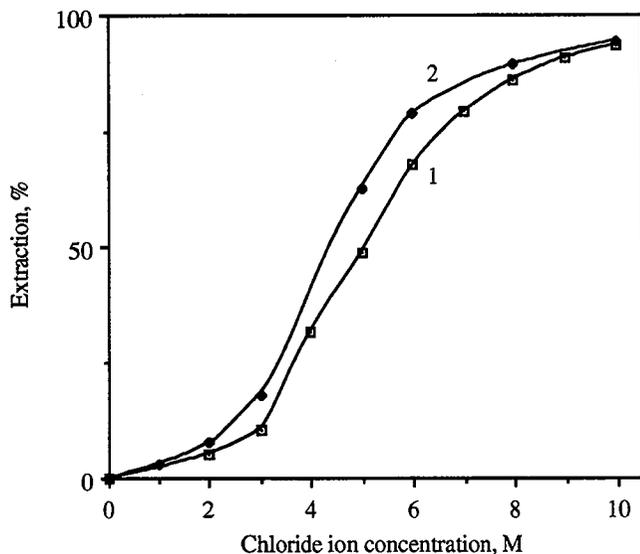


where  $K_{ex}$  is the extraction constant



with  $\beta_i = [CuCl_i^{(2-i)}] [Cu^{2+}]^{-1} [Cl^-]^{-i}$  and  $i = 1$  to 4

where L represents a molecule of extractant and aq and o subscripts refer to the aqueous and organic phases, respectively, and  $\beta_i$  is the formation constant



**Figure 3.** Extraction of copper(II) (initially  $10^{-2}$  M) by 0.2 M pyridine-3,5-dicarboxylate in toluene (1) without decanol; (2) with 20% (vol/vol) of decanol.

The apparent extraction equilibrium constants (Table 1) depend upon extractant structure, which is in agreement with the previously presented data and significantly increase with a decrease of water activity and on increase of the total concentration of ionic or molecular substances dissolved in the aqueous phase, as a result of salting-out effects.

### CONCLUSIONS

The efficiency of copper(II) extraction from chloride solutions with dipentyl pyridinedicarboxylate decreases as follows: pyridine-2,6-dicarboxylate = pyridine-2,4-dicarboxylate > pyridine-3,5-dicarboxylate >> pyridine-2,5-dicarboxylate >> pyridine-2,3-dicarboxylate. It should be pointed out that the values of the apparent copper(II) extraction constants greatly depend on the water activity and the total concentration of aqueous species, as a result of salting-out effects. The extraction ability of dipentyl pyridine-3,5-dicarboxylate changes with chloride ion concentration in a way very similar to that reported for the commercial extractant ACORGA CLX-50. Finally, the addition of decanol improves copper(II) extraction from chloride solutions by pyridine-3,5-dicarboxylate.

**TABLE 1**  
Values of  $K_{ex}$  for model pyridine carboxylates and ACORGA CLX-50

Aqueous phase	Diluent	Extractant	log $K_{ex}$
$a_w = 0.835$ (**) $\sigma = 8.0 \text{ mol L}^{-1}$ (***)	Toluene	decyl isonicotinate (*)	2.43
		decyl nicotinate (*)	2.10
		decyl picolinate (*)	1.30
		dipentyl pyridine-2,3-dicarboxylate	0.36
		dipentyl pyridine-2,4-dicarboxylate	1.49
		dipentyl pyridine-2,5-dicarboxylate	0.73
		dipentyl pyridine-2,6-dicarboxylate	1.44
		dipentyl pyridine-3,5-dicarboxylate	1.26
	Kerosene	ACORGA CLX-50 (*)	0.67
$a_w = 0.617$ $\sigma = 8.0 \text{ mol L}^{-1}$	Toluene	dipentyl pyridine-2,3-dicarboxylate	1.26
		dipentyl pyridine-2,4-dicarboxylate	2.76
		dipentyl pyridine-2,5-dicarboxylate	2.04
		dipentyl pyridine-2,6-dicarboxylate	2.82
		dipentyl pyridine-3,5-dicarboxylate	2.63
		ACORGA CLX-50 (*)	2.39
			Kerosene

(\*) from (Cote, 1994); (\*\*)  $a_w$  = water activity; (\*\*\*)  $\sigma$  = total concentration of ionic or molecular species dissolved in the aqueous phase.

### ACKNOWLEDGEMENTS

The work was supported by Polish KBN grant 1995. The authors also thank NATO for the linkage grant n° ENVIR.LG. 940602.

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## SEPARATION OF RARE EARTH METALS UTILIZING OIL-WATER INTERFACE IN LIQUID-LIQUID EXTRACTION

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### ABSTRACT

A novel synergistic agent, which is an oil-soluble polyaminocarboxylic acid alkyl derivative, has been utilized for selective separation of rare earth metals in liquid-liquid extraction. The synergistic agent has interfacial activity like that of surfactants and strongly adsorbs at an oil-water interface. A novel extraction process combined with an electrical coalescer to promote phase separation was proposed to utilize the oil-water interfaces as a separation place. Extraction of three rare earth metals (Y, Er and Yb) in the presence of the synergistic agent was carried out with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester as an extractant using the novel extraction method. The selectivity of yttrium to erbium was enhanced remarkably by the addition of a small amount of the synergistic agent. The synergistic agent was effective in a range controlled by an interfacial reaction. The enhancement of the selectivity in this work was considered to be caused by the difference in the interaction between metal ions and the new agent at the oil-water interfaces. Efficient extraction and separation of rare earth metals utilizing the oil-water interfaces were performed with the newly proposed extraction method.

### INTRODUCTION

Conventional solvent extraction is well known as one of the most effective methods for separation and purification of rare earth metals on an industrial scale. However, even in the solvent extraction method, a huge energy is required for the preparation of high-purity products, because separation factors among adjacent rare earth elements are very small. Thus it has been expected to develop more efficient techniques for separation of rare earth metals. One promising way to obtain more efficient separation is to create a new agent which enhances separation factors in rare earth metals. Recently, aqueous-soluble complexing agents such as diethylenetriamine-pentaacetic acid (DTPA) were used for selective separation of yttrium from other heavy rare earths by utilizing the difference in stability constants between metals and the complexing agent (Matsuyama et al., 1989, Komazawa et al., 1991). Although it is a very useful method for increasing the separation factors of rare earth metals, it has an inherent problem that the recovery of costly chelating agents from the product solution is very difficult. To overcome the problem, we have developed in previous work (Goto et al., 1992a,b) several new oil-soluble complexing agents which are polyaminocarboxylic acid alkyl derivatives. However, when these agents are introduced to a conventional solvent extraction process, a large amount of emulsion is produced during extraction in a mixer, because such an agent has an interfacial activity like that of surfactants. The emulsification creates extremely small droplets and leads to the promotion of the extraction rate through the large interfacial area formed by the small droplets. In this study, we have proposed a novel extraction method combined with an electrical coalescer as a promoter of phase separation and to utilize the new synergistic agents like a surfactant. The energy consumption of the electrical coalescer has already been elucidated to be very low compared with the other phase separation methods (Goto et al., 1989). Therefore, the proposed separation method, named the emulsion extraction method, would be a very economical process for the separation of rare earth metals in liquid-liquid extraction. In the present work, the novel extraction process using an oil-soluble complexing agent was applied to the separation of yttrium from heavy rare earth metals (Yb and Er). In the presence of the most effective synergistic agent, ethylenediaminediacetic acid-N,N'-dioleamide (abbreviated EDTA-N,N'-DOLA or H<sub>2</sub>S) (Goto et al., 1992b), the extraction

mechanism of rare earth metals by 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (Commercial name, PC-88A, henceforth abbreviated HR) was investigated and the key factors discussed to enhance the separation of rare earth metals in the new system.

## EXPERIMENTAL

### Reagents

The synergistic agent, EDTA-N,N'-DOLA, was synthesized from the EDTA anhydrides and oleyl amine according to the procedure in the previous paper (Goto et al., 1992a). The extractant, PC-88A, supplied from Daihachi Chemical Industry Co., Ltd., was used without further purification. Toluene of commercial GR. grade was used as the organic solvent. All other inorganic reagents used were GR. grade.

### Procedure

The interfacial tension between toluene solutions of PC-88A or EDTA-N,N'-DOLA and aqueous solutions was measured at 300 K by the drop volume method and the pendant drop method. Measurement of extraction equilibria were carried out by the normal method. Organic solutions were prepared by dissolving PC-88A and/or EDTA-N,N'-DOLA in toluene. Aqueous solutions were prepared by dissolving the chloride salt hexahydrates of three rare earth metals (Er, Y and Yb) in nitric acid solutions and adjusting the pHs and ionic strengths of the solutions with 100 mol/m<sup>3</sup> sodium nitrate and 100 mol/m<sup>3</sup> nitric acid. The concentrations of the rare earth metals were measured by ICP-atomic emission spectroscopy (SEIKO SPS-1200VR). Figure 1 shows the extraction apparatus for the emulsion extraction method. The aqueous and organic solutions were fed into the extraction mixer

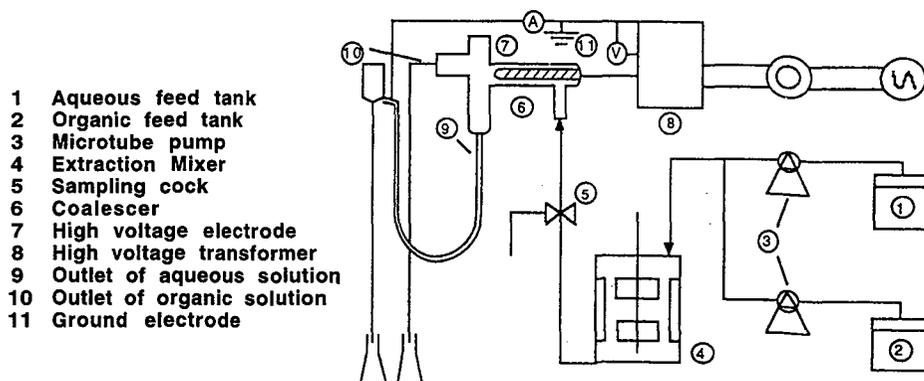


Fig. 1 Extraction apparatus of emulsion extraction method

TABLE 1

Experimental conditions for emulsion extraction method.

Aqueous phase	:rare earth metals; Y, Er, Yb, $C_{MIO}=0.5\text{mol/m}^3$ :pH=1.4-2.4 ( $100\text{mol/m}^3 \text{HNO}_3\text{-NaNO}_3$ )
Organic phase	:solvent;toluene :extractant;PC-88A, $C_{(HR)20}=50\text{mol/m}^3$ :complexing agent;EDTA-N,N'-DOLA, $C_{H2SO}=0\text{-}1\text{mol/m}^3$
Stirring speed in mixer:	1000rpm, Residence time in mixer: $\theta=50\text{-}300\text{s}$
Applied voltage: 4kV,	Temperature: 300 K

by the microtube pump. The emulsions produced in the extraction mixer were fed into the electrical coalescer and they are broken immediately under the electric field of 4kV. The volume of the mixer and coalescer are about 80 dm<sup>3</sup> and 30 dm<sup>3</sup> respectively. At the steady state, the concentration of metals in the effluent organic solution was measured. The residual amount of water in organic solutions was measured with Karl-Fischer method. The detailed experimental conditions are listed in Table 1.

## RESULTS AND DISCUSSION

### Interfacial tension

As shown in Fig.2, the interfacial tension is decreased with increasing concentration of PC-88A or EDTA-N,N'-DOLA in the organic solution due to the adsorption of the agent at the interface. The relation between the interfacial tension,  $\gamma$ , and the concentration of the agent in the organic phase is derived from the Gibbs' equation for adsorption assuming a Langmuir adsorption isotherm as follows:

$$\gamma = \gamma_0 - (RT/S_i) \cdot \ln(1 + K_{ad} \cdot C_i) \quad (1)$$

The values of the adsorption equilibrium constant,  $K_{ad}$ , obtained from the experimental results are  $2.01 \times 10^2 \text{ m}^3/\text{mol}$  for EDTA-N,N'-DOLA and  $3.28 \text{ m}^3/\text{mol}$  for PC-88A. This result indicates that the interfacial activity of EDTA-N,N'-DOLA is much higher than that of PC-88A.

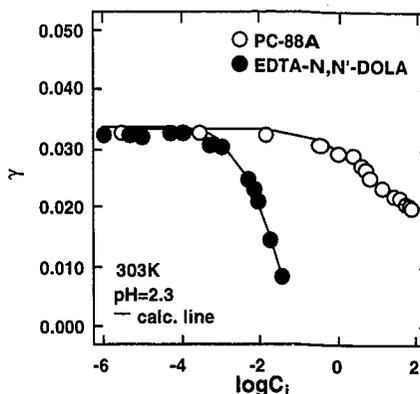
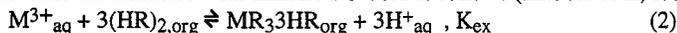


Fig.2 The relation between interfacial tension and concentration of dimeric PC-88A and new synergistic agent

### Extraction equilibrium

Rare earth metals are extracted with dimeric PC-88A as follows (Kubota et al, 1993):



The metal distribution ratio,  $D$ , defined by  $C_{\text{Morg}}/C_{\text{Maq}}$  is expressed as follows:

$$\log D \cdot C_{\text{H}}^3 = 3 \log C_{(\text{HR})_2} + \log K_{\text{ex}} \quad (3)$$

The values of extraction equilibrium constant,  $K_{\text{ex}}$ , obtained from the experimental results and the separation factors defined as the ratio of  $K_{\text{ex}}$  for each metal are shown in Table 2. The separation of Y and Er is found to be very difficult. Furthermore, it was confirmed that the extraction equilibrium is not affected by the addition of new synergistic agents.

### The evaluation of phase separation by electrical coalescence

The content of unbroken emulsions,  $Z$ , was estimated from the water content in the demulsified emulsions,  $\phi_w$ , and that in the initial emulsions,  $\phi_{w0}$ , as follows (Goto et al., 1989):

$$Z = \phi_w / \phi_{w0} \quad (4)$$

The value of  $Z$  was less than  $2 \times 10^{-3}$  under the present experimental condition. This result means that the phase separation was performed effectively by the electrical coalescer.

### Extraction of rare earth metals by emulsion extraction method

In the previous paper (Goto et al, 1992b), the effect of oil-soluble complexing agent on the extraction of rare earth metals (Ho, Y and Er) was examined using a membrane extractor. The permeation rate of Y was found to be reduced notably compared with that of the other two metals. Based on the result, the effect of the synergistic agent on the extraction rate was considered to be caused not only by the shielding effect of the agent adsorbed but also the interaction between EDTA-N,N'-DOLA and metals at the oil-water interface. The difference in the degree of the interaction makes the mutual separation factor enhanced. Experimental results suggest that there are two routes for the extraction of rare earth

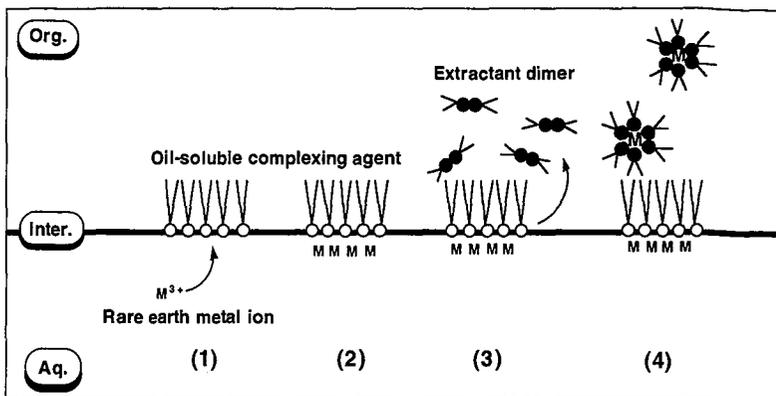
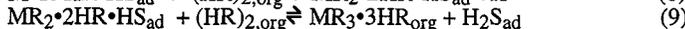
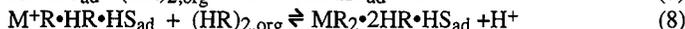
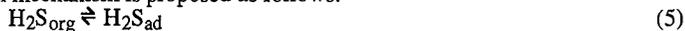


Fig.3 Schematic diagram of the synergistic extraction mechanism of rare earth metals in the presence of EDTA-N,N'-DOLA

metals in the presence of EDTA-N,N'-DOLA. One is the route that the metal is extracted directly by the extractant of which the mechanism has already been elucidated (Goto et al., 1992b, Kubota et al., 1995) and another is the route that metal extraction is achieved via interaction with EDTA-N,N'-DOLA at the oil-water interface. The degree of contribution in the two routes is considered to depend on the experimental conditions. The latter extraction behavior is schematically shown in Fig.3 and the extraction mechanism is proposed as follows:



Assuming that Eq.(9) is the rate controlling step, the interfacial reaction rate accompanied by the interaction with EDTA-N,N'-DOLA is expressed as follows:

$$R_s = k_s C_{H_2S} (C_M C_{(HR)_2}^3 / C_H^3 - C_{MR_3HR} / K_{ex}) \sigma \quad (10)$$

When the extraction is proceeded through the two routes simultaneously, the overall rate of interfacial chemical reaction is as follows:

$$R = R_f + R_s \\ = (k_f + k_s C_{H_2S}) (C_M C_{(HR)_2}^3 / C_H^3 - C_{MR_3HR} / K_{ex}) \sigma \quad (11)$$

Figure 4 shows a typical experimental result between extraction ratio, E, and residence time,  $\theta$ , in the mixer. The extraction rate of Y is found to be decreased larger than those of the other metals in the presence of EDTA-N,N'-DOLA. When the overall interfacial reaction rate is expressed as Eq.(11), the extraction rate of rare earth metal is expressed as follows:

$$R = k_0 (C_M - C_{MR_3HR} / D) \quad (12)$$

where

$$1/k_0 = 1/k_M + 1 / [(k_f + k_s C_{H_2S}) (C_{(HR)_2}^3 / C_H^3) \sigma] \quad (13)$$

Further, mass-balance of metals in the mixer was written as follows:

$$v_{aq}(C_{M0} - C_M) = v_{aq} \cdot a \cdot R \quad (14)$$

$$v_{aq}(C_{M0} - C_M) = v_{org} \cdot C_{MR_3HR} \quad (15)$$

Equation (16) are obtained from Eqs.(12), (14) and (15).

$$1/E = (d_p / 6 \cdot k_0) (1/\theta) + 1/E_{ex} \quad (16)$$

Figure 5 shows the relation between  $1/E$  and  $1/\theta$  according to Eq.(16). The linear dependence was obtained and the value of  $k_0$  for each metal was calculated on the basis of each slope.

Figure 6 shows the  $k_0$  values obtained as a function of the concentration of EDTA-N,N'-DOLA. Based on the results in Fig.6 and Fig.2, it is clear that the permeation rate was affected by EDTA-N,N'-DOLA adsorbed at the oil-water interface. Further, EDTA-N,N'-DOLA is found to enhance the separation factor between Er and Y more than 4 and this value is much larger than the value of 1.4 in conventional solvent extraction. On the basis of the obtained results,  $k_f$  and  $k_s$  in Eq.(11) were determined by a nonlinear regression method. The first term in Eq. (13) which represents the diffusion resistance on the aqueous side was considered to be negligibly small under the present experimental conditions, since the synergistic effect appeared in the range where the extraction rate is controlled by the interfacial chemical reaction. The values of  $k_f$  and  $k_s$  obtained are listed in Table 2 along with the separation factor for each metal. Evidently, the selectivity for a rare earth metal is enhanced by the synergistic agent because the separation factor via the interaction with the synergistic agent is very large compared with that of the extractant alone. The synergistic extraction behavior of rare earth metals was explained by the mechanism proposed and it was demonstrated that the oil-water interface is readily available in liquid-liquid extraction as a separation region.

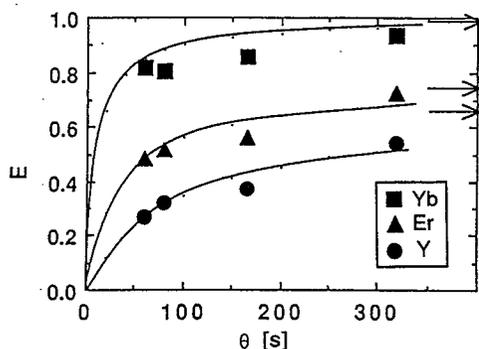


Fig.4 Relation between extraction ratio and residence time (pH=2.0,  $C_{H_2S}=0.5 \text{ mol/m}^3$ ,  $C_{(HR)_{20}}=50 \text{ mol/m}^3$ )

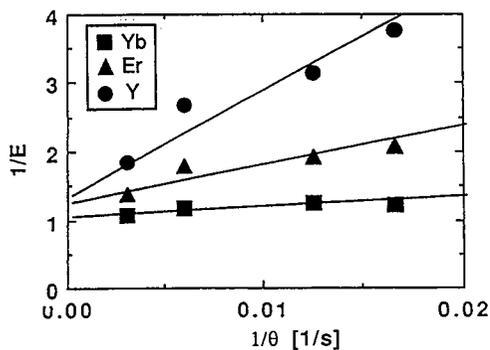


Fig.5 Relation between  $1/E$  and  $1/\theta$  (pH=2.0,  $C_{H_2S}=0.5 \text{ mol/m}^3$ ,  $C_{(HR)_{20}}=50 \text{ mol/m}^3$ )

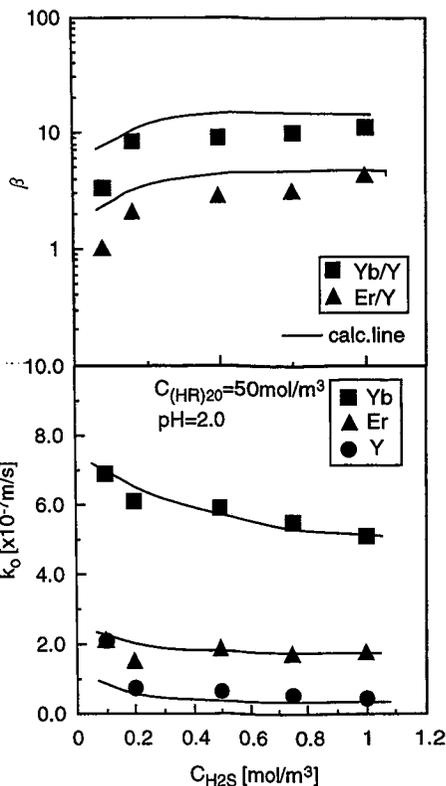


Fig.6 Relation between  $k_0$  and the concentration of EDTA-N,N'-DOLA

TABLE 2

Values of constants obtained by analysis and separation factors

Metal	$k_f$ [m/s]	$k_s$ [m <sup>4</sup> /(mol•s)]	$\beta_{Mi/Y}(k_f)$	$\beta_{Mi/Y}(k_s)$	$K_{ex}$	$\beta_{Mi/Y}(K_{ex})$
Er	2.2x10 <sup>-6</sup>	3.6x10 <sup>-6</sup>	2.3	7.7	8.4	1.4
Yb	8.9x10 <sup>-6</sup>	7.3x10 <sup>-6</sup>	9.2	15.5	110	19
Y	9.7x10 <sup>-7</sup>	4.7x10 <sup>-7</sup>	-	-	5.8	-

### CONCLUSION

A novel solvent extraction method utilizing an oil-soluble synergistic agent has been developed for the selective separation of rare earth metals. Continuous operation for extraction and separation of rare earth metals was carried out employing an electrical coalescer to facilitate the phase separation in the presence of the synergistic agent. The selectivity of Y to the heavy rare earth metals was much increased compared to that in the extractant alone system by the interaction with the synergistic agent at the oil-water interface. The adsorption ability of the agents is one of the key factors in the synergistic effect. These results indicate that the new extraction method is very effective and is a promising method for the separation of rare earth metals. Further, the extraction mechanism was examined and the result leads to the conclusion that the synergistic effect is caused by the interaction between a metal ion and the synergistic agent at the oil-water interface.

### ACKNOWLEDGMENT

The authors are grateful to Daihachi Chemical Industry Co., Ltd. for the supply of PC-88A. The authors wish to express their application to Mr. Horiuchi of Kyushu University for his technical support in constructing the glass extractor.

### NOMENCLATURE

- a = relative interfacial area
  - $d_p$  = diameter of droplet (m)
  - $k_f$  = extraction rate constant by extractant (m/s)
  - $k_s$  = extraction rate constant by extractant and synergistic agent (m<sup>4</sup>•mol<sup>-1</sup>•s<sup>-1</sup>)
  - $R_f$  = extraction rate by extractant (mol•m<sup>2</sup>•s<sup>-1</sup>)
  - $R_s$  = extraction rate by extractant and synergistic agent (mol•m<sup>2</sup>•s<sup>-1</sup>)
  - $S_i$  = interfacial area occupied by unit mole of species i (m<sup>2</sup>•mol<sup>-1</sup>)
  - $V_{aq}$  = volume of aqueous phase (m<sup>3</sup>)
  - v = volumetric flow rate (m<sup>3</sup>•s<sup>-1</sup>)
  - $\sigma$  = characteristic term of adsorption (-)
- subscript**
- ad = adsorption state

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## Cloud Point Extraction of Gold(III) from Hydrochloric Acid Solution

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### ABSTRACT

The cloud point extraction of Au(III) from hydrochloric acid media with a nonionic surfactant, polyoxyethylene nonyl phenyl ether having average chain length of 10 oxyethylene units (PONPE10), has been investigated. Phase-separation of the surfactant solutions was attained by settling it at a temperature above the cloud point. Good partitioning of Au(III) between the surfactant-rich phase and bulk aqueous phase was obtained which indicated that a high degree of the separation could be achieved. With increasing HCl concentration, the cloud point rises and the distribution ratio of Au(III) decreases on account of a deterioration of the phase-separation characteristics. However, the extraction of Au(III) could be improved by making the concentration of PONPE10 higher, adding NaCl, raising the settling temperature, or using the mixed surfactant system with PONPE7.5. Moreover, the extraction efficiencies for heavy metals such as Pd(II), Pt(IV), Zn(II), Cu(II) and Fe(III) are much lower than that for Au(III); thus a selective separation of Au(III) from these metals could be attained.

### INTRODUCTION

Purely aqueous separation methods using water-soluble surface active agents, including cloud point extraction, have attracted special attention in a viewpoint of safety because no organic solvents are required unlike conventional solvent extraction. In general, aqueous solutions of nonionic surfactants become turbid at a well-defined temperature referred as cloud point (CP), being separated into two isotropic phases by allowing it to leave at a temperature above the CP: one is a coacervate phase (surfactant-rich phase) containing a greater part of surfactant in the system and the other is a bulk aqueous phase containing a small amount of the surfactant.

Cloud point extraction utilizes the two phases as a separation field in a similar manner to solvent extraction; *i.e.*, when a nonionic surfactant is added into an aqueous solution containing a solute and the resulting solution is subject to phase-separation by heating, the solute is partitioned between the two phases according to its affinity to the surfactant. It is considered that advantages of CP extraction are as follows: safety from using nontoxic and nonvolatile surfactant, cost saving from requiring a relatively small amount of surfactant, and high ability to concentrate a variety of solutes. Moreover, CP extraction may be applicable to the recovery of bioproducts, though having to take account of degradation of heat sensitive substrates with raising temperature for the phase-separation.

In previous studies, CP extraction has been found to be applicable for separating *n*-alcohols and 4-*tert*-butylphenol -Gullickson (1989)- and membrane proteins -Bordier (1981), Ganong *et al.* (1991). Hoshino *et al.* (1983) reported a quantitative description for the partitioning of such an analytical reagent as 8-quinolinol between surfactant-rich and water phases. Watanabe *et al.* (1978) also applied the extraction to trace analysis of zinc(II) via chelate formation with PAN. Most recently, the authors (1995) have reported CP extraction of phenol and pyridine derivatives from aqueous solutions. In these studies were used *iso*-octylphenoxy polyethoxyethanol (Triton X series) and polyoxyethylene-4-nonyl phenyl ether (PONPE) as nonionic surfactant. Moreover, another types of surfactants have been used by Schmid *et al.* (1993) and Saitoh *et al.* (1991).

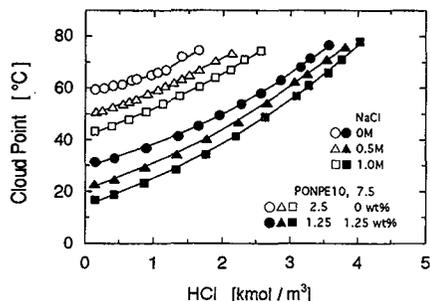


Fig. 1 Effect of HCl concentration on cloud point of aqueous PONPE solution.  $[Au(III)]=5 \times 10^{-4} M$

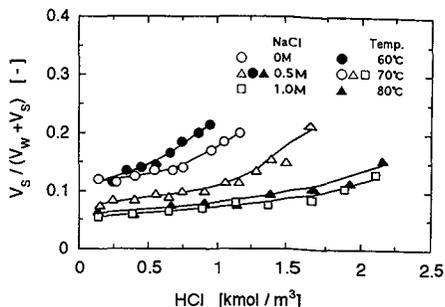


Fig. 2 Effect of HCl concentration on equilibrium volume ratio of surfactant-rich phase after phase-separation.  $[PONPE10]=2.5 \text{ wt\%}$ ,  $[Au(III)]=5 \times 10^{-4} M$

There is, however, little study on the applicability of CP extraction to a direct recovery of metals from aqueous solutions. In the present study, a possibility of CP extraction of metal ion will be demonstrated on the separation of gold(III) from hydrochloric acid media.

## EXPERIMENTAL

Two polyoxyethylene nonyl phenyl ethers having the average ethylene oxide unit of 10 (PONPE10) and 7.5 (PONPE7.5) were obtained from Tokyo Kasei Kogyo Co., Ltd., and used without further purification. Each aqueous stock solution was prepared by dissolving the nonionic surfactants and metal chlorides in deionized water; a desired feed solution was obtained by blending the stock solutions at an appropriate volume ratio. The concentrations of the surfactant and metal in the aqueous feed were 2.5 wt% and  $5 \times 10^{-4}$  mol/L, respectively, except otherwise stated. All chemicals used were of reagent grade.

An aqueous feed (20 mL) was well mixed in a 25 mL graduated glass tube, and heated slowly in a thermostatted water bath until the solution became turbid, whereby this temperature was recorded as CP of the solution. Subsequently the solution was allowed to be phase-separated by settling it overnight in an incubator at 70 °C except for studying the effect of the settling temperature, and both equilibrium volumes of the surfactant-rich and aqueous phases were measured. Metal concentration of the aqueous phase was determined by atomic absorption spectroscopy, that of the surfactant-rich phase being evaluated on the basis of a mass balance.

## RESULTS AND DISCUSSION

### Cloud Point and Phase Separation

Figure 1 shows the effect of HCl concentration on the CP of PONPE10 solution and of the mixed solution with PONPE7.5 in the presence of a small amount of Au(III). At a temperature above CP, the solution is in a state of clouding and ready to be phase-separated. In all runs, the CP rose with an increase in HCl concentration, so that it was necessary to raise the settling temperature for attaining phase-separation. The addition of NaCl gave rise to a significant decrease in CP: the lowering was of ca. 8 °C with 0.5 M and of ca. 15 °C with 1.0 M.

Mixed surfactant solution of PONPE10 and PONPE7.5 gave much lower CP than the former single solution; thus the mixed system allows CP extraction to use much higher HCl concentration. Such lowering of CP of the mixed solution is attributable to more hydrophobicity of PONPE7.5 as compared to PONPE10. This leads to a possibility of controlling CP to a desired temperature with a combination of salt and surfactant system.

Figure 2 shows the effect of HCl concentration in PONPE10 solutions on the equilibrium volume

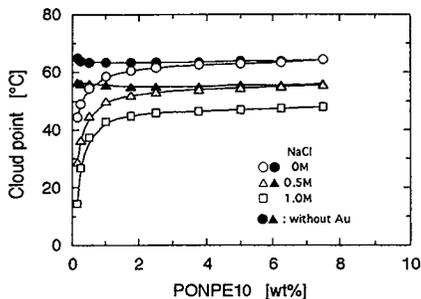


Fig.3 Effect of PONPE10 concentration on cloud point of aqueous solution with and without Au(III).  
[HCl]=0.5M, [Au(III)]= $5 \times 10^{-4}$ M

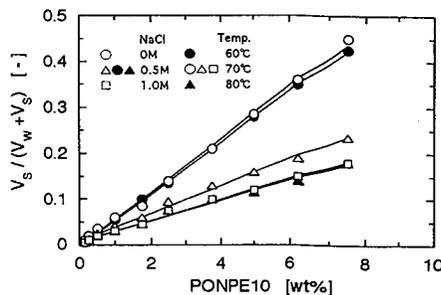


Fig.4 Effect of PONPE10 concentration on equilibrium volume ratio of surfactant-rich phase after phase-separation.  
[HCl]=0.5M, [Au(III)]= $5 \times 10^{-4}$ M

ratio of the surfactant-rich phase,  $V_S / (V_W + V_S)$ , where  $V$  denotes the volume; the subscripts S and W do the surfactant-rich and aqueous phases, respectively. In the present system it is to be noted that the surfactant forms a coacervate as the lower phase, whose volume is below 20 % of the feed solution in all runs; thus a high recovery of solutes could be expected in CP extraction.

The volume ratio increases with increasing HCl concentration. On adding NaCl or on raising settling temperature, however, the volume ratio decreased: the addition to 1.0 M or the raise to 80 °C gave the volume ratio as small as 0.07. This indicates that the larger the difference between CP and settling temperature, the smaller the volume ratio. Also,  $\text{Na}_2\text{SO}_4$  had much significant effect on both the CP and the volume ratio, though the data are not shown here. In all measurements of the volume ratio, the equilibria were attained within 40 min.

Figure 3 shows the relationship between CP and feed PONPE10 concentration, indicating that CP of the solution without Au(III) is substantially independent of the surfactant concentration, except at the extremely low concentration where the CP gives a little higher value. The presence of Au(III), however, caused a significant decrease of CP at lower surfactant concentrations. This implies that there is a strong interaction between PONPE10 and Au(III).

Figure 4 shows the effect of feed PONPE10 concentration on the volume ratio of the surfactant-rich phase after phase-separation. The volume ratio increases with the concentration as a result of an increasing amount of the surfactant in the whole system, whereby the addition of the salt and raising temperature also have the same effect as in Fig.2. When phase-separating 5 wt% PONPE10 solution (20 mL) in the absence of NaCl at 70 °C, we obtained the surfactant-rich phase of 5.7 mL, containing PONPE10 of *ca.* 1.0g, which is still occupied by water of *ca.* 80 % in weight, while the surfactant concentration of the bulk aqueous phase is only several-fold of the CMC, though the data are not shown here; thus, loss of the surfactant is not very serious in CP extraction. This also suggests an applicability of CP extraction to the separation of bioproducts as in aqueous two-phase partitioning by use of polyethylene glycol.

### Cloud Point Extraction of Au(III)

For a nonionic surfactant solution with multiple solutes, we can expect that each solute is distributed between the surfactant-rich and aqueous phases according to affinity to the surfactant during phase-separation. Here, we attempted the CP extraction of some precious metals from hydrochloric acid media.

The results for the CP extraction of Au(III) from 0.5 M HCl solutions at 70°C are shown in Figure 5, as a function of feed PONPE10 concentration, wherein the percent extraction,  $E$ , is based on the amount of the metal instead of its concentration because of a volumetric variation of the surfactant-rich phase under experimental conditions, and defined by

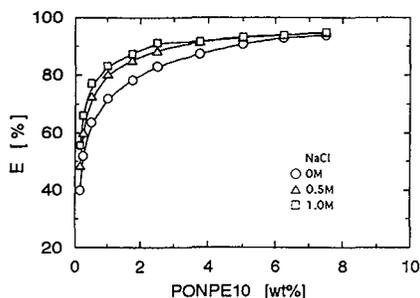


Fig. 5 Relationship between percent extraction of Au(III) and PONPE10 concentration at 70°C. [HCl]=0.5M, [Au(III)]= $5 \times 10^{-4}$ M

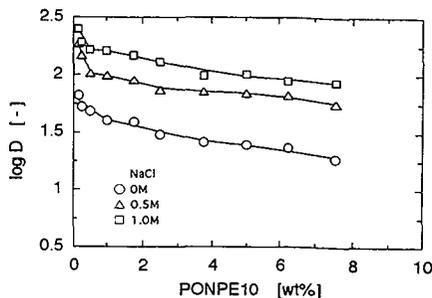


Fig. 6 Effect of PONPE10 concentration on distribution ratio of Au(III) at 70°C. [HCl]=0.5M, [Au(III)]= $5 \times 10^{-4}$ M

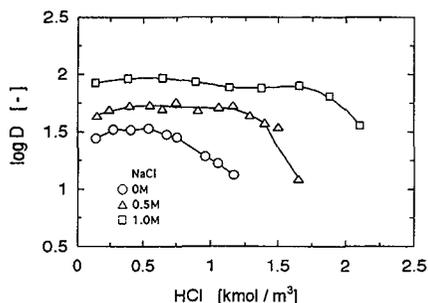


Fig. 7 Effect of HCl concentration on distribution ratio of Au(III) at 70°C. [PONPE10]=2.5wt%, [Au(III)]= $5 \times 10^{-4}$ M

$$E = 100 (M_S / (M_S + M_W)) \quad (1)$$

$$M_S = V_S C_S \quad (2)$$

$$M_W = V_W C_W \quad (3)$$

where  $M$  and  $C$  denote the amount and concentration of metal, respectively.

As Fig. 5 shows, the extraction efficiency of Au(III) increases with an increase in the PONPE10 concentration, and attained more than 90 % at a surfactant concentration above 5 wt%. Thus, CP extraction would provide an effective method for the recovery of Au(III). The addition of NaCl to the solution had no significant effect on the extraction efficiency. It seems that the extraction is

attributable to the formation of a complex between chloroauric acid,  $\text{HAuCl}_4$ , and ethylene oxide unit of the surfactant molecule.

**Figure 6** shows the effect of PONPE10 concentration on the distribution ratio of Au(III),  $D$ , defined as

$$D = C_S / C_W \quad (4)$$

The  $D$ -values are so large that a high concentration of Au(III) can be expected from the small equilibrium volume of the surfactant-rich phase, even when taking account of a little lowering with an increase in the PONPE10 concentration. Moreover, the distribution ratio increases with NaCl concentration, then reaching around 100 at 1.0 M of NaCl. Such a salt concentration dependence of the distribution ratio results from the decrease of volume of the surfactant-rich phase as can be seen in Fig. 4.

The effect of HCl concentration on the distribution ratio of Au(III) is shown in **Figure 7**. Although having a constant value depending on NaCl concentration, the ratio tends to decrease sharply above a critical concentration of HCl. Such decrease is caused from a deterioration of the phase-separation characteristics, viz., the CP rise, as described in the previous section. The addition of NaCl allows the CP extraction to give a positive effect on both of the distribution ratio of Au(III) and an extent of HCl concentration in the acid media. As Fig. 7 shows, the logarithmic ratio of *ca.* 2 is found over the HCl concentration range of 0.15-1.7 M for 1.0 M NaCl compared with *ca.* 1.5 for the HCl solution below 0.7 M in the absence of NaCl.

In a practical situation it is crucial to separate gold from strong acidic media. **Figure 8** shows the

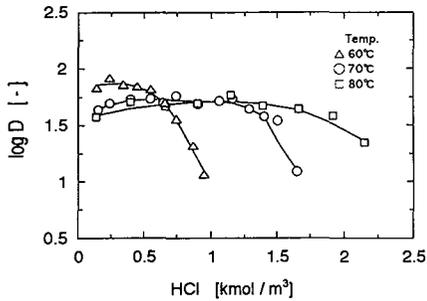


Fig. 8 Effect of settling temperature for phase-separation on distribution ratio of Au(III).  
 [PONPE10]=2.5wt%, [Au(III)]= $5 \times 10^{-4}$ M, [NaCl]=0.5M

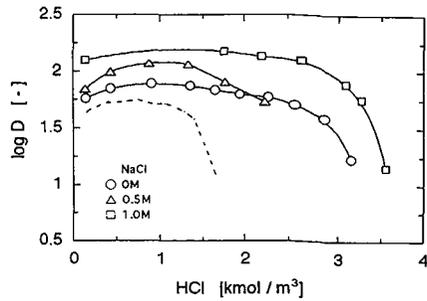


Fig. 9 Effect of HCl concentration on distribution ratio of Au(III) for mixed surfactant solution of PONPE10 and PONPE7.5 at 70°C.  
 [PONPE10]=[PONPE7.5]=1.25wt%, [Au(III)]= $5 \times 10^{-4}$ M

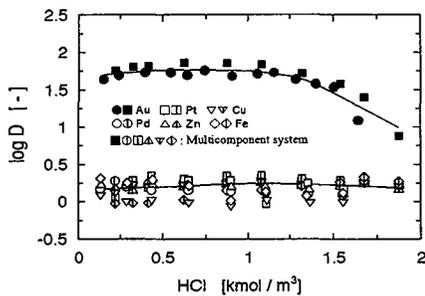


Fig. 10 Distribution ratio of heavy metals between surfactant-rich and aqueous phases at 70°C.  
 [PONPE10]=2.5wt%, [M]= $5 \times 10^{-4}$ M, [NaCl]=0.5M

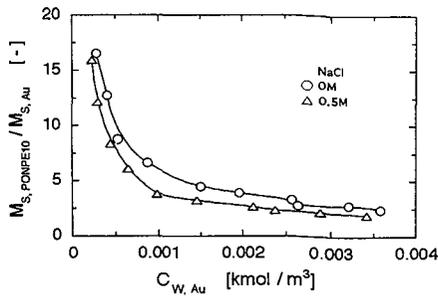


Fig. 11 Relationship between molar ratio of PONPE10 to Au(III) in surfactant-rich phase and aqueous Au(III) concentration at 70°C.  
 [HCl]=0.5M, [Au(III)]= $5 \times 10^{-3}$ M

effect of settling temperature of the PONPE10 solution on the distribution ratio of Au(III) for 0.5 M NaCl, as a function of HCl concentration. Raising temperature extends the HCl concentration to a higher region favorable to the separation: the extraction from 2 M HCl media can be realized at 80 °C of the settling temperature. In the region below the critical concentration of HCl, there is no significant difference in the distribution ratio at the three temperatures. Thus in the practical application we can determine the lowest temperature suitable to the separation in the acidity of aqueous media to be treated.

**Figure 9** shows the results of the CP extraction of Au (III) at 70 °C for the binary surfactant solution of PONPE10 and PONPE7.5, along with that for the single system of PONPE10 with 0.5 M NaCl (dashed line). Comparing with the single system, the binary system gives much larger distribution ratio even at higher HCl concentration because of a significant lowering of CP. The addition of NaCl has the same effects as in the single system shown in Fig. 7; thus the extraction from the HCl solution up to 3 M could be attained with 1.0 M NaCl.

Unfortunately an incomplete phase-separation occurs in the region of HCl concentration higher than 2 M with 0.5 M NaCl and around 1.0 M HCl with 1.0 M NaCl for the binary surfactant solution. This may be due to that the densities of both phases are very close and hence there is an ambivalent region of HCl concentration for the phase inversion. In fact the mixed surfactant system formed a coacervate as the lower phase below the transient concentration and *vice versa*. The additional problem in using the binary system is a rise in the solution viscosity with increasing PONPE7.5.

Further experiments were made on the applicability of CP extraction to the separation of several metals; the results for each single metal system are shown in **Figure 10** as a plot of  $D$  vs. HCl concentration. For HCl concentration below 1.5 M, no preferential extraction of palladium(II), platinum(IV), zinc(II), copper(II) and iron(III) is observed. The same tendency is also observed for the extraction in the multicomponent system with these metals, and only Au(III) is extracted from the acid media. This will lead to developing an effective separation method of Au(III) from the other metals in acidic media.

**Figure 11** shows the molar ratio of PONPE10 to Au(III) in the surfactant-rich phase,  $M_{S,PONPE10} / M_{S,Au}$ , as a function of Au(III) concentration of the aqueous feed,  $C_{W,Au}$ . As the Au(III) concentration increases, the molar ratio decreases and approaches an asymptotic value of 2, not much depending on the NaCl concentration. This stoichiometry implies that Au(III) is partitioned in the surfactant-rich phase in a form of chloroauric complex combined with two PONPE10 molecules.

Furthermore, the recovery of Au(III) from the loaded surfactant-rich phase was examined by use of dilute aqueous HCl solutions. The stripping efficiency was, however, very low because of the strong interaction between Au(III) and PONPE10. Consequently, we recommend a direct burning of the loaded surfactant-rich phase with a view to recovering Au(III) as a precious metal.

## CONCLUSION

The cloud point extraction of Au(III) from hydrochloric acid solutions was studied using a nonionic surfactant, PONPE10, and the following conclusions were obtained.

For aqueous PONPE10 solutions, CP rises with an increase in the HCl concentration, but can be lowered by adding NaCl into it or by use of the mixed surfactant with PONPE7.5. The phase-separation of the surfactant solution can be attained by allowing it to settle at a temperature above the CP; when the difference between the settling temperature and CP of the solution is larger, smaller quantity of the surfactant-rich phase is formed as a coacervate.

The cloud point extraction of Au(III) was successfully attained for dilute HCl solutions. For the extraction from acidic media, however, it is desirable to make the concentration of PONPE10 and of NaCl higher, to raise the settling temperature, or to use the mixed surfactant system. The present system provides a preferential extraction of Au(III) over some heavy metals without the exclusion though being low in the stripping efficiency from the surfactant-rich phase.

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# SYNERGIC EXTRACTION ENHANCEMENT OF LANTHANOID ELEMENTS WITH VERSATIC 10 AND 5,6-DIMETHYL-1,10-PHENANTHROLINE

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## ABSTRACT

Synergic extraction of lanthanoid elements, La(III), Nd(III), Tb(III), Tm(III) and Lu(III), with Versatic 10 (VA10; HA) and a neutral bidentate ligand, 5,6-dimethyl-1,10-phenanthroline (dmp; S) in benzene was investigated. The constants for the distribution of dmp and related equilibria including the association with VA10 were evaluated, and the equilibrium concentration of dmp was calculated by using these constants. The extraction of lanthanoids with VA10 was enhanced in the presence of dmp through the formation of a ternary complex,  $MA_3(HA)S$ . The separation factor among lanthanoids was also enhanced in the synergic extraction.

## INTRODUCTION

Extraction separation of rare earth elements has been performed by using various kinds of extractants. The improvement of separation factors among these elements in extraction is important for the mutual separation of these chemically similar elements. The synergic extraction of lanthanoids with an acidic extractant,  $\beta$ -diketone, and a neutral bidentate heterocyclic amine has been published in detail elsewhere by Nakamura, Imura, and Suzuki (1984,1985) and Nakamura and Suzuki(1986). Large extraction enhancement was observed and the separation factors among lanthanoids were further improved in some extraction systems, such as 2-thenoyltrifluoroacetone and 1,10-phenanthroline. The synergic enhancement is attributable to adduct formation in the organic phase and the improvement of separation seems to be due to the powerful donating ability of the bidentate ligand.

A bulky alkyl carboxylic acid, Versatic 10 (VA10), has been employed for extraction of rare earths in industrial fields. The extractabilities of rare earths with VA10, reported by Preston(1985) and Du Preez and Preston(1992), are rather low, compared with organophosphate extractants. Further, no synergic enhancement with a neutral ligand such as tributylphosphate was observed.

In the present paper, the synergic extraction of several lanthanoid elements was investigated by employing VA10 and a neutral bidentate ligand, 5,6-dimethyl-1,10-phenanthroline, and synergic enhancement in extraction separation was demonstrated.

## EXPERIMENTAL

### Materials

Radioisotopes,  $^{140}\text{La}$ ,  $^{147}\text{Nd}$ ,  $^{160}\text{Tb}$ ,  $^{170}\text{Tm}$ , and  $^{177}\text{Lu}$ , used as tracers, were produced by neutron irradiation of 0.1-5 mg of each oxide in a nuclear reactor (JRR-4) of the Japan Atomic Energy Research Institute at a thermal neutron flux of  $5.5 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$  for 6 h, and dissolved in  $\text{HNO}_3$ . Versatic 10 (VA10) was obtained from Shell Chemical Co., and its purity was checked to be 98.6% by potentiometric titration in ethanol with a sodium hydroxide solution. 5,6-Dimethyl-1,10-phenanthroline (dmp; Tokyo Kasei Kogyo Co., Ltd.) was used without further purification. Unless otherwise stated, reagents used were of guaranteed reagent grade.

### Distribution of Dmp

An aqueous solution ( $10 \text{ cm}^3$ ) containing 0.1 M ( $M = \text{mol dm}^{-3}$ )  $\text{NaNO}_3$  buffered with  $5 \times 10^{-3}$  M piperazine-1,4-bis(2-ethanesulfonic acid) (PIPES) and a benzene solution ( $10 \text{ cm}^3$ ) containing dmp alone and in the presence of VA10 were placed in a  $50 \text{ cm}^3$  extraction vial, and the vial was shaken for 30 min at  $25^\circ\text{C}$ . The dmp concentration in the organic phase was determined after stripping into

0.1 M HCl by the measurement of the absorbance of protonated dmp at 285 nm. On the other hand, dmp in the aqueous phase was extracted into fresh benzene at high pH around 12 adjusted with a NaOH solution, stripped into 0.1 M HCl, and determined by measuring the absorbance at 285 nm.

### Extraction of Lanthanoids(III)

An aqueous solution (4 cm<sup>3</sup>) containing 10<sup>-5</sup> M lanthanoid(III) labeled with its radioisotope was placed in a 30 cm<sup>3</sup> extraction vial. A benzene solution (4 cm<sup>3</sup>) containing VA10 and dmp was added, and the vial was shaken for 1 h at 25°C. After centrifugal phase separation, an aliquot was taken from each phase and the  $\gamma$ -activity was measured with a NaI(Tl) well-type scintillation detector. The pH of the aqueous phase was adjusted with 5 × 10<sup>-3</sup> M PIPES and NaOH solutions. Ionic strength was kept at 0.1 with sodium nitrate.

## RESULTS AND DISCUSSION

### Distribution Behavior of Dmp

Dmp distributes between aqueous and organic solutions, forming protonated species in the aqueous phase. The equilibrium concentration of dmp in the organic phase is important for an understanding of the extraction equilibria of metals, and hence distribution behavior of dmp was examined.

Direct determination of the dmp concentration in the organic phase was unfavorable after the distribution experiment, because the absorption peak at 273 nm of neutral dmp overlaps with strong absorption of benzene. The absorbance for protonated dmp was measured after stripping into 0.1 M HCl. On the other hand, the absorption peak of dmp in the aqueous phase overlapped with absorption of NO<sub>3</sub><sup>-</sup>. In order to avoid this interference, dmp was recovered into fresh benzene at high pH with a 98% yield, and then stripped into 0.1 M HCl to measure the absorbance at 285 nm. The molar absorption coefficient was calculated as 36400 at 285 nm.

Figure 1 shows the distribution ratio (D<sub>s</sub>) of dmp (S) as a function of pH. The value of log D<sub>s</sub> increased linearly with increasing pH and then became constant in the higher pH region. The distribution ratio of dmp can be expressed as,

$$D_{s,0} = \frac{[S]_{\text{org}}}{[S]_{\text{aq}} + [\text{HS}^+]_{\text{aq}}} = \frac{P_s}{1 + [\text{H}^+]_{\text{aq}} / K_{\text{HS}}} \quad (1)$$

where P<sub>s</sub> and K<sub>HS</sub> denote the partition coefficient of dmp and the acid dissociation constant of protonated dmp, respectively. The values of P<sub>s</sub> and K<sub>HS</sub> were evaluated by a least-squares fitting method based on Eq.(1) as 1.70 for log P<sub>s</sub> and -5.85 for log K<sub>HS</sub>. The solid line indicates the calculated value from Eq. (1), and is in good agreement with the experimental plots. The values of P<sub>s</sub> and K<sub>HS</sub> for the 5,6-dimethyl derivative of 1,10-phenanthroline obtained in this work are very close to the corresponding values for the 2,9-dimethyl derivative, i. e., log P<sub>s</sub> = 1.79 and log K<sub>HS</sub> = -5.81. Two methyl groups contribute to a similar extent of the enhancement of partition and basicity irrespective of their bonding positions, compared with the constants, log P<sub>s</sub> = 0.78 and log K<sub>HS</sub> = -5.04 for 1,10-phenanthroline.

The variation in log D<sub>s</sub> in the presence of 0.1 M VA10 is also illustrated in Fig. 1. The distribution ratio of dmp was enhanced by the addition of VA10; this may be attributed to association of dmp and VA10 (HA) in the organic phase,



where  $\beta_{m,n}$  denotes the association constant. Here, VA10 is expressed in the dimer form, (HA)<sub>2</sub>, because a dimeric species seems to be dominant in nonpolar diluents.

The distribution ratio of dmp in the presence of VA10 is written as

$$D_s = \frac{[S]_{\text{org}} + \sum_{m=1}^m \sum_{n=1}^n (n[(\text{HA})_m \text{S}_n]_{\text{org}})}{[S]_{\text{aq}} + [\text{HS}^+]_{\text{aq}}} = \frac{P_s \left( 1 + \sum_{m=1}^m \sum_{n=1}^n (n\beta_{m,n} [(\text{HA})_2]_{\text{org}}^{m/2} [\text{S}]_{\text{org}}^{n-1}) \right)}{1 + [\text{H}^+]_{\text{aq}} / K_{\text{HS}}} \quad (3)$$

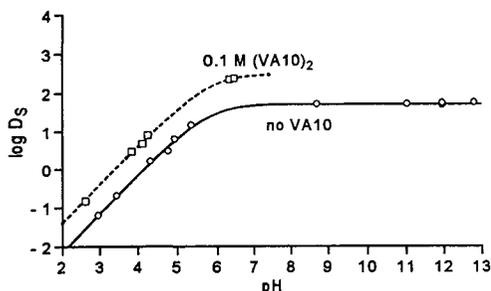


Figure 1. The distribution ratio of dmp in benzene.

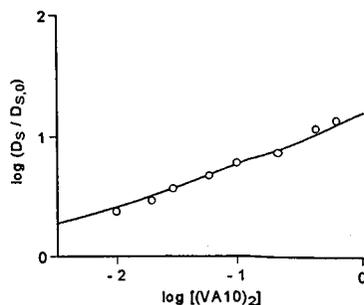


Figure 2. The increment of the distribution ratio of dmp with VA10.

From Eqs. (1) and (3), we obtain the following equation.

$$\frac{D_s}{D_{s,0}} = 1 + \sum_{m=1}^m \sum_{n=1}^n (n\beta_{m,n} [(HA)_2]_{org}^{m/2} [S]_{org}^{n-1}) \quad (4)$$

Since the  $D_s/D_{s,0}$  values were found to be independent of the dmp concentration, the value of  $n$  was approximated to be unity. As Fig. 2 shows the values of  $D_s/D_{s,0}$  gradually increased with increasing VA10 concentration. In the higher concentration of VA10, the slope of the plots was asymptotic to 0.5, and then Eq. (4) can be simplified by employing  $m = 1$  and  $n = 1$ .

$$\frac{D_s}{D_{s,0}} = 1 + \beta_{1,1} [(HA)_2]_{org}^{1/2} \quad (5)$$

This implies that dmp in the organic phase is present as the free form and the associated one with VA10 monomer, and the association reaction can be expressed by



The solid line in Fig. 2 indicates the calculated value from Eq. (5) using 1.18 for  $\log \beta_{1,1}$ , and is in good agreement with the experimental plot.

The equilibrium concentration of free dmp in the organic phase is thus related to the initial dmp concentration,  $[S]_{init}$ , as:

$$[S]_{org} = \frac{[S]_{init}}{1 + \beta_{1,1} [(HA)_2]_{org}^{1/2} + (1 + [H^+]_{aq} / K_{HS}) / P_s} \quad (7)$$

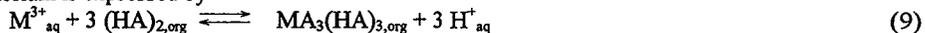
where  $[(HA)_2]_{org}$  is related to the initial VA10 concentration,  $[(HA)_2]_{init}$ , as:

$$[(HA)_2]_{init} = [(HA)_2]_{org} + 1/2 \cdot \beta_{1,1} [(HA)_2]_{org}^{1/2} \cdot [S]_{org} \quad (8)$$

The equilibrium concentration of S and  $(HA)_2$  can be numerically evaluated based on Eqs.(7) and (8).

### Synergic Extraction of Tb(III)

Extraction of Tb(III) with 0.1 M  $(VA10)_2$  was investigated in the absence and presence of dmp in benzene. As Fig. 3 shows, plots of  $\log D$  vs. pH gave individual straight lines with slopes close to 3, and the addition of dmp caused large synergic enhancement. The experimental data without PIPES-buffer followed the same line as indicated by closed symbols, and then no effect of PIPES on the extraction behavior of Tb(III) was verified. Extraction of Tb(III) with dmp alone was also verified to be negligibly small. Figure 4 shows the effect of the extractant concentration on the extraction of Tb(III). The slope of a plot for VA10 alone was about 3, and then extraction equilibrium is expressed by



and the distribution ratio ( $D_0$ ) is written as

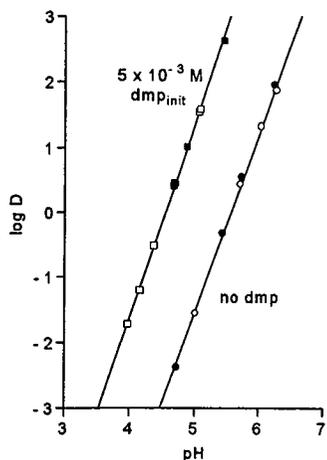


Figure 3. The extraction of Tb(III) with 0.1 M (VA10)<sub>2</sub> in benzene. Open: 5 × 10<sup>-3</sup> M PIPES; Closed: no PIPES.

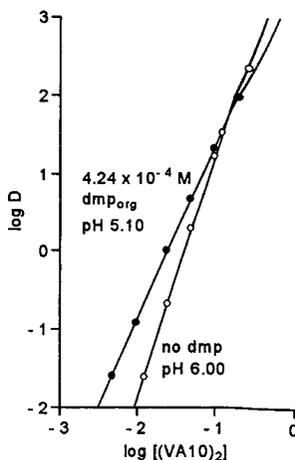


Figure 4. The effect of the VA10 concentration on the Tb(III) extraction.

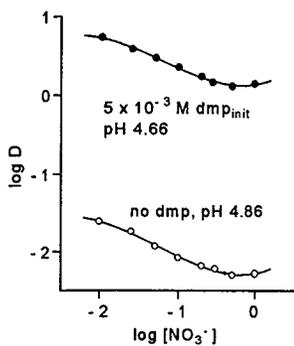


Figure 5. The effect of the NO<sub>3</sub><sup>-</sup> concentration on the Tb(III) extraction.

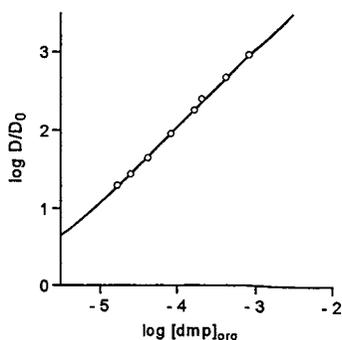


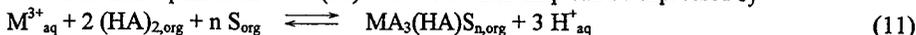
Figure 6. The synergic enhancement of Tb(III) in the variation of the dmp concentration.

$$D_0 = \frac{[\text{MA}_3(\text{HA})_3]_{\text{org}}}{[\text{M}^{3+}]_{\text{aq}}} = K_{\text{ex}} \cdot \frac{[(\text{HA})_2]_{\text{org}}^3}{[\text{H}^+]_{\text{aq}}^3} \quad (10)$$

where  $K_{\text{ex}}$  denotes the extraction constant.

In the synergic extraction, the equilibrium concentration of dmp in the organic phase was kept at constant by varying the initial concentration of dmp, taking into account the association of dmp and VA10. The slope of a plot in the presence of dmp was about 2; this implies that two molecules of (HA)<sub>2</sub> combine to Tb(III). Figure 5 shows the effect of the concentration of NO<sub>3</sub><sup>-</sup>. The distribution ratio of Tb(III) decreased gradually with increasing [NO<sub>3</sub><sup>-</sup>] in a similar manner irrespective of dmp, probably due to the formation of Tb-NO<sub>3</sub> complexes in the aqueous phase. This finding implies that NO<sub>3</sub><sup>-</sup> ion is not involved in extracted species in the presence of dmp.

The extraction equilibrium of Tb(III) with VA10 and dmp can be expressed by



and the distribution ratio (D) is written as

$$D = \frac{[\text{MA}_3(\text{HA})_3]_{\text{org}} + \sum_{n=1}^n [\text{MA}_3(\text{HA})\text{S}_n]_{\text{org}}}{[\text{M}^{3+}]_{\text{aq}}} = \frac{K_{\text{ex}}[(\text{HA})_2]_{\text{org}}^3 \left( 1 + \sum_{n=1}^n \frac{K_{\text{exs},n}[\text{S}]_{\text{org}}^n}{K_{\text{ex}}[(\text{HA})_2]_{\text{org}}} \right)}{[\text{H}^+]_{\text{aq}}^3} \quad (12)$$

where  $K_{\text{exs},n}$  is the synergic extraction constant. From Eqs. (10) and (12), we obtain the following equation.

$$\frac{D}{D_0} = 1 + \sum_{n=1}^n \frac{K_{\text{exs},n}[\text{S}]_{\text{org}}^n}{K_{\text{ex}}[(\text{HA})_2]_{\text{org}}} \quad (13)$$

A logarithmic plot of  $D/D_0$  against the concentration of dmp is shown in Fig. 6. The slope of the plot in the higher concentration region of dmp was found to be unity. The solid line calculated by employing  $n = 1$  agrees with the experimental plots, suggesting the extracted species of  $\text{MA}_2(\text{HA})\text{S}$  in the synergic extraction.

### Extraction of Lanthanoid elements

The extraction behavior of other lanthanoids, La(III), Nd(III), Tm(III) and Lu(III), was also investigated. Figure 7 shows the extraction by VA10 and its mixture with dmp as a function of pH. The synergic enhancement was also brought about in the presence of dmp for every lanthanoid. Figure 8 illustrates the distribution ratios of the lightest lanthanoid, La(III), and the heaviest one, Lu(III), as a function of the VA10 concentration. The slopes of plots for VA10 alone were about 3 for both lanthanoids, and those in the presence of dmp were about 2, as well as the findings for Tb(III) presented in Fig. 4. Logarithmic plots of  $D/D_0$  against the dmp concentration are shown in Fig. 9, and the slopes of these plots were close to unity. Thus, the synergic extraction is attributed to the formation of the ternary complex,  $\text{MA}_2(\text{HA})\text{S}$ , for each lanthanoid.

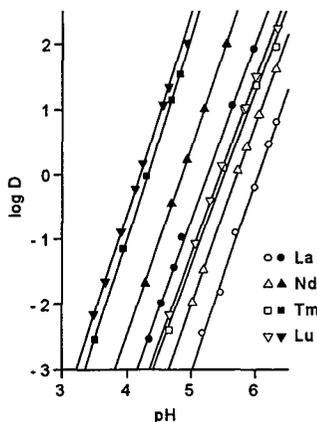


Figure 7. The extraction of La(III), Nd(III), Tm(III) and Lu(III) with 0.1 M  $(\text{VA10})_2$ . Open: no dmp; closed:  $5 \times 10^{-3}$  M  $\text{dmp}_{\text{init.}}$ .

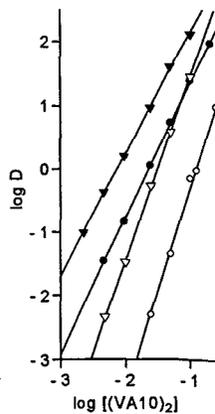


Figure 8. The effect of the VA10 concentration. La(III):  $\circ$  no dmp, pH 6.00;  $\bullet$   $4.31 \times 10^{-4}$  M  $\text{dmp}_{\text{org}}$ , pH 5.90. Lu(III):  $\nabla$  no dmp, pH 6.00;  $\blacktriangledown$   $4.22 \times 10^{-4}$  M  $\text{dmp}_{\text{org}}$ , pH 5.00.

### Trend of Extractability for Lanthanoids

In order to compare the extractability of a series of lanthanoids, the distribution ratios at pH 5 in the absence and the presence of dmp are illustrated in Fig. 10. The difference in the distribution ratios among lanthanoids was enhanced by the addition of dmp. The values of  $K_{\text{ex}}$  and  $K_{\text{exs},1}$ , and the separation factors,  $\alpha_{\text{ex}}$  and  $\alpha_{\text{exs},1}$ , defined by the ratio of the extraction constants between two

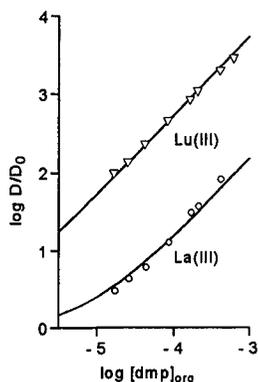


Figure 9. The synergic enhancement of La(III) and Lu(III) in the variation of the dmp concentration.

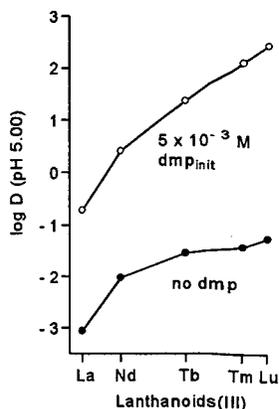


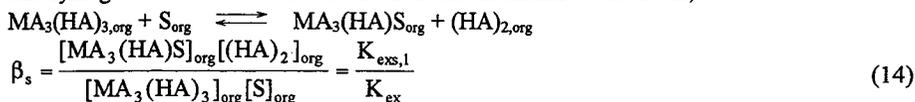
Figure 10. Extractability of lanthanoids in the absence and the presence of dmp.

**TABLE 1**  
Equilibrium constants in the extraction of lanthanoids

Lanthanoids	log $K_{ex}$	$\alpha_{ex}$	log $K_{exs,1}$	$\alpha_{exs,1}$	log $\beta_s$
La	-15.16		-10.72		4.44
		9.33		17.0	
Nd	-14.19		-9.49		4.70
		3.09		9.33	
Tb	-13.70		-8.52		5.18
		1.28		4.79	
Tm	-13.59		-7.84		5.75
		1.62		2.34	
Lu	-13.38		-7.47		5.91

lanthanoids are listed in Table 1. The separation factors in the synergic extraction were larger than those with VA10 alone.

The synergic enhancement was attributed to the substitution reaction as;



The substitution reaction constant,  $\beta_s$ , are also listed in Table 1. The values of  $\beta_s$  increased with increasing atomic number of lanthanoids, and this trend led to the improvement of the separation of lanthanoids.

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## SEPARATION OF RARE METALS BY PHOTOREDUCTIVE STRIPPING IN LIQUID-LIQUID EXTRACTION PROCESSES

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### ABSTRACT

The separation and purification of rare metals, such as Eu and V, by photoreductive stripping in liquid-liquid extraction processes has been studied. The extracted Eu in the organic solution (bis(2-ethylhexyl)phosphoric acid (D2EHPA) diluted with xylene or cyclohexane) was photoreduced from trivalent state to divalent form by using low-pressure or high-pressure mercury lamp in the presence of radical scavenger such as isopropyl formate, formic acid and 2-propanol. The reduced Eu was stripped into the aqueous phase selectively and precipitated as  $\text{EuSO}_4$ . The recovery of Eu was 93% and the purity of Eu in the  $\text{EuSO}_4$  precipitate was 99%, while the stripping of Sm and Gd was less than 1%. In the case of the separation of V from Mo, pentavalent V extracted by tri-*n*-octylmethylammonium chloride (TOMAC) was reduced to tetravalent form by using halogen lamp, and thus the V was stripped selectively, leaving Mo in the organic phase. The recovery of V reached 96% and the separation factor of about 300 was obtained. The effects of diluent, light source and scavenger on the recovery and separation of the metals were studied, to develop the separation process of high performance.

### INTRODUCTION

The solvent extraction method is widely used for the separation of the rare metals on the industrial scale. The traditional solvent extraction process consists of three stages: extraction, scrubbing, and stripping. Extractive separation is effected, in the majority of cases, on the basis of a difference in distribution ratio between the metals in the feed solution. In the rare-earth series, however, the chemical properties of adjacent members are very similar, making it very difficult to separate and purify the individual elements. Selective stripping of the target metal is one of the effective methods for the separation of the rare metals. Trivalent Eu ion is known to be more reducible to the divalent form than the other rare-earth elements. Peppard et al. (1962) reported that the distribution ratio of  $\text{Eu}^{2+}$  was much smaller than that of  $\text{Eu}^{3+}$ , and was stripped effectively into the aqueous phase when using bis(2-ethylhexyl)phosphoric acid (D2EHPA) as extractant. The trivalent Eu can also be reduced electrochemically by using a titanium plate electrode and separated from Sm and Gd (Hirai and Komasaawa, 1992). As for V, the chemical- and electro-reductive stripping for separation of V and Mo was found to be feasible (Hirai and Komasaawa, 1990, 1993a)

In previous works, the photoreductive stripping of Eu from D2EHPA/xylene solution containing Eu, Sm, and Gd (Hirai et al., 1993b), and the photoreductive stripping of V from tri-*n*-octylmethylammonium chloride (TOMAC)/benzene solution containing V and Mo (Hirai et al., 1993c) were studied, using isopropyl formate as a radical scavenger for removing OH radical. In this work, the more selective photoreductive stripping process of Eu and V were studied. The effects of UV and visible light wavelength, organic solvent (diluent), and radical scavenger on the separation, recovery, and purity of Eu and V were studied. The reusability of the organic phase after photoreductive stripping was also examined.

### EXPERIMENTAL

D2EHPA was supplied by Daihachi Chemical Ind. Co., Ltd. and was diluted with xylene, cyclohexane,

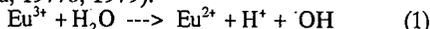
or hexane. TOMAC was supplied by Koci Kagaku Kogyo Co., Ltd. The extraction of Sm, Eu and Gd was carried out by shaking equal volumes of aqueous solution containing ca. 5 mM  $\text{SmCl}_3$ ,  $\text{EuCl}_3$ , and  $\text{GdCl}_3$  at a pH value of 6.8 with the organic solution (0.2 M D2EHPA) at 298 K ( $M = \text{mol/L}$ ). Extraction efficiencies were about 90% for the xylene system and about 99% for the cyclohexane and hexane systems, and the concentration of each metal in the resulting organic solution was about 4.5 and 5 mM respectively for the above systems. Extraction of V and Mo was carried out by shaking equal volumes of the 0.015 M TOMAC/benzene and pH 7 aqueous solution containing ca. 0.01 M  $\text{NaVO}_3$ , 0.01 M  $\text{Na}_2\text{MoO}_4$  and 0.07 M NaCl. The extraction percentages of V and Mo were greater than 98% and less than 8%, respectively, and the resulting organic solution contained ca. 0.01 M V and ca. 0.9 mM Mo.

Photoreductive stripping was carried out in a beaker-type glass bottle (32 mm in diameter). A 20 W low-pressure mercury lamp (LPML) was used as a light source, which had emission peaks of 184.9 and 253.7 nm. When only the 253.7 nm line was used, the 184.9 nm line was cut off by glass filter. The tip of the LPML was immersed in the solution and the irradiation area was about  $2.8 \times 10^{-3}$  and  $3.1 \times 10^{-3} \text{ m}^2$  for the cases without filter and with filter, respectively. A 300 W high-pressure mercury lamp (HPML) having emission peaks of about 310 and 365 nm and 500 W halogen lamp were also used, and irradiated from outside the glass bottle. Since the glass bottle absorbs short-wavelength light, wavelengths above 300 nm are thus utilized for photoreduction. The irradiated area was about  $1.5 \times 10^{-3} \text{ m}^2$ . The aqueous solution (15 mL, 1 M  $(\text{NH}_4)_2\text{SO}_4$ , pH 5 for the case of Eu and 0.1M HCl-NaCl for the case of V), the metal-loaded organic solution (15 mL), and scavenger (isopropyl formate, formic acid, or 2-propanol) were agitated and irradiated. The precipitate ( $\text{EuSO}_4$ ) was separated by centrifuge. The concentration of the elements in the aqueous solution were determined by the use of an inductively coupled argon plasma emission spectrophotometer.

## RESULTS AND DISCUSSION

### Photoreductive Stripping of Eu

The trivalent Eu is reduced photochemically by electron transfer from a binding ligand such as  $\text{H}_2\text{O}$  in its charge-transfer (C-T) band (Donohue, 1977a, 1977b, 1979).



The radical ( $\cdot\text{OH}$ ) must be scavenged immediately by radical scavenger to avoid a reverse reaction. The absorption spectra of 0.2 M D2EHPA when diluted by the three organic solvents are shown in figure 1a. Cyclohexane and hexane solutions show rather weak absorption in the UV region in comparison with the xylene solution, and thus, LPML can be utilized in these diluent systems. The absorption spectra of Eu in cyclohexane and hexane show absorption peaks around 210 nm as shown in figure 1b. A weak absorption around 300 nm is also seen. These findings indicate that LPML (184.9 and 253.7 nm lines) and HPML can be utilized for photoreduction of Eu in the organic phase.

The time course for the precipitation of  $\text{EuSO}_4$  and the stripping yields of Sm and Gd in the cyclohexane system is shown in figure 2, for LPML used as a light source. In this figure, the feed amounts of the elements in the organic phase are set at the base level of 100% and the pH values

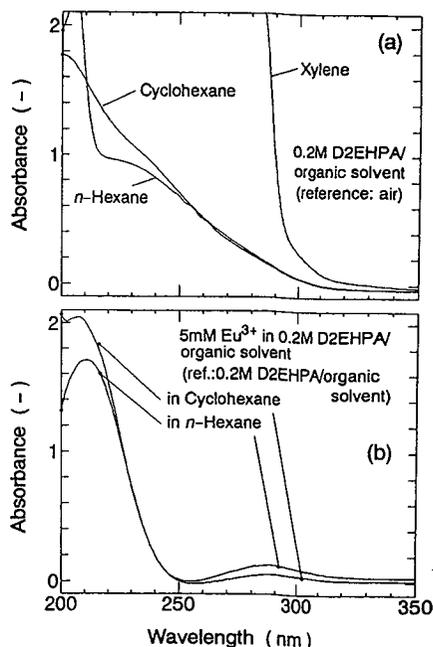


Figure 1. Absorption spectra of (a) 0.2 M D2EHPA/organic solvents and (b) 5 mM  $\text{Eu}^{3+}$  in 0.2 M D2EHPA/organic solvent systems.

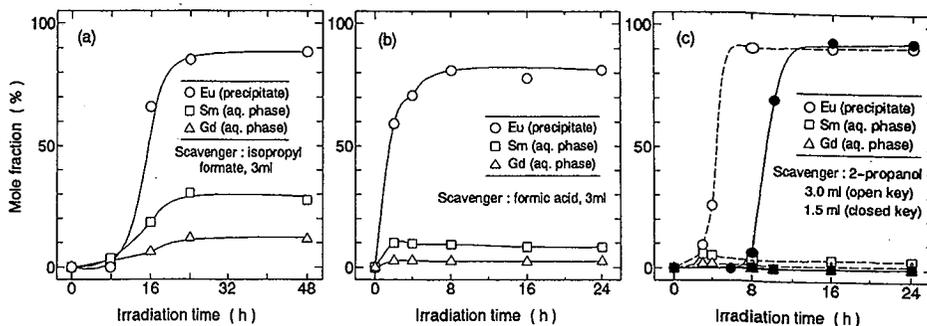


Figure 2. Effect of irradiation time on precipitation of  $\text{EuSO}_4$  and stripping yield of Sm and Gd in cyclohexane system using LPML (184.9 + 253.7 nm lines).

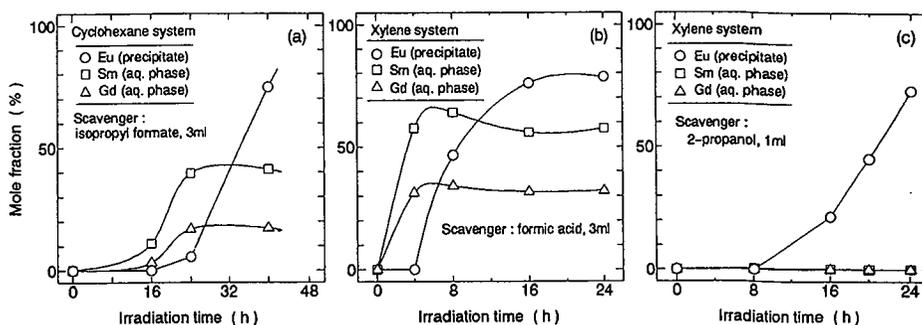


Figure 3. Effect of irradiation time on precipitation of  $\text{EuSO}_4$  and stripping yield of Sm and Gd in the cases using HPML ( $\lambda > 300$  nm lines).

show the final pH of aqueous phase. Eu ions extracted into the organic phase were stripped selectively and were precipitated as  $\text{EuSO}_4$ . The photoreductive stripping of Eu was also feasible in the hexane system when LPML and isopropyl formate were used (Hirai et al., 1993d). These results differ from those obtained for the xylene diluent system, where the photoreduction of Eu hardly occurred in the two-phase system when a glass bottle and LPML were used (Hirai et al., 1993b). A comparison of these results shows that  $\text{Eu}^{3+}$  is photoreduced mainly in the organic phase in the cyclohexane and hexane systems and not in the aqueous phase. HPML was found to be effective for the photoreductive stripping of Eu in both cyclohexane and xylene systems, as shown in figure 3.

The diluents used in this study are characterized from the viewpoints of light absorption, water content, and dielectric constant. The photoreduction of  $\text{Eu}^{3+}$  in the xylene phase with LPML was difficult, except for the case when formic acid was used as a scavenger. This is due to the large absorption of UV light by xylene, as shown in figure 1a. When cyclohexane was employed, both LPML and HPML were utilized for the photoreduction.

The water content of the metal-loaded organic phase was 0.031 and 0.017 M for the xylene and cyclohexane systems, respectively. Since water is necessary for the photoreduction of  $\text{Eu}^{3+}$  as shown by equation 1, the xylene system may be more practical. The greater water content also allows the water-soluble scavengers (formic acid and 2-propanol) to approach the  $\text{Eu}^{3+}$  ion and the photochemical reaction site in the organic phase.

The dielectric constants of xylene, cyclohexane, and hexane are 2.420, 2.052, and 1.874, respectively, and the extraction ability for the metals increases with a decrease in the dielectric constant. The

high extraction ability makes the stripping of Sm and Gd low and, therefore, the purity of Eu in the precipitate high. Thus, the cyclohexane and hexane systems are more practical for selective stripping of Eu.

The effect of the amount of the scavenger on the precipitation of  $\text{EuSO}_4$ , on the stripping yield of Sm and Gd, and on the aqueous phase pH is shown in figure 4 for the cyclohexane system. The amount of scavenger dissolved in the organic phase is also shown. The purity of Eu in the precipitate is shown in Table 1.

There are some disadvantages for using isopropyl formate. About half the amount of isopropyl formate added was distributed into the organic phase, as shown in figure 4a. This increases the dielectric constant of the solution and decreases the extraction ability of the organic phase. The addition of isopropyl formate also decreases the pH of the aqueous phase by hydrolysis of the ester. These results increase the stripping of Sm and Gd and therefore decrease the purity of the precipitate. Furthermore, the addition of the bulky molecule of isopropyl formate to the extract complex may be rather difficult, resulting in a longer induction period prior to the precipitation (figure 1a).

Table 1. Purity of Eu (%) in  $\text{EuSO}_4$  precipitate<sup>a</sup>

scavenger	amount of scavenger (mL)				
	1.5	2.0	3.0	4.0	5.0
isopropyl formate			94.8	94.6	93.5
formic acid	95.7	95.5	94.9	93.0	93.1
2-propanol	99.1	98.4	96.7	95.4	95.0

<sup>a</sup> Photoreductive stripping was done in the cyclohexane system with 24 h irradiation by LPML.

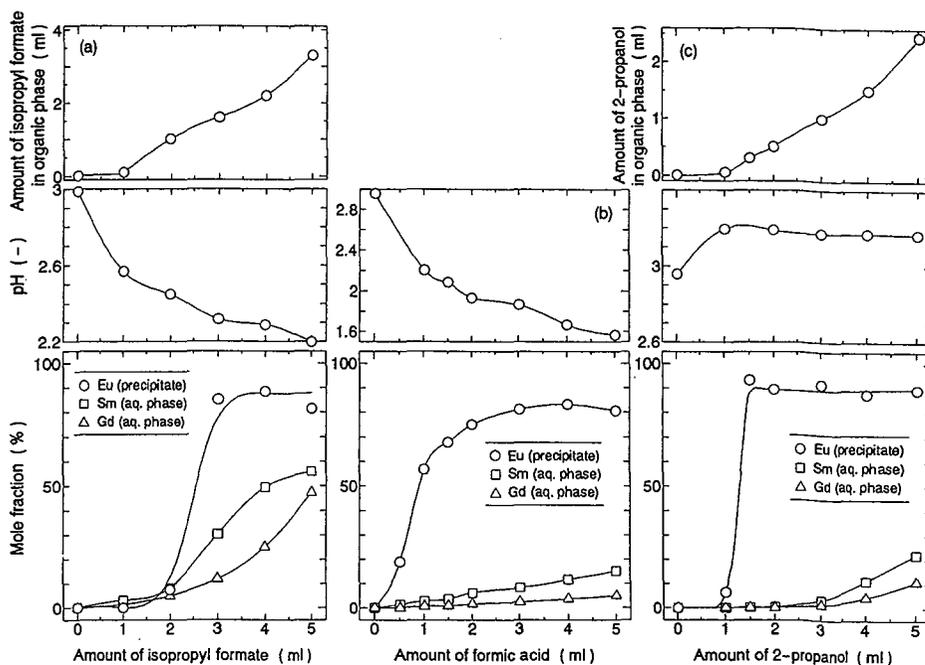


Figure 4. Effect of amount of (a) isopropyl formate, (b) formic acid, and (c) 2-propanol on precipitation of  $\text{EuSO}_4$ , stripping yield of Sm and Gd, aqueous phase pH, and amount of scavenger in organic phase in cyclohexane system. Irradiation: 24 h by LPML (184.9 + 253.7 nm lines).

Formic acid is water-soluble and is not solubilized in the organic phase. The stripping yield of Sm and Gd is, however, increased by the decrease in the pH value. The photoreductive stripping of Eu occurred more rapidly with formic acid. This is because the COOH formed by the photodecomposition of formic acid (Allmand and Reeve, 1926) acts as a reducing agent.

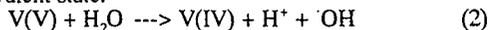
With 2-propanol, the pH of the aqueous phase was maintained greater than a value of 3. The stripping of Sm and Gd was, however, enhanced by the addition of 2-propanol as shown in figure 4c. The addition of 2-propanol increases the dielectric constant of the organic diluent, resulting in the decrease in the extraction ability, since 2-propanol has solubility in the organic phase. Thus, decreasing the amount of 2-propanol added to the system from 3 to 1.5 mL brought about a decrease in the rate of photoreduction, together with a low stripping percentage of Sm and Gd (less than 1%) and a high purity of the precipitate (about 99%, Table 1) as shown by the filled symbols in figure 1c. 2-Propanol is thus the most appropriate scavenger in this photoreductive stripping system.

In the present experiment, a rather long time was needed for the photoreductive stripping. A better result is expected through improvement of the photoreduction cell by means of a larger irradiation area and by a more powerful light to obtain greater irradiation intensity.

The reusability of the organic phase after photoreductive stripping was examined. Xylene became light yellow by irradiation using LPML, whereas cyclohexane changed only slightly in color, indicating that xylene is not a practical diluent. When formic acid was used as a scavenger, the rate of precipitation was low and the precipitate was found to be at the interface between the organic and aqueous phases at the second photoreductive stripping stage. Thus, the system of cyclohexane and isopropyl formate or 2-propanol was examined for repeated extraction and photoreductive stripping. The typical result obtained in the case of 2-propanol is shown in Table 2. The performance of the second and third extractions and subsequent photoreductive stripping was quite similar to that of the first extraction-stripping, indicating that the organic phase can be reused for repeated use.

### Photoreductive Stripping of V

Vanadium is photoreduced from pentavalent to tetravalent state.



Since the distribution ratio of the reduced V is much smaller than that of pentavalent V, it is stripped into the aqueous phase. Figure 5 shows the stripping yield of vanadium and molybdenum by photo-irradiation using halogen lamp. 2-Propanol was added as a radical scavenger. Vanadium was stripped selectively, leaving Mo in the organic phase. The recovery of V reached 96%. The separation factor was calculated by dividing

Table 2. Reusability of organic phase.  
Scavenger, 2-propanol (1.5 mL); Stripping, 16 h  
Irradiation by LPML (184.9 + 253.7 nm Lines)<sup>a</sup>

	extraction (%)			stripping (precipitation)	
	Sm	Eu	Gd	Eu (%)	purity (%)
first	99.0	99.5	99.7	93.7	98.8
second	98.9	99.5	99.7	93.8	99.0
third	98.9	99.5	99.7	92.5	99.0

<sup>a</sup> Organic phase after photoreductive stripping was washed with 6 M HCl prior to second (or third) extraction.

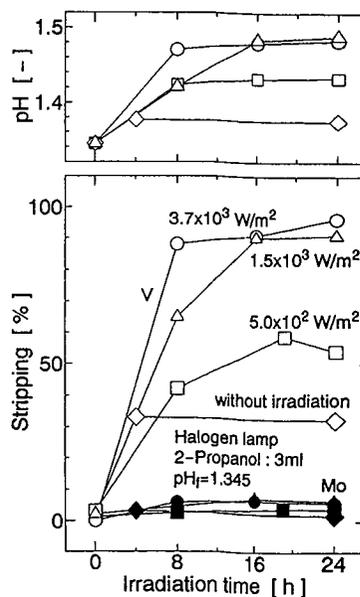


Figure 5. Effect of irradiation time on stripping of V and Mo using halogen lamp and 2-propanol.

the molar ratio of V and Mo in the stripping solution by that in the feed solution, and was about 300. The stripping rate was affected by the irradiation intensity of the light. This indicates the photoreduction of V shown by equation 2 was rate-controlling step. In the case with formic acid, stripping occurred more rapidly, since the acid could reduce the pentavalent V chemically. Furthermore, COOH radical formed by photodecomposition of formic acid by UV-irradiation (Allmand and Reeve, 1926) reduced V(V) when LPML was employed, which enhanced the stripping rate.

The reusability of the organic solution after the photoreductive stripping was examined. Figure 6 shows the metal concentration in the organic phase during the repeated extraction-photoreductive stripping process. The organic phase was washed with 6 M HCl to remove the remaining metals prior to the second extraction. The organic phase showed sufficient loading and stripping capacities in the repeated processes.

### CONCLUSION

The photoreductive stripping of Eu and V from organic phase was investigated with the following results.

- 1) Eu was photoreduced in the organic phase and stripped selectively into the aqueous phase to precipitate as  $\text{EuSO}_4$  by using a low-pressure mercury lamp (LPML) or high-pressure mercury lamp (HPML) in the presence of a radical scavenger. The photoreduction occurred more rapidly when LPML was employed. Cyclohexane was found to be a more suitable diluent than xylene, because of its weak absorption in the UV region and low dielectric constant. These properties make the photoreduction of Eu in the organic phase relatively easy and the selective stripping of Eu feasible, since Sm and Gd are retained in the organic phase. The use of LPML and 2-propanol in the cyclohexane system was found to be most suitable. In this case, the recovery of Eu as  $\text{EuSO}_4$  was greater than 93%, while the stripping yield of Sm and Gd was less than 1%. The purity of Eu in the precipitate was about 99%.
- 2) V was photoreduced in the organic phase and stripped selectively into the aqueous phase by using a halogen lamp in the presence of 2-propanol as a radical scavenger. The recovery of V and the separation factor were 96% and about 300, respectively. The stripping rate was found to be influenced by the irradiation intensity of lights.
- 3) The organic solutions after the photoreductive stripping was successfully reusable for repeated extraction.

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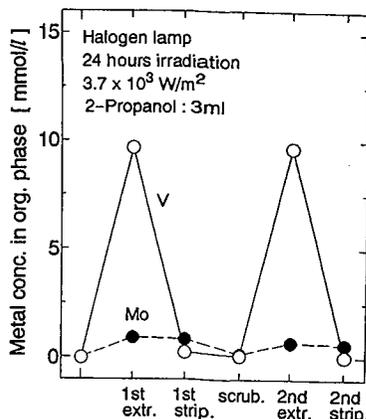


Figure 6. Metal concentration in organic phase during repeated extraction-photoreductive stripping processes.



## SOLVENT EXTRACTION OF RHODIUM WITH CYCLOHEXANOL FROM HCl/SnCl<sub>2</sub> MEDIA

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### ABSTRACT

Solvent extraction of rhodium(III), ruthenium(III) and iridium(III) with cyclohexanol from HCl/SnCl<sub>2</sub> media was investigated in this paper. Tin(II) chloride increases the extraction of rhodium much more than that of ruthenium or iridium. Under the conditions ([HCl]=4.0 M, [SnCl<sub>2</sub>]=0.20 M, [cyclohexanol]=5.0 M, phase contact time 1 min and phase ratio 1:1), Rh is extracted 95.5%, Ru 23.1% and Ir 3.6% respectively. The formation of rhodium-tin(II) chloride complexes may be confirmed by UV-spectra in both aqueous and organic solutions.

Keywords: cyclohexanol, rhodium, ruthenium, iridium, tin chloride.

### INTRODUCTION

It has been long known that the interaction of tin(II) chloride with some of platinum group metals gives coloured species which have been utilized analytically (Elizarova, 1973; Al-Bazi, 1984; Milner, 1955; Sandell, 1944; Young, 1964; Yan, 1987), though the exact nature of some species present in solution was uncertain until recently (Kostanski, 1991; Koch, 1983). Treatment of acidic solutions containing rhodium(III) chloride with tin(II) chloride leads to an intense red-orange colour depending on Sn(II):Rh(III) ratio as well as concentration of hydrochloric acid in the solution. It is fairly certain that the SnCl<sub>3</sub><sup>-</sup> binds with rhodium forming a variety of labile complexes [RhCl<sub>6-n</sub>(SnCl<sub>3</sub>)<sub>n</sub>] (n=1-6) (Garralda, 1981; Crosby, 1971; Uson, 1980; Davies, 1963) which can be quantitatively extracted from acidic solution. In general, tin(II) chloride is reported to exert a favorable influence on the rate and efficiency of rhodium extraction from aqueous acidic solution due to a labilizing effect of SnCl<sub>3</sub><sup>-</sup> which acts both as ligand and as reductant where the reduction of Rh(III) to Rh(I) is accompanied by the oxidation of Sn(II) to Sn(IV) (Koch, 1983; Iwasaki, 1984). The extraction of rhodium-tin complex is easier than that of its aquochloro complex, even though there are some reports on the extraction of rhodium as compounds of its hydrated cation (Ali Khan, 1967; Wang, 1986; Yan, 1994), since they are non-aquated and therefore more lipophilic than hydrated cation complexes (Koch, 1993; Benguerel, 1993).

Benguerel and Demopoulos have recently reported on extraction of the rhodium-tin(II) chloride complexes with Kelex 100. With only some alcohols as extractant this paper presents the results of our studies, since 1990, of the use of tin(II) chloride in the extraction of rhodium, ruthenium and iridium.

### EXPERIMENTAL

Cyclohexanol supplied by Merck, Germany, was diluted to 5.0 M in toluene. Tin(II) chloride was from Schuchardt, Germany. RhCl<sub>3</sub> was from Fluka, Switzerland, IrCl<sub>3</sub> from Alfa Inorganics Ventron, Mass., USA, and ruthenium powder (200 mesh) from Aldrich Chem. Co Wi, USA. Tracers of <sup>99</sup>Rh, <sup>101</sup>Rh and <sup>102</sup>Rh were produced in a (p,n) and (p,2n) reaction by irradiating ruthenium powder with 15 MeV protons in the cyclotron at the Institute of Physics, University of

Oslo. The powder was suspended in an indium metal melt which was solidified on a target holder. From the cyclotron irradiation of the indium metal the tracer of  $^{113}\text{Sn}$  could be separated after dissolution in HCl. The ruthenium powder after irradiation were melted together with KOH and  $\text{KNO}_3$  at about 1000 °C for 5 hr, then dissolved in water. The tracers of  $^{103}\text{Ru}$  as well as  $^{192}\text{Ir}$  and  $^{194}\text{Ir}$  were produced by neutron activation of 2-5 mg of the metal chloride in the JEEP II reactor at Institutt for Energiteknikk, Kjeller, Norway.

#### Analysis procedure

At preselected phase contact times ratios of the concentrations of metals in both aqueous and organic phases were obtained by measuring  $\gamma$ -intensities in samples of equal volumes of the two phases with a Ge detector and a multi-channel analyzer. The half-lives and  $\gamma$ -energies used in the measurement of the radio-tracers of rhodium, ruthenium and iridium are shown in Table 1. The distribution ratio is given as:

**D = The  $\gamma$ -activity of a metal tracer in the organic phase / The  $\gamma$ -activity of the metal tracer in the aqueous phase**

The standard deviation of the measurements of samples with  $\gamma$ -spectrometry was <5%.

**TABLE 1**  
Properties of radionuclides utilized as tracers

Nuclide	Half life	$E_\gamma$ (keV)	$\Delta E_\gamma$ (keV)	*I $\gamma$ (%)	$\Delta I_\gamma$ (%)
$^{99}\text{Rh}$	16d	89.76	0.06	33	1.5
		353.05	0.06	34.6	1.0
		528.24		38	1
$^{101}\text{Rh}$	4.5d	306.86	0.02	87	1
$^{102}\text{Rh}$	2.9y(206d)	475.06	0.04	94.8 (45)	0.3 (4)
$^{103}\text{Ru}$	39.45d	497.08	0.02	86.4	3.5
		610.33	0.02	6.3	0.3
$^{192}\text{Ir}$	74.2d	316.497	0.007	82.9	0.1
		468.06	0.01	48.1	0.7
$^{194}\text{Ir}$	19.38h	328.448	0.014	13.0	1.8
$^{113}\text{Sn}$	115.1d	391.69	0.02	64	1

\*I $\gamma$  - relative intensity (number of photons per 100 disintegrations)

#### Extraction procedure

The formation of the rhodium-tin complexes at elevated temperature is much faster than at room temperature, at which some few days or even longer are normally needed reaction time depending on concentration of both tin(II) chloride and acidity in the solution. All samples in the experiments were put in oven and kept at 60 °C for 30 min to complete the formation of rhodium-tin complexes and then cooled to room temperature. The complexes of rhodium-tin with intense red or orange colour is stable in solution for months or even for years at room temperature.

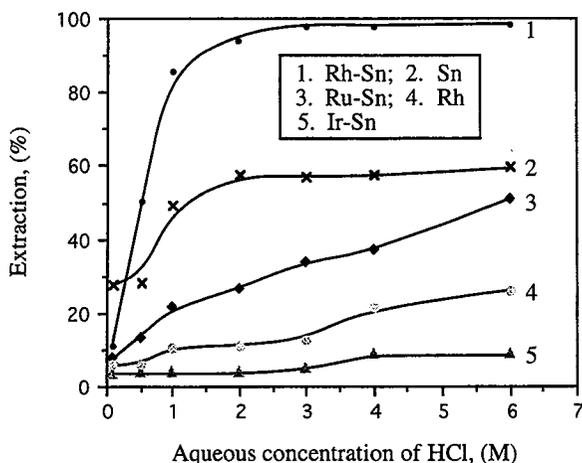
A 5 mL portion of the aqueous phase containing rhodium ions of about 100 mg/L (about  $10^{-3}$  M), rhodium, ruthenium and iridium radio-tracers, tin(II) chloride and acid in appropriate concentrations was contacted with an equal volume of a solution of cyclohexanol which had been preequilibrated with the selected acid concentration of the aqueous phase. The phase contact was performed by hand shaking for a predetermined time.

The adopted value of a distribution ratio was obtained from the average result of at least three parallel extraction experiments. The ionic strength of the aqueous solution was adjusted with  $\text{NaClO}_4$  and all the experiments were carried out at room temperature.

## RESULTS AND DISCUSSION

### Extraction of metals at different concentrations of hydrochloric acid

The variation in extraction of rhodium, ruthenium and iridium on the acidity from 0.10 M to 6.0 M HCl solutions is shown in Figure 1. The extraction of rhodium treated with tin(II) chloride is much higher than that of rhodium without tin(II) chloride, and is also much higher than that of ruthenium or iridium in the same solution of rhodium with tin(II) chloride as long as the concentration of HCl is over 1.0 M. By adding tin(II) chloride rhodium is forming extractable species more easily than ruthenium and iridium at high hydrochloric acidic concentrations. For example, rhodium, ruthenium and iridium are extracted 95.5%, 23.1% and 3.6% respectively at  $[HCl]=4.0$  M,  $[SnCl_2]=0.20$  M in the aqueous phase,  $[cyclohexanol]=5.0$  M in toluene as the organic phase and phase contact time 1.0 min. The loaded organic phase was stripped 95.5% with 0.50 M NaCl in two steps.



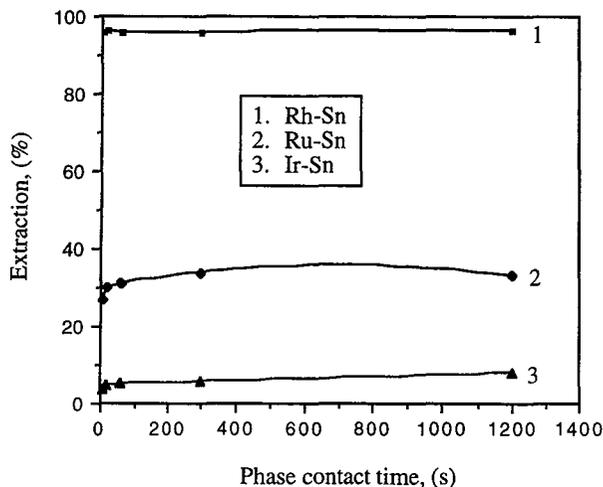
**Figure 1.** Extraction of Rh, Ru, Ir and Sn from aqueous HCl concentrations up to 6 M;

**Organic phase:** 5.0 M cyclohexanol in toluene; **aqueous phase:** 0.20 M  $SnCl_2$ ; ionic strength controlled with  $NaClO_4$ ; **phase contact time** 1.0 min; **curve 2:** 0.20 M  $SnCl_2$ , rhodium free; **curve 4:** 0.001 M Rh,  $SnCl_2$  free.

Similar results can be obtained by using some other alcohols as extractant, for example, rhodium was extracted 93.8%, ruthenium 33.5% and iridium 5.9% by 50% n-octanol in Isopar-M and rhodium 92.5%, ruthenium 30.1% by 50% n-decanol in Isopar-M at  $[HCl]=4.0$  M,  $[SnCl_2]=0.20$  M in the aqueous phase.

### Extraction of metals at different phase contact time

The results of extraction with changing phase contact time given in Figure 2 show that the equilibrium of extraction for rhodium, ruthenium and iridium was incredibly fast reached (at the condition of  $[HCl]=2.0$  M and  $[SnCl_2]=0.20$  M in aqueous solution,  $[cyclohexanol]=5.0$  M in toluene as organic phase) and in particularly for rhodium the equilibrium can even be reached in a few seconds. This is an advantage that may be utilized for rhodium separation from other coextracted impurity metals.



**Figure 2.** Extraction of Rh, Ru and Ir at increasing phase contact time (from 5 sec to 1200 sec); Aqueous phase: 2.0 M HCl and 0.20 M SnCl<sub>2</sub>; organic phase: 5.0 M cyclohexanol in toluene.

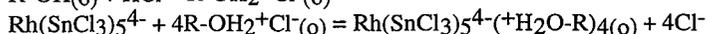
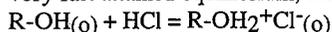
#### Extraction of metals at various concentrations of tin(II) chloride

The addition of tin(II) chloride increases the extraction of rhodium significantly in acidic solution. It is therefore of interest to examine the extraction dependence of rhodium, ruthenium and iridium on the concentration of tin(II) chloride. The experiment was carried out with [cyclohexanol]=5.0 M in toluene as organic phase, [HCl]=2.0 M, [RhCl<sub>3</sub>]=0.01 M in aqueous phase, shaking time 2.0 min and the ionic strength kept constant with NaClO<sub>4</sub>. The results given in Figure 3 show that the extraction of ruthenium, iridium and especially rhodium increases with increasing tin(II) chloride concentration in the solution. At a certain tin to rhodium molar ratio the extraction of rhodium is not significantly affected by a further increase in concentration of SnCl<sub>2</sub>. The initial ratio of Sn:Rh is about 12 for this experiment according to Figure 3, but the real ratio of Sn:Rh might be about 5:1 as 55% tin itself (see Figure 1) is extracted. The main compound of rhodium-tin complexes which are extracted is thus consistent with [Rh(SnCl<sub>3</sub>)<sub>5</sub>]<sup>4-</sup>, which have been conceived by others (Garraalda, 1981; Benguerel, 1993).

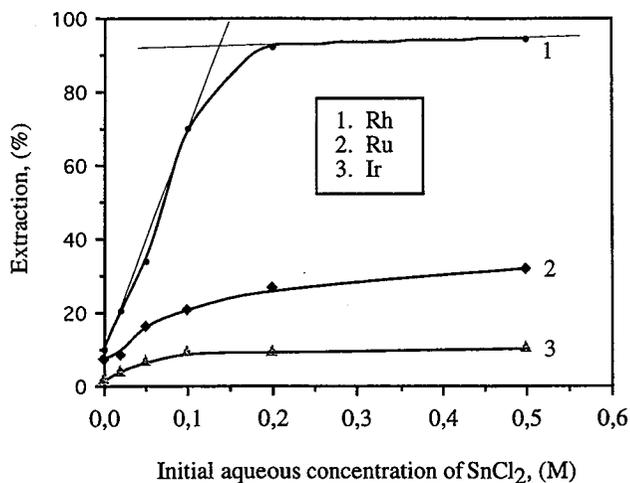
#### Study of UV-vis spectra of rhodium

The spectra obtained by using Hitachi U-2000 Spectrophotometer may confirm the formation of rhodium-tin(II) chloride complexes in both aqueous and organic phases, though the exact composition of the complex is unknown in this experiment. The UV-vis spectra of rhodium in Figure 4 show the difference between rhodium solutions with tin(II) chloride and without tin(II) chloride. The similar spectra of rhodium-tin(II) chloride complex in aqueous phase and organic phase are observed by using a 5 mL 5 M cyclohexanol in toluene in extracting from an equal volume of rhodium-tin(II) chloride solution containing 2.0 M HCl and 0.20 M SnCl<sub>2</sub>. They are completely different from that of rhodium-aquochloro complex not containing tin(II), and may suggest the similar structure of rhodium-tin(II) complex in both phases.

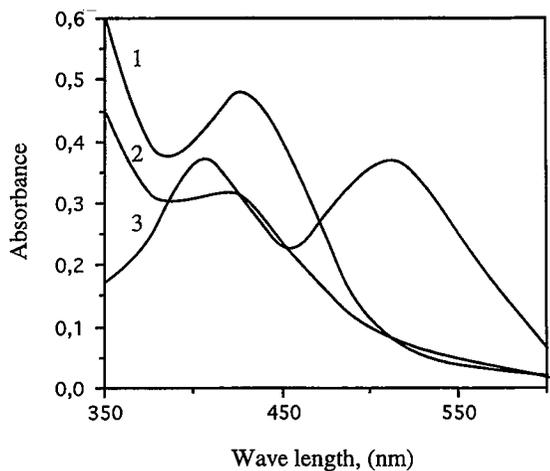
Considering the evaluated molar ratio of Sn:Rh, the effect of acid on rhodium extraction and its very fast attained equilibrium, the equations of extraction for rhodium may be expressed as:



R-OH = cyclohexanol, n-octanol, n-decanol



**Figure 3. Extraction of Rh, Ru and Ir at various concentrations of tin(II) chloride;**  
Organic phase: 5.0 M cyclohexanol in toluene; phase contact time 10 min.; aqueous phase: 2.0 M HCl and 0.01 M rhodium; ionic strength kept constant with NaClO<sub>4</sub>, I = 3.6.



**Figure 4. UV-spectra of rhodium;**  
1. rhodium in 2.0 M HCl and 0.20 M tin(II) chloride aqueous solution; 2. rhodium-tin complexes in 5.0 M cyclohexanol solution; 3. 0.01 M rhodium in 2.0 M HCl aqueous solution.

## CONCLUSION

Rhodium(III) can be quantitatively extracted from ruthenium(III) and iridium(III) with cyclohexanol or other alcohols in presence of tin(II) chloride in HCl solution. The equilibrium for the rhodium extraction is reached in a very short time.

## ACKNOWLEDGEMENTS

The authors are very grateful for the financial support from *Stefi og Lars Fylkesakers Vitenskapelige Stiftelse* and the help from staff and students in Nuclear Section of Department of Chemistry, University of Oslo.

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## CHEMISTRY OF SOLVENT EXTRACTION OF RARE METALS BY QUATERNARY AMMONIUM SALTS

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### ABSTRACT

An investigation of the liquid-liquid extraction of Ti, Nb, Ta, Cr(VI), Mo(VI), W(VI), U(VI), Th(IV), Sc, Y and lanthanoids, as well as mineral acids and alkaline metals, using quaternary ammonium salts, alone, and with mixtures of other classes of extractants is reported. The composition of extracted compounds and the mechanism of their extraction are discussed.

### INTRODUCTION

Quaternary ammonium salts (Q.A.S.) are being used widely in the solvent extraction of non-ferrous and rare metals. This is due to the possibility of extracting metals from different aqueous solutions using both anion-exchange and solvation mechanisms (Shmidt, 1980). Another reason is the possibility of forming synergistic mixtures with other classes of extractants, such as acidic (Cholkin and Kuzmin, 1984), neutral phosphoric compounds (Gaikwad and Damodaram, 1990) and chelating reagents (Dukov and Genov, 1986). Thus the solvent extraction properties of Q.A.S. or their synergistic mixtures have made possible the recovery of rare metals from carbonate, hydroxide and neutral solutions, and solutions in different mineral acids. In some cases Q.A.S. may show unusual properties and extract metals salts as crown ethers (Stepanov, 1994).

This report discusses the results of systematic investigations of the solvent extraction chemistry of the rare-metals, alkaline metals salts and mineral acids with Q.A.S., which have been carried out at the Department of Technology of Rare-Metals of the Mendeleev University. Some examples of the application of these extractants in the technology of rare metals are also considered.

### EXPERIMENTAL

The main investigations were carried out using methyltrioctylammonium sulphate (TOMA sulphate), which was synthesised as described elsewhere (Frolov et. al., 1975) and an industrial reagent, methyltrialkylammonium sulphate (TAMA sulphate) (mixture of C<sub>7</sub>H<sub>15</sub> - C<sub>9</sub>H<sub>19</sub> carbon chains), was manufactured under the assistance of the Mendeleev University. The purity of the industrial reagent was 96-98%, with 2-4% tertiary and secondary amine impurities. For both reagents, the required anionic form was achieved by mixing with the appropriate ammonium or sodium salts. The compositions of the extractable complexes were determined using methods, including partition, loading and isomolar methods, slope analysis, and IR, UV and NMR - spectroscopy. Mathematical modelling method of the

extraction isotherms, taking into account hydration of the organic phase components was also used (Sergievsky, 1981). Metals investigated were Ti, Nb, Ta, Cr(VI), Mo(VI), W(VI), U(VI), Th(IV), Sc, Y, all of which are industrially important.

## RESULTS AND DISCUSSION

Table I summarises the compositions of the extracted complexes, which were obtained from the present work. The data from Table I only shows the ratios between the extractant and the extracted metal, and does not show the structures of the extracted complex.

### Hydration of Q.A.S.

In organic solutions Q.A.S. formed non-stoichiometric hydrates, which have been determined as "hydration degree",  $h$ . It can also be determined as:  $h = (C_w - C_w^0) / C_c$ , where:  $C_w$  and  $C_w^0$  - water concentration in Q.A.S. solution and pure solvent corresponding under current water activity ( $a_w$ ),  $C_c$  - concentration of Q.A.S. in the same solution. For solutions of Q.A.S. two types of isotherms were established: linear and non-linear (usually S-form). The values of  $h$  for linear isotherm and integrated  $h$  for the non-linear isotherm are directly proportional to  $a_w$ . The values of  $h$  increase in the order:  $I^- < NO_3^- < Br^- < Cl^- < HSO_4^- < SO_4^{2-} < CO_3^{2-} < OH^-$  for Q.A.S. with the same cation. The effect of diluent on  $h$  is more complicated.  $h$  decreased in the order: nitrobenzene > chlorobenzene > benzene > toluene > xylene >  $CHCl_3$  >  $CCl_4$ . The displacement of water from organic phase was observed for the mixtures of Q.A.S. with different anions or in the presence of other extractants, due to their joint association. Aggregation of Q.A.S. also decrease the values of  $h$ .

### Mineral acids.

The extraction of four main industrial acids: chloride, nitrate, phosphoric and sulphuric acids was investigated in this work. The formation solvation and the distribution of the acid molecules which are partially dissociate in the organic phase, were established for the extraction of the mineral acids except HCl, which does not form monosolvate. Table I shows the formulae of the mineral acids investigated and the extractant used. It also shows the extracted species and the dissociated form of the acids in organic phase.

### Alkaline metals.

The extractions of lithium, sodium and potassium chlorides, nitrates, sulphates and carbonates by the same kind of Q.A.S. were investigated. The distribution of alkaline metals salts into the organic phase under  $a_w$  near 1 was established for tetralkylsubstituted salts. The extraction of LiCl by quaternary chlorides is better described in term of non-stoichiometric solvates formation. The solvate numbers obtained range from 0.77 to 1.57 depend on the initial concentration of extractant. Analogous results were obtained for  $NH_4NO_3$  extraction by Q.A.S.

The extractions of  $Li_2SO_4$ ,  $Na_2SO_4$ ,  $K_2SO_4$  and  $LiNO_3$ ,  $NaNO_3$ ,  $KNO_3$  by methyl cyclohexyldioctylammonium sulphate or nitrate involve the formation of monosolvates. This was due to the introduction of the negative charged anion partially or wholly into the cavity of the cyclohexyl substituent, which was connected to the positive charged atom of nitrogen.

**Table 1. Composition of extracted species of rare metals with quaternary ammonium salts and synergic mixtures.**

Aqueous media	Extractant	Extracted species (organic phase)
1	2	3
<b>Hydration</b>		
H <sub>2</sub> O	(R <sub>4</sub> N <sup>+</sup> ) <sub>x</sub> An <sup>x-</sup>	(R <sub>4</sub> N <sup>+</sup> ) <sub>x</sub> An <sup>x-</sup> ·hH <sub>2</sub> O
<b>Mineral acids</b>		
HCl	R <sub>4</sub> NCl	HC l ; (H <sup>+</sup> +Cl <sup>-</sup> )
HNO <sub>3</sub>	R <sub>4</sub> NNO <sub>3</sub>	R <sub>4</sub> NNO <sub>3</sub> · HNO <sub>3</sub> ; HNO <sub>3</sub> ; (H <sup>+</sup> +NO <sub>3</sub> <sup>-</sup> )
H <sub>2</sub> SO <sub>4</sub>	(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub>	(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub> · H <sub>2</sub> SO <sub>4</sub> ; H <sub>2</sub> SO <sub>4</sub> ORG. ; (H <sup>+</sup> +HSO <sub>4</sub> <sup>-</sup> ) ORG.
H <sub>3</sub> PO <sub>4</sub>	R <sub>4</sub> NH <sub>2</sub> PO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub> ;(H <sup>+</sup> +H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> )
<b>Alkaline metals</b>		
Li(Na, K)NO <sub>3</sub>	R <sub>4</sub> NNO <sub>3</sub>	MeNO <sub>3</sub> ; (Me <sup>+</sup> +NO <sub>3</sub> <sup>-</sup> )
Li(Na, K)NO <sub>3</sub>	**R <sub>4</sub> NNO <sub>3</sub>	R <sub>4</sub> NNO <sub>3</sub> . Li(Na, K)NO <sub>3</sub>
Na(K)Cl	R <sub>4</sub> NCl	MeCl ; (Me <sup>+</sup> +Cl <sup>-</sup> )
LiCl	R <sub>4</sub> NCl	qR <sub>4</sub> NCl · LiCl
Li(Na, K) <sub>2</sub> CO <sub>3</sub>	(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	Li(Na, K) <sub>2</sub> CO <sub>3</sub>
Li(Na, K) <sub>2</sub> SO <sub>4</sub>	(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub>	Li(Na, K) <sub>2</sub> SO <sub>4</sub>
Li(Na, K) <sub>2</sub> SO <sub>4</sub>	** (R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub>	(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub> . Li(Na, K) <sub>2</sub> SO <sub>4</sub>
<b>Uranium</b>		
UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>	(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	
Na <sub>2</sub> (K,NH <sub>4</sub> )CO <sub>3</sub> pH>9.5		(R <sub>4</sub> N) <sub>4</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>
pH 7.5-9.5		(R <sub>4</sub> N) <sub>4</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>
pH~7.0		(R <sub>4</sub> N) <sub>2</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> (R <sub>4</sub> N) <sub>4</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (R <sub>4</sub> N) <sub>2</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> (R <sub>4</sub> N) <sub>6</sub> (UO <sub>2</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> pH 2.0-3.0	R <sub>4</sub> NNO <sub>3</sub>	3R <sub>4</sub> NNO <sub>3</sub> ·UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> 2R <sub>4</sub> NNO <sub>3</sub> ·UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> R <sub>4</sub> NNO <sub>3</sub> ·UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> R <sub>4</sub> NNO <sub>3</sub> ·2UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> R <sub>4</sub> NNO <sub>3</sub> ·3UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>
UO <sub>2</sub> Cl <sub>2</sub> pH 2.0-3.0	R <sub>4</sub> NCl	2R <sub>4</sub> NCl·UO <sub>2</sub> Cl <sub>2</sub> R <sub>4</sub> NCl·UO <sub>2</sub> Cl <sub>2</sub> R <sub>4</sub> NCl·2UO <sub>2</sub> Cl <sub>2</sub>

1	2	3
UO <sub>2</sub> SO <sub>4</sub> pH 2.0-3.0	(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub>	2(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub> ·UO <sub>2</sub> SO <sub>4</sub> (R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub> ·UO <sub>2</sub> SO <sub>4</sub> (R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub> ·2UO <sub>2</sub> SO <sub>4</sub>
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> H <sub>3</sub> PO <sub>4</sub> / HNO <sub>3</sub>	R <sub>4</sub> NNO <sub>3</sub> + (RO) <sub>2</sub> POOH	2(RO) <sub>2</sub> POOH·UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · R <sub>4</sub> NNO <sub>3</sub>
<b>Thorium</b>		
Th(NO <sub>3</sub> ) <sub>4</sub> HNO <sub>3</sub>	R <sub>4</sub> NNO <sub>3</sub>	(R <sub>4</sub> N) <sub>2</sub> Th(NO <sub>3</sub> ) <sub>6</sub>
Th(NO <sub>3</sub> ) <sub>4</sub> H <sub>3</sub> PO <sub>4</sub> + HNO <sub>3</sub>	*R <sub>4</sub> NNO <sub>3</sub> +(RO) <sub>3</sub> PO	(R <sub>4</sub> N) <sub>2</sub> Th(NO <sub>3</sub> ) <sub>6</sub> ·3(RO) <sub>3</sub> PO
Th(NO <sub>3</sub> ) <sub>4</sub> HNO <sub>3</sub>	*R <sub>4</sub> NNO <sub>3</sub> +(RO) <sub>3</sub> PO+ R <sub>3</sub> PO	(R <sub>4</sub> N) <sub>2</sub> Th(NO <sub>3</sub> ) <sub>6</sub> ·n(RO) <sub>3</sub> PO· (3-n) R <sub>3</sub> PO; n=1-3.
<b>Scandium</b>		
Sc(NO <sub>3</sub> ) <sub>3</sub> HNO <sub>3</sub> + NH <sub>4</sub> NO <sub>3</sub>	R <sub>4</sub> NNO <sub>3</sub>	6R <sub>4</sub> NNO <sub>3</sub> ·Sc(NO <sub>3</sub> ) <sub>3</sub> 3R <sub>4</sub> NNO <sub>3</sub> ·Sc(NO <sub>3</sub> ) <sub>3</sub>
H <sub>3</sub> PO <sub>4</sub> + HNO <sub>3</sub>	*R <sub>4</sub> NNO <sub>3</sub> + (RO) <sub>2</sub> POOH	[(RO) <sub>2</sub> POO] <sub>3</sub> Sc·nR <sub>4</sub> NNO <sub>3</sub> n=1-2.
Sc <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> Na <sub>2</sub> (K,NH <sub>4</sub> )CO <sub>3</sub> pH>9.0	(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	(R <sub>4</sub> N) <sub>5</sub> Sc(CO <sub>3</sub> ) <sub>4</sub> or 2(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub> ·(R <sub>4</sub> N)Sc(CO <sub>3</sub> ) <sub>2</sub>
<b>Lanthanoids</b>		
Ln(NO <sub>3</sub> ) <sub>3</sub> pH=2,0-3,0	*R <sub>4</sub> NNO <sub>3</sub>	n R <sub>4</sub> NNO <sub>3</sub> · Ln(NO <sub>3</sub> ) <sub>3</sub> ; n=9-5 3R <sub>4</sub> NNO <sub>3</sub> · Ln(NO <sub>3</sub> ) <sub>3</sub> 2R <sub>4</sub> NNO <sub>3</sub> · Ln(NO <sub>3</sub> ) <sub>3</sub>
La(NO <sub>3</sub> ) <sub>3</sub> -Sm(NO <sub>3</sub> ) <sub>3</sub> 0,1MHNO <sub>3</sub> +NH <sub>4</sub> NO <sub>3</sub>	*R <sub>4</sub> NNO <sub>3</sub> +(RO) <sub>3</sub> PO	n R <sub>4</sub> NNO <sub>3</sub> ·m(RO) <sub>3</sub> PO· La(NO <sub>3</sub> ) <sub>3</sub> n=1-3, m=3-n
Er <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> Na <sub>2</sub> (K,NH <sub>4</sub> )CO <sub>3</sub> pH>9.0	(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	(R <sub>4</sub> N) <sub>7</sub> Er(CO <sub>3</sub> ) <sub>5</sub> or 2(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub> ·(R <sub>4</sub> N) <sub>3</sub> Er(CO <sub>3</sub> ) <sub>3</sub>
<b>Titanium</b>		
TiOSO <sub>4</sub> 0,5-2,0 M H <sub>2</sub> SO <sub>4</sub>	(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub>	(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub> ·2 TiOSO <sub>4</sub>
TiOSO <sub>4</sub> 0,5-2,0 M H <sub>2</sub> SO <sub>4</sub>	*(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub> + (RO) <sub>2</sub> POOH	4(RO) <sub>2</sub> POOH·0,5(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub> · nTiOSO <sub>4</sub> ; n=2-3
<b>Chromium</b>		
Cr <sup>6+</sup> , pH<7,0	(R <sub>4</sub> N) <sub>2</sub> SO <sub>4</sub>	(R <sub>4</sub> N) <sub>2</sub> Cr <sub>n</sub> O <sub>(3n+1)</sub> ; n=2-4

1	2	3
Cr <sup>6+</sup>	(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	(R <sub>4</sub> N) <sub>2</sub> CrO <sub>4</sub>
Na <sub>2</sub> (K,NH <sub>4</sub> )CO <sub>3</sub> pH=7,0-9,5		(R <sub>4</sub> N) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
<b>Molybdenum</b>		
Mo <sup>6+</sup>	*(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	(R <sub>4</sub> N) <sub>2</sub> MoO <sub>4</sub>
Na <sub>2</sub> (K,NH <sub>4</sub> )CO <sub>3</sub> pH≥7,0		
Cr <sup>6+</sup>	*(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	(R <sub>4</sub> N) <sub>2</sub> MoO <sub>4</sub>
Na <sub>2</sub> (K,NH <sub>4</sub> )CO <sub>3</sub> pH=7,0-9,5		
S <sup>2-</sup>		(R <sub>4</sub> N) <sub>2</sub> MoO <sub>n</sub> S(4-n); n=1-4
<b>Tungsten</b>		
W <sup>6+</sup>	*(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	(R <sub>4</sub> N) <sub>2</sub> WO <sub>4</sub>
Na <sub>2</sub> (K,NH <sub>4</sub> )CO <sub>3</sub> pH>9,5		
W <sup>6+</sup>	*(R <sub>4</sub> N) <sub>2</sub> CO <sub>3</sub>	(R <sub>4</sub> N) <sub>2</sub> WO <sub>4</sub>
Na <sub>2</sub> (K,NH <sub>4</sub> )CO <sub>3</sub> pH=7,0-9,5		(R <sub>4</sub> N) <sub>6</sub> W <sub>7</sub> O <sub>24</sub>
S <sup>2-</sup>		(R <sub>4</sub> N) <sub>2</sub> WO <sub>n</sub> S(4-n); n=1-4

Where: (RO)<sub>2</sub>POOH = DEHPA, R<sub>4</sub>N = CH<sub>3</sub>(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N, \*R<sub>4</sub>N = CH<sub>3</sub>(C<sub>7</sub>H<sub>15</sub>-C<sub>9</sub>H<sub>19</sub>)<sub>3</sub>N, \*\*R<sub>4</sub>N=CH<sub>3</sub>(C<sub>6</sub>H<sub>11</sub>)(C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>N, (RO)<sub>3</sub>PO = TBP and R<sub>3</sub>PO = TAPO = (C<sub>7</sub>H<sub>15</sub>-C<sub>9</sub>H<sub>19</sub>)(i-C<sub>5</sub>H<sub>11</sub>)CH<sub>3</sub>PO.

#### Uranium.

Tricarbonatouranilate, which is the most stable uranium complex, was extracted into the organic phase from carbonate solutions at pH>9.5. At pH 7.5-9.5 the dicarbonatouranilate complex began to be extracted and extraction of this complex increases with decreasing pH. At pH 7.0, a polynuclear complex was also extracted. The composition of this complex is, as well as the other two complexes, shown in Table 1.

There are a number of extractable solvates from the nitrate solutions. The composition of the extracted species depends on the ratio of the extractant and metal concentrations and varies from three to 1/3 solvate system when the organic phase was loaded. It was possible that the [UO<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>]<sup>-</sup> complex was extracted, which is further solvated in the organic phase with either the extractant or the other uranium nitrate molecules. This has also been observed in the extraction of uranium sulphate and uranium chloride from neutral solutions.

Uranium was extracted as a synergistic complex, containing two molecules of the organic acid and one Q.A.S. from mixed phosphate-nitrate acidic solutions.

#### Thorium.

Thorium was extracted from nitrate solutions as (R<sub>4</sub>N)<sub>2</sub>Th(NO<sub>3</sub>)<sub>6</sub> (Bac, 1966). In the presence of trialkylphosphine oxide (TAPO) or tributylphosphate (TBP) a synergistic effect has been observed, which was caused by an additional solvation of the initial complex. Mixtures of Q.A.S., TAPO and TBP show an even higher synergistic effect.

### **Scandium.**

Two compounds were extracted from low acidic nitrate solutions with TOMA nitrate, which contain 6 and 3 extractant molecules. It is possible, that the complex  $[\text{Sc}(\text{NO}_3)_4]^-$  was extracted into the organic phase where it was further solvated by free extractant molecules. Analogous results were observed for Sc extraction from carbonate solutions in which the organic phase complex contains five extractant molecules. This can be represented as either the 1:1 or 3:1 complex with additional solvation by the free extractant.

Two different complexes were found for the extraction of Sc with a synergistic mixture of DEHPA and TAMA nitrate from acidic nitrate and phosphate-nitrate solutions, the composition of which are shown in Table 1.

### **Y, La, lanthanoid.**

These metals were extracted from neutral or weak acidic nitrate solutions as solvates of different composition. The increase of metal nitrate concentrations in the aqueous phase gives the extracted complex a lower solvation number. Additional solvation of the extracted complexes by free extractant appears similar to that shown by the uranium and scandium extraction.

Mixtures of Q.A.S. and the neutral phosphoric extractant TBP, show a synergistic effect in the solvent extraction of lanthanoids from nitrate solutions, which produced solvates of different compositions, as shown in Table 1.

### **Titanium.**

Ti was extracted as a polymeric compound from low concentration sulphuric acid solutions. Mixtures of DEHPA and TAMA sulphate are synergistic mixtures over a wide range of sulphuric acid concentrations, extracting dimers or trimers of titanyl sulphate into the organic phase.

### **Chromium, molybdenum, tungsten.**

These elements of group VI are extracted as monooxanions  $\text{MeO}_4^{2-}$  at  $\text{pH} > 9.50$  and as polyoxanions of different composition below  $\text{pH} 9.0$ . The degree of polymerisation of oxanions increases with decreasing  $\text{pH}$  of the aqueous phase and with the increase of mineral acid concentrations in the organic phase.

## **CONCLUSIONS**

Investigations of the chemistry and thermodynamics of solvent extraction systems with Q.A.S. has allowed the selection of more effective extractants and their synergistic mixtures for the recovery and separation of rare metals from different acidic, neutral and carbonate solutions.

## **ACKNOWLEDGMENTS**

The author would like to thank Professor Michael Cox and Dr Neil Kelly from the Division of Chemical Sciences, University of Hertfordshire for their help and support in the preparation of this paper.

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# SOLVENT EXTRACTION OF TRIVALENT GALLIUM, INDIUM AND THALLIUM FROM HYDROCHLORIC ACID SOLUTIONS BY TOPO AND TBP

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## ABSTRACT

The extraction of trivalent gallium, indium and thallium from aqueous solutions containing hydrochloric acid and/or lithium chloride by trioctyl phosphine oxide (TOPO) and tributyl phosphate (TBP) in benzene has been examined under different conditions. The organic extracts are also checked by infrared spectroscopy. As a result, it is found that the extraction efficiency for metals of TOPO and TBP is in the order  $Tl > Ga > In$ , although the extraction efficiency of TOPO is higher than that of TBP. These extractions are expressed by the following equilibrium equations:  $GaCl_3(a) + TOPO(o) \rightleftharpoons GaCl_3 \cdot TOPO(o)$ ,  $InCl_3(a) + 2TOPO(o) \rightleftharpoons InCl_3 \cdot 2TOPO(o)$ , at low aqueous acidity  $TlCl_3(a) + 2TOPO(o) \rightleftharpoons TlCl_3 \cdot 2TOPO(o)$  and at higher acidities  $TlCl_3(a) + HCl(a) + 2TOPO(o) \rightleftharpoons HTlCl_4 \cdot 2TOPO(o)$  where (a) and (o) denote aqueous and organic phases, respectively.  $GaCl_3(a) + 2TBP(o) \rightleftharpoons GaCl_3 \cdot 2TBP(o)$ ,  $InCl_3(a) + 3TBP(o) \rightleftharpoons InCl_3 \cdot 3TBP(o)$ , at low aqueous acidity  $TlCl_3(a) + 2TBP(o) \rightleftharpoons TlCl_3 \cdot 2TBP(o)$  and at higher acidities  $TlCl_3(a) + HCl(a) + 2TBP(o) \rightleftharpoons HTlCl_4 \cdot 2TBP(o)$  and in addition with increasing the concentration of thallium in aqueous phase  $TlCl_3(a) + HCl(a) + 3TBP(o) \rightleftharpoons HTlCl_4 \cdot 3TBP(o)$ .

## INTRODUCTION

The extraction of metals belonging to the IIIB group is important in the development of high-technology electronics. Therefore we have investigated the extraction of trivalent aluminium, gallium, indium and thallium from aqueous acid solutions by acid organophosphorus compounds (Sato et al., 1984, 1987, 1988, 1989) and  $\alpha$ -hydroxyoxime (Sato et al., 1989). The present paper extends the work in order to obtain further information on the extraction of trivalent gallium, indium and thallium from hydrochloric acid solutions by trioctyl phosphine oxide (TOPO) and tributyl phosphate (TBP).

## EXPERIMENTAL

### Reagents

The TOPO (Hokko Chemical Industry Co., Ltd.) was of high purity and used without further purification by dissolving in benzene. The TBP (Daiichi Chemical Industry Co., Ltd.) was purified by boiling with dilute caustic soda solution and was diluted with benzene. The aqueous solutions of metals were prepared by dissolving their chlorides ( $InCl_3 \cdot xH_2O$  and  $TlCl_3 \cdot 4H_2O$ ), except for aqueous gallium chloride solution which was prepared by dissolving gallium metal (99.9999%, Swiss Aluminium Ltd.) in concentrated hydrochloric acid and diluted with deionized water to a required concentration. In general, the concentrations of their metal salts were  $1 \text{ g dm}^{-3}$  except for the loading test. Other chemicals were of analytical reagent grade.

### Extraction and analytical procedures

Equal volumes ( $15 \text{ cm}^3$  each) of the aqueous and organic phases were shaken for 10

min in 50 cm<sup>3</sup> stoppered conical flasks in a thermostatted water at 20°C, except for the experiments on temperature effect. Preliminary experiments showed that the equilibrations were achieved in 10 min. The mixture was centrifuged and separated, and aliquots of both phases were analysed to determine the distribution coefficient ( $E_a^0$ , the ratio of the equilibrated concentration of metal in organic phase to that in aqueous phase). Metals in organic phases were stripped with 0.1 mol dm<sup>-3</sup> hydrochloric acid for gallium and indium, and 0.1 mol dm<sup>-3</sup> sodium hydroxide solution for thallium. The concentrations of metals in aqueous solutions were determined by EDTA titration using xylenol orange (XO) as indicator. The chloride concentration and water content in the organic phase were determined by adding 2 cm<sup>3</sup> to 25 cm<sup>3</sup> of 75% ethyl alcohol and the use of Volhard's method in the presence of nitrobenzene and by the Karl Fisher's titration method, respectively.

#### IR spectrophotometry

Infrared (IR) spectra of the organic extracts were determined on JASCO models IRA-1 (4000-650 cm<sup>-1</sup>) and IR-F (700-200 cm<sup>-1</sup>) using a capillary film between thallium halide plates or polyethylene films.

#### Measurement of apparent molecular weight

The apparent molecular weight was determined in benzene using a Hitachi model 115 isothermal molecular weight apparatus.

## RESULTS AND DISCUSSION

#### Extraction isotherm by TOPO

In order to investigate the extraction behaviours of trivalent gallium, indium and thallium from hydrochloric acid solutions by TOPO in benzene at 20°C, the distribution of these metals between the organic and aqueous phases has been examined with varying concentration of hydrochloric acid. The results are shown in Figs. 1-3. The results show that although the extraction efficiency for metals of TOPO is in the order Tl > Ga > In, the distribution coefficients of gallium(III) and indium(III) rise with increasing aqueous acidity to maxima which occur at initial hydrochloric acid concentrations of 6 and 4 mol dm<sup>-3</sup>, respectively, and then fall. The distribution coefficient of thallium(III) reveals maxima at about 0.02 mol dm<sup>-3</sup> and 5 mol dm<sup>-3</sup> hydrochloric acid concentrations, and decreases gently with increasing acidity. For the extraction of gallium(III) and indium(III), however, when hydrochloric acid in the aqueous phase is partly replaced by lithium chloride, it is observed that the distribution coefficient from aqueous mixed hydrochloric acid-lithium chloride solution by TOPO increases monotonously with the total chloride ion concentration, as illustrated in Fig. 2 for the extraction of indium(III). Further, the extraction of thallium(III) by TOPO from mixed hydrochloric acid-lithium chloride solution at [HCl] > 3 mol dm<sup>-3</sup> gives the distribution behaviour similar to the case of gallium(III) and indium(III). From these results it is deduced that the controlling factor for the extraction of trivalent gallium, indium and thallium from hydrochloric acid solutions is the total chloride ion concentration. Accordingly, the replacement of hydrochloric acid by lithium chloride checks the decrease in the distribution coefficient at higher aqueous acidities because of the removal of hydrochloric acid competition for available TOPO. In the extraction of thallium(III) from mixed hydrochloric acid-lithium chloride solution at a constant total chloride ion concentration, at low acidity (in 0.05 mol dm<sup>-3</sup>) the increase of the hydrogen ion concentration has little effect on the distribution coefficient, but at higher acidity (in 4 mol dm<sup>-3</sup>) raises the distribution coefficient. Besides the results for the variations of the molar ratios of [Cl<sup>-</sup>]/[Tl] and [H<sup>+</sup>]/[Tl] in the organic phase suggest that hydrochloric acid is accompanied by the extraction of thallium(III) at higher aqueous acidities. These imply that hydrochloric acid has no effect on the extraction of thallium(III) at

low aqueous acidity, but affects its extraction at higher acidities. The log-log plots of  $E_a^0$  vs.  $[\text{TOPO}] - n[\text{M}]_{\text{org}}$ , where  $n$  is the solvation number and  $\text{M} = \text{Ga}, \text{In}$  or  $\text{Tl}$ , at hydrochloric acid concentrations of 3-8, 0.1-9 and 0.01-9  $\text{mol dm}^{-3}$  give straight lines with slopes of  $\sim 1, \sim 2$  and  $\sim 2$  for gallium, indium and thallium, respectively. These results suggest the first-, second- and second-power dependencies on TOPO concentration for the extraction of gallium(III), indium(III) and thallium(III), respectively. The stoichiometry of the extracted species was examined by a loading test of metal in the organic phase. With increasing metal concentration in aqueous phase, the molar ratio  $[\text{Ga}]/[\text{Cl}]/[\text{TOPO}]/[\text{H}_2\text{O}]$  approaches to 1 : 3 : 1 : 0;  $[\text{In}]/[\text{Cl}]/[\text{TOPO}]$  to 1 : 3 : 2 : 0;  $[\text{Tl}]/[\text{Cl}]$

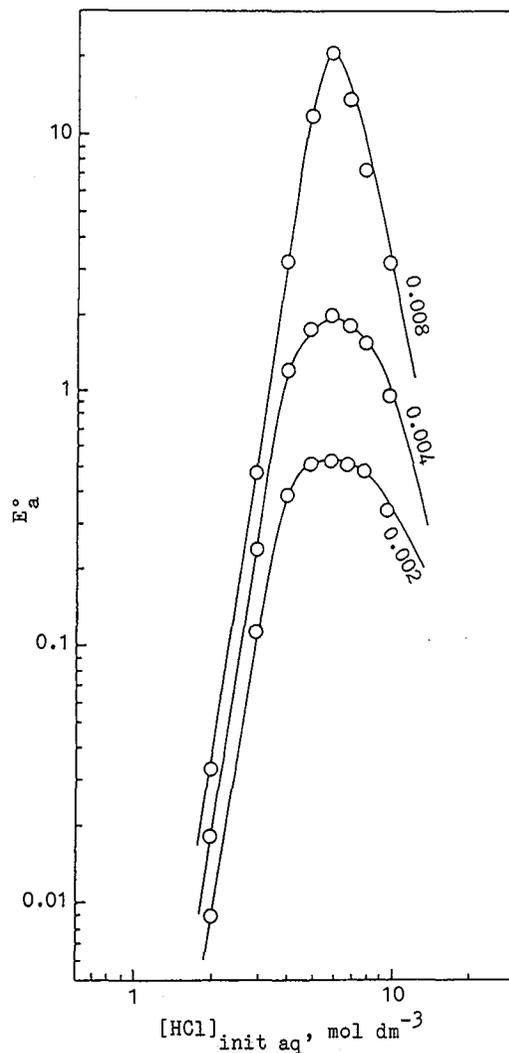


Figure 1. Extraction of gallium(III) from HCl solutions by TOPO in benzene at 20°C (numerals on curves are TOPO concs.,  $\text{mol dm}^{-3}$ ).

/[TOPO]/[H<sub>2</sub>O] to 1:3:2:0 at [HCl] < 0.3 mol dm<sup>-3</sup> and 1:4:2:0 at [HCl] > 0.3 mol dm<sup>-3</sup>. The results indicate the formation of the stoichiometric compositions of GaCl<sub>3</sub>·TOPO, InCl<sub>3</sub>·2TOPO and TlCl<sub>3</sub>·2TOPO and HTlCl<sub>4</sub>·2TOPO at low and high acidities, respectively.

Hence it is proposed that the extraction of gallium(III), indium(III) and thallium(III) from hydrochloric acid solutions by TOPO is expressed as the following reactions:

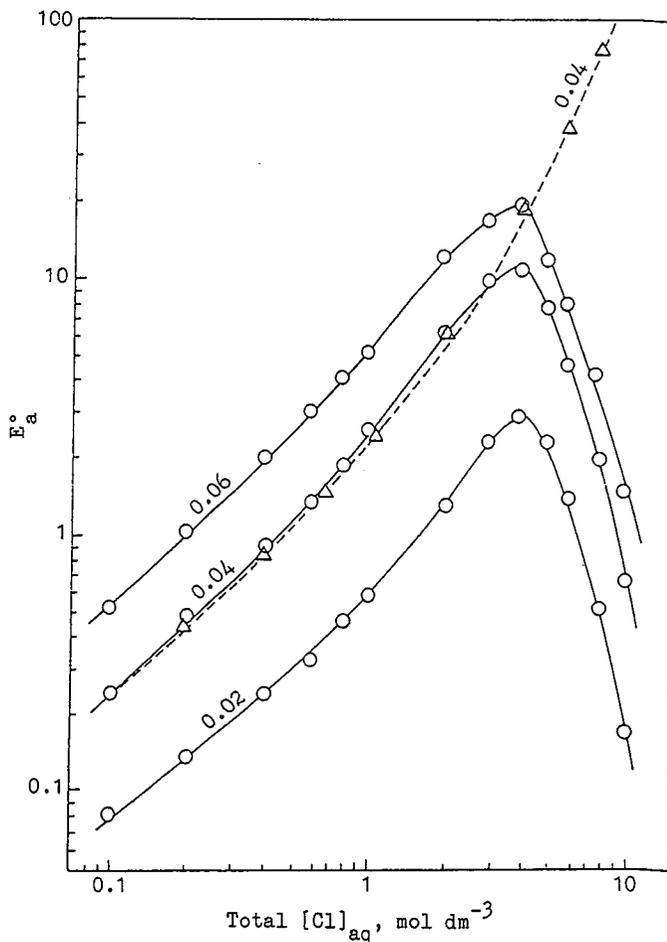
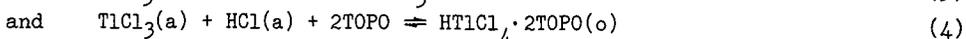
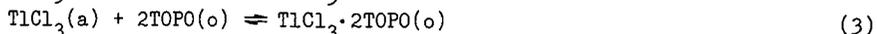
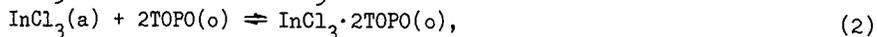
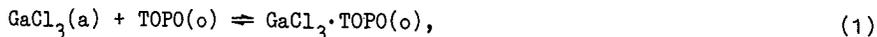


Figure 2. Extraction of indium(III) from HCl solutions by TOPO in benzene at 20°C (continuous and broken lines represent the extraction from HCl solns. and mixed 0.1 mol dm<sup>-3</sup> HCl/LiCl solns., respectively; numerals on curves are TOPO concns., mol dm<sup>-3</sup>).

in which (a) and (o) denote aqueous and organic phases, respectively, and Eqs. (3) and (4) are valid at  $[HCl] < 0.3$  and  $[HCl] > 0.3$  mol dm<sup>-3</sup>, respectively.

#### IR spectra

The organic extracts of trivalent gallium, indium and thallium from hydrochloric acid solutions by TOPO in benzene at 20°C were examined by IR spectrophotometry. With increase in metal concentration in the organic phase, the P→O stretching band for the compound HCl·TOPO·H<sub>2</sub>O (Sato et al., 1991) at 1150 cm<sup>-1</sup> shifts to lower frequencies at 1085, 1110 and 950 cm<sup>-1</sup> for the organic extracts of gallium(III), indium(III) and thallium(III), respectively. The shift of the P→O stretching band is in the order Tl>Ga>In, corresponding to the extraction efficiency of TOPO for trivalent gallium, indium and thallium. Further, the organic extracts exhibit the following absorptions: the M-O stretching bands at 395 cm<sup>-1</sup>, 442 and 415 cm<sup>-1</sup> and 412 and 390 cm<sup>-1</sup> for gallium, indium and thallium, respectively; the M-Cl stretching bands at 357 cm<sup>-1</sup>, 333 cm<sup>-1</sup> and 305, 298, 292 and 277 cm<sup>-1</sup> for gallium, indium and thallium, respectively. Accordingly the IR spectra indicate the formation of the chloride coordinated metal ion species which is also supported by the results determined for the chloride concentration in the organic phase.

The Data obtained using the apparent molecular weights indicate that the complexes extracted by TOPO exist as monomer for gallium and indium and as dimer for thallium. This suggests that the extracted species of gallium(III), indium(III) and thallium(III) according to Eqs. (1)-(4), consist of the complexes GaCl<sub>3</sub>·TOPO, InCl<sub>3</sub>·2TOPO and Tl<sub>2</sub>Cl<sub>6</sub>·4TOPO or H<sub>2</sub>Tl<sub>2</sub>Cl<sub>8</sub>·4TOPO, respectively, displaying the coordination number of four, five and six, respectively.

#### Extraction by TBP

The extraction of trivalent gallium, indium and thallium from hydrochloric acid solutions by TBP in benzene has been examined under different conditions, accord-

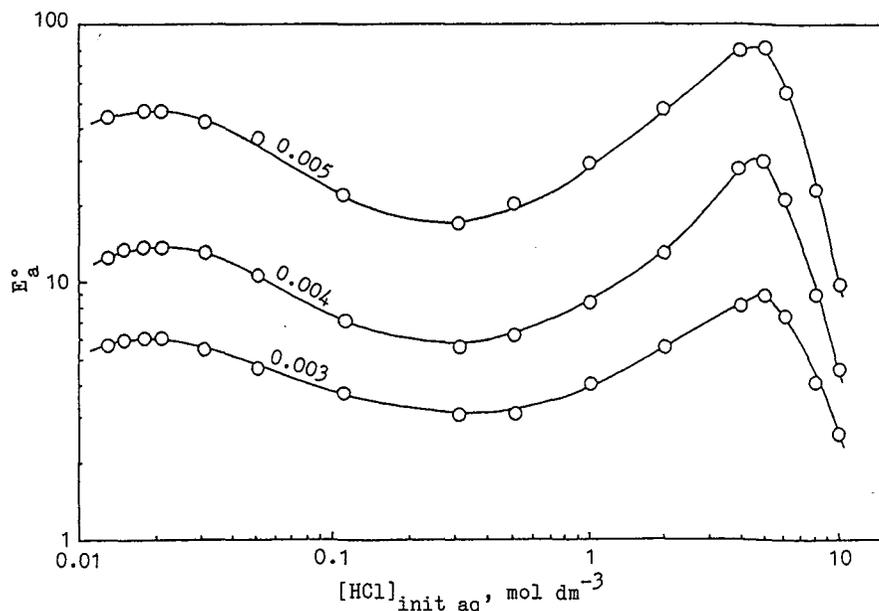
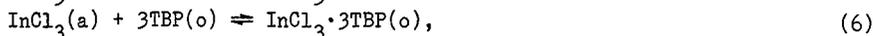
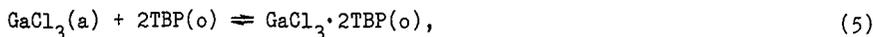


Figure 3. Extraction of thallium(III) from HCl solutions by TOPO in benzene at 20°C (numerals on curves are TOPO concns., mol dm<sup>-3</sup>).

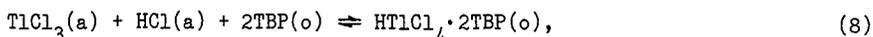
ing to the same manner as the extraction by TOPO. The results showed that although the extraction efficiency for metals using TBP is lower than that of TOPO, their extraction behaviour resembles each other and the extraction efficiency of TBP is in the order  $Tl > Ga > In$ . With increasing aqueous acidity, the distribution coefficients of gallium(III) and indium(II) reveal maxima at initial hydrochloric acid concentrations of 9 and 8 mol dm<sup>-3</sup>, respectively, while the distribution coefficient of thallium(III) exhibit two maxima at initial hydrochloric acid concentrations of 0.02 and 8-9 mol dm<sup>-3</sup>. The extractions are expressed by the following equilibrium equations:



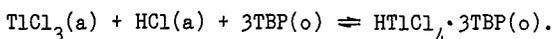
at low aqueous acidity



and at higher acidities



and in addition with increasing the concentration of thallium in aqueous phase



#### ACKNOWLEDGEMENTS

We wish to thank Messrs. S.Ishikawa and T.Nishimura for assistance with partial experimental work, and also thank the Hokko Chemical Industry Co., Ltd. for the sample of TOPO and the Daihachi Chemical Industry Co., Ltd. for the sample of TBP.

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# THE OXIDATION DURING SOLVENT EXTRACTION OF TETRAVALENT RARE EARTHS USING SALEN AS OXYGEN TRANSPORT REAGENT

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## INTRODUCTION

N,N'-Ethylene - bis(Salicylideneimine) (SALEN)[1] has been synthesized and studied since 1986 at Hanoi University for its ability in form of chelates. The special property of SALEN complexes for oxygen transportation was discovered in 1989. SALEN is insoluble in water but is soluble in low polarity organic solvents.

Studies of complexes of SALEN and R.E.E. [2] showed that no stable complexes are formed with trivalent R.E.E. However complexes of SALEN and tetravalent R.E.E. such as Ce(IV), Pr(IV) etc. are very stable.

In this paper we describe the ability of oxygen transportation of the complex of SALEN with Ce(IV) which is playing a very important role in the separation of R.E.E. and in other oxidation-reduction processes.

## EXPERIMENTAL

In the past, our publication showed that the structure of the complex between SALEN and Ce(IV) is as shown in figure 1 [3]. On the other hand, SALEN does not form any complexes with trivalent Cerium (as mentioned above). But Ce(III) (in aqueous solution) can be extracted by SALEN (dissolved in an organic solvent) and is extracted as a complex between SALEN and Ce(IV).

This means that, during the extraction, when SALEN in the organic phase is in contact with trivalent Cerium ions in the aqueous phase, the following reaction occurs. The trivalent Cerium is oxidizing to tetravalent Cerium in parallel with the process of forming the SALEN - Ce(IV)

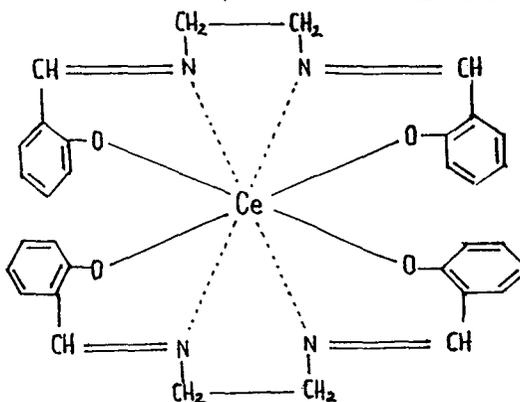


Figure 1. Structure of the SALEN-Ce(IV) chelate

complex. In this way, that Cerium is transported into the organic phase.

This process can be assumed to following three steps:

(1) - When contacting with Ce(III) ions, SALEN forms an intermediate compound which has structure as shown in figure II. In this form, the fourth valence electron of Cerium is less strongly held and the hydrogen atom is easier to remove from the hydroxyl group in the SALEN molecule.

(2) - In the presence of oxygen in the medium, the trivalent Cerium ion is oxidized to tetravalent Cerium.

(3) - The hydrogen ion is separated from the hydroxyl group and the complex SALEN - Ce(IV) is formed.

In the reverse reaction, the SALEN - Ce(IV) complex can be destroyed by reducing compounds. When tetravalent Cerium in the SALEN - Ce(IV) complex is reduced to the trivalent state, the chelate is destroyed and the trivalent Cerium ion just dissolves back into the aqueous phase. The oxidation - reduction process is something like that as hemoglobin in blood.

On the basis of the special properties of the SALEN - Ce(IV) chelate a study could made in two directions: To use SALEN as a selective reagent for the separation of Cerium from other R.E.E.; or a study of the of the application of the SALEN - Ce(IV) chelate in other oxidation and catalyzed oxidation processes.

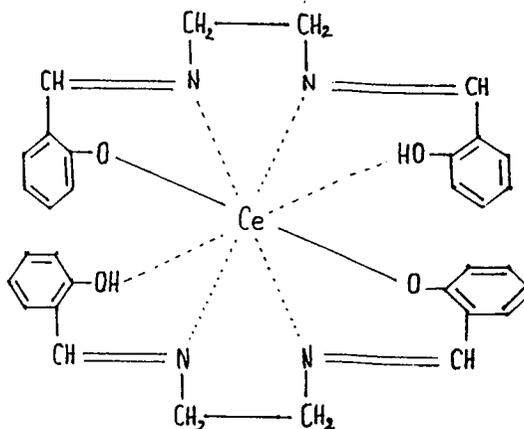


Figure II. Intermediate compound of SALEN - Ce(IV)

This report presents some results of the first direction. It is well-known that the general way for the separation of cerium from other R.E.E. is to first oxidized the Cerium to the tetravalent state. Then it can be separated by one of the well-known methods such as fractional precipitation, selective dissolution or extraction.

Using SALEN dissolved in an organic solvent as the extraction reagent, we can directly extract trivalent Cerium from aqueous solutions in an open system and obtain pure trivalent Cerium.

Our detailed investigation has shown that the extraction of Cerium is good in a weak acidic medium. The influence of the acid concentration on the extraction ability is shown in figure III. From the extraction curve in figure III it can be seen that:

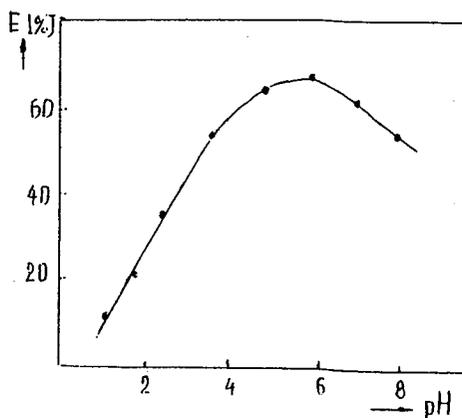


Figure III. The influence of acid concentration on the extraction of Cerium

- (a) There is no extraction when the  $H^+$  ion concentration is greater than 1M.
- (b) In the pH range from 1 to 7, the extraction increases and reaches a maximum at the pH value of about 5-6.
- (c) For pH values higher than 7 the extraction decreases.

The reason for this extraction behavior can be explained by the following factors. The ability of the dissociation of the  $H^+$  ion in the SALEN molecule increases with the decrease of acidic concentration. In a strong acidic solution, the SALEN molecule is undissociated but SALEN is destroyed in a strong basic solution. The case of oxidation of Ce(III) to Ce(IV), the oxidized ability increase if decrease the concentration of  $H^+$  ion in solution. In a strong acidic solution, the oxidation potential of the redox couple Ce(III)/Ce(IV) is so high, therefore it is difficult to oxidize the Ce(III) ion. The final factor is in fact Cerium ion is hydrolyzed in basic solution.

Thus, the extraction of Cerium by SALEN is possible from solutions that have pH values as high as better.

The influence of different acids and its salts on the extraction process should be paid attention (figure IV).

The overall extraction rate depends on the oxidation of trivalent Cerium, the formation of complexes and the establishment of the extraction equilibrium. There are three factors which determine this and also determine the extraction efficiency of SALEN. There are:

- (1) - The efficiency of the contact between SALEN and Ce(III) ions.
- (2) - The oxygen transportation into the extraction system and oxygen diffusion in solution.
- (3) - The rate of formation of the extracted complexes and of the mass transportation between the two phases.

Practically, the three above-mentioned factors happen simultaneously. If air is blown constantly through the solution, it will take 30 - 40 minutes for establishing the extraction equilibrium (figure V).

Generally, when describing an extraction system, the molar ratio of the reactants must be suitable. In this system the best

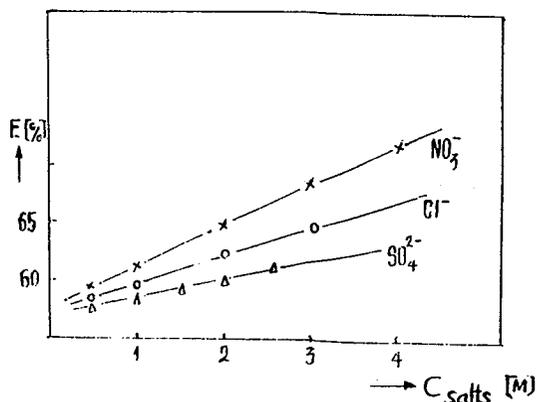


Figure IV. The influence of leaching salts on the extraction

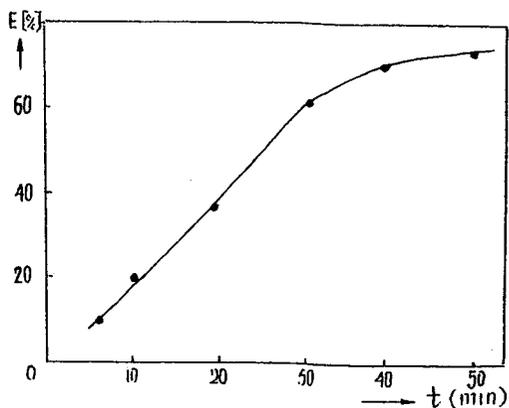


Figure V. The influence of extracting time on the extraction Ce(III) by SALEN

extraction of Cerium by SALEN occurs at a molar ratio of about 1 to 2.0 - 2.5 (figure VI).

In conclusion, we report that the conditions for extraction of Ce(III) by SALEN dissolved in organic solvent as follows:

- (1) The pH values for aqueous solution are from 5 to 6.
- (2) The aqueous phase includes nitrate ion with a total concentration is more than 3M.
- (3) The molar ratio of SALEN and Ce(III) is more than 2.5.
- (4) Air is constantly blown through the extraction system during the extraction.

Under the optimal conditions we have successfully separated Cerium from a mixture of the light R.E.E. by SALEN using air oxygen for the extraction process and hydrogen per-oxide for the re-extraction process.

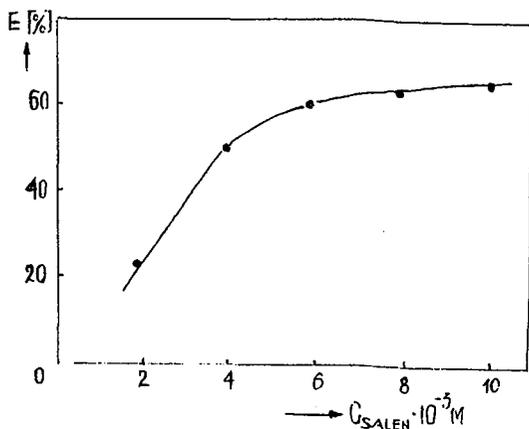


Figure VI. The molar ratio for extraction Cerium by SALEN (concentration of Ce(III) is  $10^{-2}M$ )

## OTHER OXIDATION REACTION

As mentioned before, there is another application of the SALEN - Ce(IV) chelate for oxidation processes

Firstly, there is the use of this complex in controlling oxidation of some organic compounds.

Secondly, this complex can be used as oxygen transport reagent for continuous oxidation by air. In this case, the conditions under which cycle operates must be determined.

We would like to suggest that this is a new direction for the use and application of the SALEN - Ce(IV) complex.

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## COPPER (II) EXTRACTION FROM CHLORIDE SOLUTIONS WITH MODEL HYDROPHOBIC PYRIDINECARBOXAMIDES

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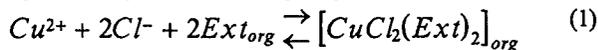
### ABSTRACT

Extraction of copper(II) from its chloride solutions at constant water activity and constant total concentrations of dissolved species with individual hydrophobic pyridinecarboxamides is studied and modelled. The extraction ability of the studied extractants changes in the following order: N-monoalkylamides > N,N-dialkylamides > N,N,N',N'-tetraalkyldiamides. The extraction is, however, still stronger when compared to pyridinecarboxylic acids esters and especially to commercial ACORGA CLX-50. Thus, there is a need to reduce extraction in order to permit stripping with aqueous solutions of low chloride concentration. The chemical model agrees well with the experimental extraction data.

### INTRODUCTION

Copper is present mainly in complex sulphide ores which can be efficiently leached by aqueous chloride solutions. The development of a new hydrometallurgical process would be a milestone in copper recovery and hydrometallurgy [Szymanowski, 1990, Szymanowski, 1993].

In 1982 ICI (now ZENECA), U.K., proposed a new extractant ACORGA DS 5443 (now ACORGA CLX-50) for copper recovery from its chloride solutions [Dalton et al., 1982, Dalton et al., 1983]. Stripping is carried out with aqueous solutions of low chloride concentration, which include hot water. The process is forced by a difference in the chloride ion concentration between extraction and stripping according to the following simplified equation:



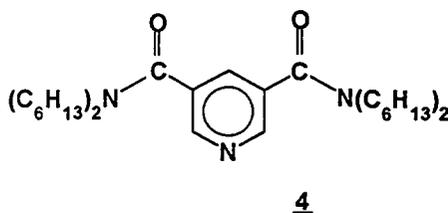
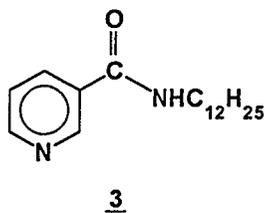
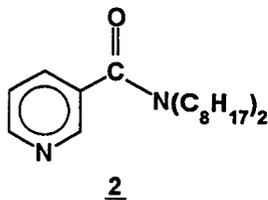
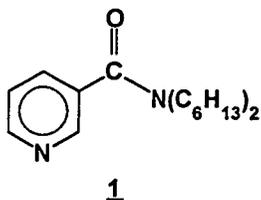
The active component of ACORGA CLX-50 is an ester of 3,5-pyridinedicarboxylic acid. Amide derivatives of pyridinecarboxylic acids were also claimed by ICI as copper extractants [Dalton et al., 1982]. Extraction properties of model N-alkyl- and N,N-dialkylpyridinecarboxamides were recently described by us [Borowiak-Resterna et al., 1993, Borowiak-Resterna, 1994]. The extraction was carried out in a typical way and the effect of reagent concentrations was studied keeping a constant ionic strength of the aqueous phase.

In other parallel work [Cote et al., 1994, Szymanowski et al., 1993] the extraction of copper from chloride solutions with esters of pyridinemonocarboxylic acids was studied. The experiments were carried out at constant water activity according to the approach developed by Ly (1984), Ly et al. (1986), Pitsch (1986), Pitsch et al. (1989), Thibaudeau (1990), Dannus (1991), Mokili (1992). The fundamentals of this approach were described in our previous work [Cote et al., 1994].

The aim of this work is to study the extraction of copper from its chloride solutions with model pyridinecarboxamides at constant water activity.

## EXPERIMENTAL

N,N-dihexyl-3-pyridinecarboxamide (**1**), N,N-dioctyl-3-pyridinecarboxamide (**2**), N-dodecyl-3-pyridinecarboxamide (**3**) and N,N,N',N'-tetrahexyl-3,5-pyridinedicarboxamide (**4**) were studied as copper extractants:



Copper(II) chloride, lithium nitrate, sodium nitrate and sodium chloride of analytical grade were used to prepare aqueous solutions of constant water activity and constant total concentration of ionic and molecular species dissolved in the aqueous solution ( $\sigma$ ). The composition of the studied aqueous solutions is given in Table 1.

**TABLE I**

Concentrations of NaCl, LiNO<sub>3</sub> and NaNO<sub>3</sub> required for obtaining a constant water activity ( $a_w = 0.8352$ ) and a constant total concentration ( $\sigma = 8.0$ ) with a variable concentration of chloride ions

[Cl <sup>-</sup> ]	NaCl	LiNO <sub>3</sub>	NaNO <sub>3</sub>
M	M	M	M
3.00	3.00	0.64	0.36
2.50	2.50	0.96	0.54
2.00	2.00	1.28	0.72
1.50	1.50	1.60	0.90
1.00	1.00	1.91	1.08
0.50	0.50	2.24	1.26
0.10	0.10	2.50	1.41
0.05	0.05	2.53	1.42
0.03	0.03	2.54	1.43
0.01	0.01	2.55	1.44

The copper(II) concentration was constant and equal to  $1.25 \cdot 10^{-2}$  M in all experiments. The total water activity was 0.8352 and the total concentration  $\sigma = 8.0$  M. The chloride concentration was changed from 0.1 M to 3 M. In all experiments, the pH of the aqueous phase was close to 3.

Toluene was used as diluent and the extractant concentration was changed from 0.07 to 0.5 M. Only in the case of **3** its concentration was 0.02 M as a result of a poor solubility of this compound.

Extraction was carried out in a typical way at room temperature using 10 cm<sup>3</sup> volumes of each phase [Borowiak-Resterna, 1994]. Copper(II) was completely stripped from the organic phase by pure water. Copper concentration was determined in the initial aqueous solutions and in the aqueous phase after extraction and after stripping by titration with EDTA or by the spectrophotometric method using sodium diethyldithiocarbamate [Borowiak-Resterna, 1994].

### RESULTS AND DISCUSSION

Figure 1 shows the effect of chloride concentration upon percentage of copper extracted in to the organic phase. For comparison, Figure 1 also contains the data obtained by Cote et al., (1994), for copper extraction with decyl nicotinate (**5**) and commercial ACORGA CLX-50 under the same experimental conditions. The obtained results imply that N,N-dialkylamides are more soluble in the organic phase than N-monoalkylamides which results in higher extractant concentrations. N,N-dialkylamides extract lower amounts of copper than N-alkylamide at comparable chloride concentrations. The extraction falls with the addition of the second N,N-dialkylamide group but is still higher than with the ester **5** and especially with ACORGA CLX-50. The change of the alkyl group length (compounds **1** and **2**) has a secondary effect upon copper extraction in comparison to the parameters presented above.

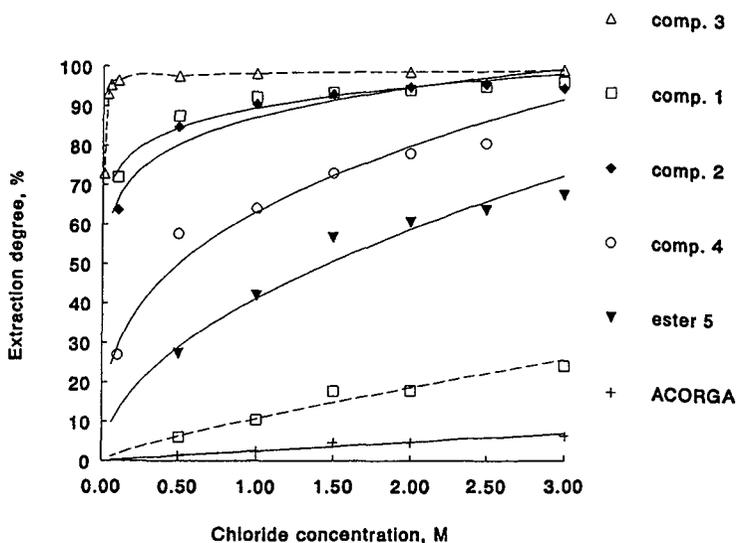


Figure 1. Copper(II) extraction from chloride solutions with hydrophobic pyridinecarboxylic acids derivatives (—,  $c = 0.2$  M; ---,  $c = 0.02$  M)

If one takes into account that extraction is followed by stripping with an aqueous solutions and the difference of the chloride concentrations in extraction and stripping is the process driving force then the extraction of copper should not be observed at a low chloride concentration, as in the case of ACORGA CLX-50. It means that the considered extractants have too high an extraction ability and thus can not be used alone without modification.

Thus, N-alkylamides should be disregarded as copper extractants and further studies should be carried out with N,N-dialkylamides, especially with N,N,N',N'-tetraalkyldiamides, e.g. compound 4 and its analogs. They contains basic nitrogen in pyridine ring and two oxygen and two nitrogen atoms capable of forming hydrogen bonds with hydrophobic alcohols (e.g., tridecanol) and alkylphenols (e.g., nonylphenol) that should depress extraction and shift the extraction curves in the region of higher chloride concentrations, as in the case of hydroxyoximes [Szymanowski, 1994].

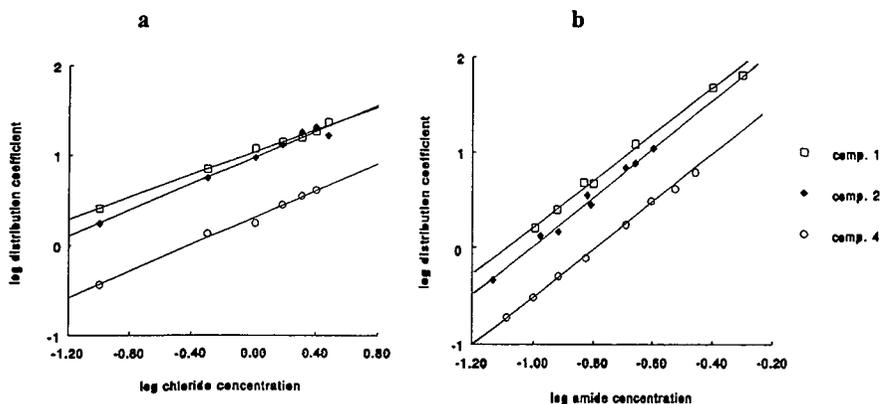


Figure 2. The influence of reagent concentration (a, chloride; b, extractant) on the copper distribution coefficient (a, amide concentration, 0.2 M; b, chloride concentration, 1 M)

Logarithmic plots of the distribution coefficient of copper(II) versus extractant concentration or chloride concentration are shown in Figure 2 (a) and (b), respectively. Approximately linear relations were obtained with large deviation of the slopes from those expected from equation 1. The slopes of  $\log D$  vs.  $\log [Cl^-]$  obtained were 0.62, 0.72 and 0.74 for copper extraction with extractants 1, 2 and 4, respectively. The slopes of  $\log D$  vs.  $\log [Ext]$  are equal to 2.34, 2.54 and 2.40 for the same compounds, respectively.

The results deviate, in the same way as those reported previously for pyridinemonocarboxylic acid esters [Cote et al., 1994]. Thus the formation of copper chlorocomplexes must also be considered



with  $i = 1$  to 4.

Using the TOT program [Rosset et al., 1991] the extraction results were analysed using equations (1) and (2), and assuming the stability constants of copper chlorocomplexes equal to  $\log \beta_1 = 0.60$  and  $\log \beta_2 = -0.40$  (Cote et al., 1994). The higher chlorocomplexes were not considered. The model agrees well with the experimental data as presented in Figure 3.  $CuCl_2Ext_2$  species are extracted in to the organic phase, while  $Cu^{2+}$  and  $CuCl^+$  dominate in the aqueous phase at the chloride concentrations considered. The extraction constants ( $\log K_{ex}$ ) obtained are 3.25, 3.13 and 2.50 for extractants 1, 2 and 4, respectively.

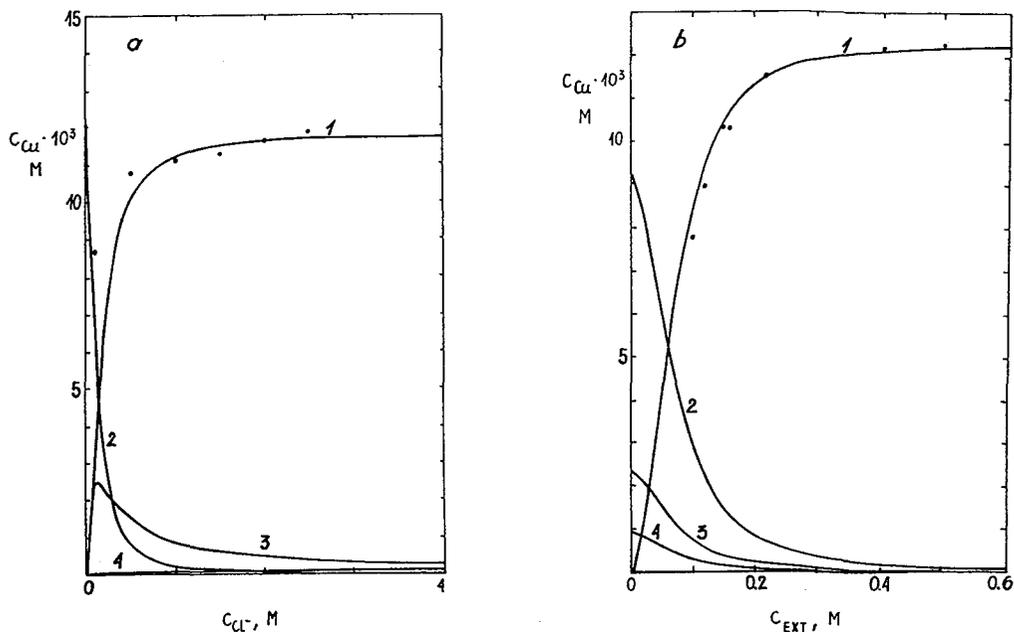


Figure 3. Effect of reagent concentration (a, chloride; b, extractant 1) upon concentration of complex (1),  $\text{Cu}^{2+}$  (2),  $\text{CuCl}^+$  (3) and  $\text{CuCl}_2$  (4) in organic and aqueous phase, respectively (a, extractant concentration = 0.2 M; b, chloride concentration = 1 M)

### CONCLUSIONS

N-monoalkylamides have a strong extraction ability and a very low solubility in the organic phase to be considered as perspective extractants for copper extraction from chloride solutions. N,N,N',N'-tetraalkyldiamides seem the most plausible from the group of amides considered. Their extraction ability must be, however, further depressed, e.g., by the addition of modifiers having a hydroxyl group capable of forming hydrogen bondings with oxygen and/or nitrogen atoms of amide groups. The results again proved the superiority of the commercial well-tailored extractant, **ACORGA CLX-50**. The chemical model agrees well with extraction results obtained at constant water activity.

### ACKNOWLEDGEMENT

The work was supported by KBN grant 1995. The authors thank the NATO for the linkage grant SA. 12-2-02 (ENVIR.LG 6940602) 5010(94) LVdC and Dr. G.Cote for fruitful discussions concerning experiment design and use of the TOT program.

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## DYNAMIC SEPARATION OF SOME d- AND f-ELEMENTS BY LIQUID-LIQUID EXTRACTION

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### ABSTRACT

On the basis of a physical model of the extraction processes for d- and f-elements by organic acids, the steps were determined which had different rates even for the substances with almost the same properties. The influence of the kinetic and transport parameters on the value of the dynamic separation coefficient and its time dependence were considered. Experimental data for the systems Pr(III), Nd(III) / di-(2-ethylhexyl)phosphoric acid (HDEHP), toluene and Co(II), Ni(II), HNO<sub>3</sub> / HDEHP, toluene were obtained, which confirm the possibility of obtaining better selectivity of separation by using kinetic factors.

### INTRODUCTION

It is known that multistage equipment is widely used in liquid extraction. Equilibrium is reached at each stage and the separation factor is determined by thermodynamic parameters which are characterized by the distribution of the components between phases. The separation factor is close to one in the case of elements which have similar properties. For example, the separation factor for Pr(III)/Nd(III) equals 1.38 in liquid extraction by a HDEHP solution in toluene (Pierce, Peck, 1963) and the separation factor for Co(II)/Ni(II) equals 1.4 (Ritcey, Lucas, 1971). However, the selectivity of the separation is strongly increased under nonequilibrium conditions. In this manuscript the influence of some factors on the value of the dynamic separation factor are considered and the results of the experimental research are given.

### THEORY

Dynamic separation of the elements which have similar properties in liquid extraction is based on the difference of the kinetic and transport parameters. In systems with organic acids as extractant several possible stages define the dynamic separation such as chemical reactions forming the salts of the extracted ion with the extractant, adsorbed accumulation of the complex and diffusion. The reaction involving successive substitution of ligands in the extracted complex ion by anions from the organic acid can occur at the interface and in the bulk phase. If the surface activity of the extractant is high, the solubility in the aqueous phase will be low, and it is more probably that the reaction will be interfacial one. Otherwise the reaction will be a bulk phase one but because of its high speed the reaction area will be near the interface. However it can proceed both on the surface and near the aqueous phase layer under the condition of finite concentrations of the extractant and the extracted elements. Salt molecules of the extracted element with the extractant also possess surface activity and are adsorbed at the interface. Their interaction among themselves and with extractant molecules results in the formation of aggregates or large particles before and phase separation takes place. The condensed interfacial film appears for compounds which are able to form polymeric metalorganic molecules

but not for cases which cannot. It takes place for instance in systems with organophosphoric acids. Molecules of the normal salt are solvated by molecules of the extractant and pass into the organic phase. The interfacial film dissipates a little near the organic phase and it is formed near the aqueous phase. The interfacial film near the aqueous phase is formed by ions of the extracted element and of the extractant molecules which diffuse through it. The thickness of the interfacial film changes however on reaching a quasiequilibrium condition but it is not zero. The generalized physical model given reflects the main details of the extraction mechanism for d- and f-elements by organophosphoric acids which were determined as a result of our investigations as well as from many investigations of other authors. We have analysed the influence of the process parameters on the value of the dynamic coefficient of separation by postulating the following possible extraction mechanisms.

a). *Extraction is accompanied by the surface reactions.*

Let the extraction of two elements proceed in an immovable two phase system which is accompanied by a fast surface reaction of pseudofirst order for the first element and a comparatively slow surface reaction of the same order for the second element. We express the dynamic coefficient of separation as follows

$$\beta = \frac{\langle C_{12}(t) \rangle}{\langle C_{11}(t) \rangle} \bigg/ \frac{\langle C_{22}(t) \rangle}{\langle C_{21}(t) \rangle} \quad (1)$$

where  $C_{ij}$  - average concentration of the  $i$ -component in the  $j$ -phase

$$\langle C_{ij}(t) \rangle = \frac{1}{l_j} \int_0^{l_j} C_{ij}(x, t) dx$$

Expressions for the average concentrations were obtained by one of the authors (1992) by means of solving the corresponding boundary problem by the method of Laplace transformation in approaching diffusion independence in following way

$$\begin{aligned} \langle C_{11}(t) \rangle &= \frac{C_{11}^0}{1 + K_1 l_0} - \sum_{n=1}^{\infty} \frac{C_{11}^0 \cdot F_4(\mu_n)}{\mu_n \cdot F_2(\mu_n)} \cdot \exp\left(-\frac{D_{11}}{l_1^2} \mu_n^2 t\right); \\ \langle C_{12}(t) \rangle &= \frac{C_{11}^0}{l_0 + 1/K_1} + \sum_{n=1}^{\infty} \frac{2 C_{11}^0 K_1 \sin \mu_n \cdot \sin \mu_{1n}}{\mu_n l_0 \cdot F_2(\mu_n)} \cdot \exp\left(-\frac{D_{12}}{l_2^2} \mu_{1n}^2 t\right); \\ \langle C_{21}(t) \rangle &= \frac{C_{21}^0 + C_{22}^0 l_0}{1 + K_c l_0} + \sum_{n=1}^{\infty} \frac{\alpha \cdot \sin \bar{\mu}_n \cdot \sin \bar{\mu}_{1n}}{\bar{\mu}_n \cdot F_6(\bar{\mu}_n)} \cdot \exp\left(-\frac{D_{21}}{l_1^2} \bar{\mu}_n^2 t\right); \\ \langle C_{22}(t) \rangle &= \frac{K_c (C_{21}^0 + C_{22}^0 l_0)}{1 + K_c l_0} - \sum_{n=1}^{\infty} \frac{\alpha \cdot \sin \bar{\mu}_n \cdot \sin \bar{\mu}_{1n}}{\bar{\mu}_n \cdot F_6(\bar{\mu}_n)} \cdot \exp\left(-\frac{D_{22}}{l_2^2} \bar{\mu}_{1n}^2 t\right), \end{aligned}$$

where  $F_2(\mu_n) = \mu_n \left[ (1 + K_1 l_0) r \cos \mu_n \cos \mu_{1n} - (K_1 + r^2 l_0) \sin \mu_n \sin \mu_{1n} \right]$

$F_4(\mu_n) = 2 K_1 \sin \mu_n \sin \mu_{1n}$ ;  $F_6(\bar{\mu}_n) = \frac{1}{2} \bar{\mu}_n \left( \frac{3 D_{21}}{l_1} + k_1 + k_2 \bar{r}^2 l_0 \right) \sin \bar{\mu}_n \sin \bar{\mu}_{1n} +$

$+(h - k_1) \cos \bar{\mu}_n \cos \bar{\mu}_{1n} + (h l_0 - k_2) \sin \bar{\mu}_n \cos \bar{\mu}_{1n} - \frac{1}{2} \bar{r} \bar{\mu}_n (k_1 l_0 + k_2) \cos \bar{\mu}_n \cos \bar{\mu}_{1n}$ ;

$\mu_{1n} = \mu_n l_0 r$ ;  $l_0 = l_2 / l_1$ ;  $\bar{\mu}_{1n} = \bar{\mu}_n l_0 \bar{r}$ ;  $\alpha = k_1 C_{21}^0 - k_2 C_{22}^0$ ;  $h = D_{21} \bar{\mu}_n^2 / (2 l_1)$ ;

$r^2 = D_{11} / D_{12}$ ;  $\bar{r}^2 = D_{21} / D_{22}$ ;  $K_c = k_1 / k_2$ ;  $\mu_n$  and  $\bar{\mu}_n$  roots of equations

$$(K_1 / r) \operatorname{tg}(\mu r l_0) + \operatorname{tg} \mu = 0, \quad \sin \bar{\mu} \cdot \left( \bar{\mu} \frac{D_{21}}{k_1 l_1} \sin \bar{\mu}_1 - \frac{k_2 \bar{r}}{k_1} \cos \bar{\mu}_1 \right) - \cos \bar{\mu} \sin \bar{\mu}_1 = 0$$

The analysis of these equations provides the main parameters influencing the value  $\beta$ . Fig.1 shows the calculated dependencies ( $\beta=f(t)$ ) for several possible values of the parameters. The complex character of the dependence attracts attention (curve 6) which shows the definite relationship between the parameters and is controlled by the difference in rate between the diffusion and the chemical processes. Other mechanisms were considered by Kizim, Tarasov, Yagodin (1980).

b). Extraction controlled by the formation of the extracted form as a result of a bulk reaction.

Suppose, that extraction of the first element is controlled by the formation of the extracted form of the element as a result of ion reaction with the extractant molecules. This will be considered as a reverse pseudofirst order reaction and the second element extraction proceeds according to the mechanism of "physical" distribution.

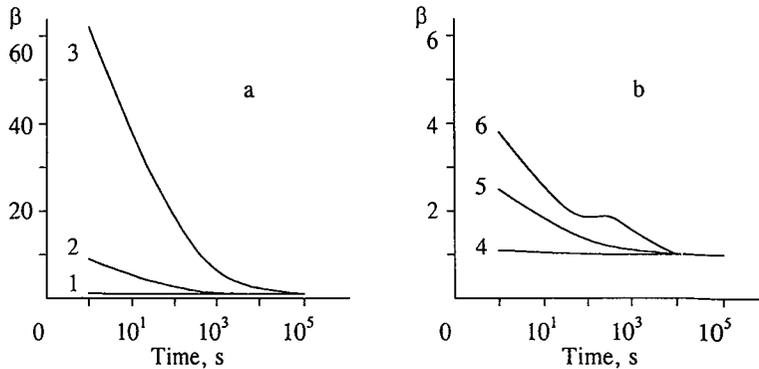


Fig. 1. The influence of the rate constant of the direct (a) and reverse (b) reactions on the dependence of the dynamic coefficient of separation with time. Calculated according to the equation (1) when:  $D_{12}=1 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ ;  $k_1, \text{ cm} \cdot \text{s}^{-1}$ :  $1 \cdot 10^{-3}$  - (1),  $1 \cdot 10^{-4}$  - (2);  $1 \cdot 10^{-5}$  - (3);  $k_2, \text{ cm} \cdot \text{s}^{-1}$ :  $1 \cdot 10^{-3}$  - (1,4);  $1 \cdot 10^{-4}$  - (2);  $1 \cdot 10^{-5}$  - (3)

The dynamic coefficient of separation in this case is expressed by the equations determined by the defining the auxiliary parameter  $a_0=r_1/\alpha_1+(1+r_1/\alpha_1)K_c$ . If  $a_0 < 1$ , then

$$\beta = a_{11} / F_1(t) \quad (2)$$

where

$$F_1(t) = 1 + a_{12}F_{11}(t) - F_{12}(t); \quad F_{11}(t) = \left[ \text{erf}((k_{12} + b_0)t)^{0.5} - \text{erf} \sqrt{b_0 t} \right] \exp(b_0 t);$$

$$F_{12}(t) = \sqrt{\pi} \cdot \text{erf} z(t) / (2a_0 z(t)); \quad a_{11} = a_2 r_{31} / (1 + r_2 / \alpha_2); \quad a_{12} = \sqrt{\pi(1 - a_0^2)} / (2a_0);$$

$$a_2 = 1 + r_1(1 + K_c) / (\alpha_1 K_c); \quad b_0 = a_0^2 k_{12} / (1 - a_0^2); \quad k_{12} = k_1 + k_2; \quad K_c = k_1 / k_2;$$

$$r_1^2 = D_{11} / D_{21}; \quad r_2^2 = D_{31} / D_{32}; \quad r_{31}^2 = D_{31} / D_{11}; \quad z(t) = \sqrt{k_{12} t}$$

The expression for another definition of  $a_0$  is given by the authors (1992). Fig. 2 represents the results of the calculation according to equation (2) with finite values for the rate constant and diffusion coefficient.

If the mutual influence of the components is not disregarded and the reaction is considered to be second order, the solution to next problem can be obtained by numeral methods. Implicit finite-difference procedures were used. For approximation of the boundary conditions the fictitious point method is used. Solving of differential equations is

carried out by the method of common iteration. Some the results of calculations are given in fig. 3.

c). *Accumulation of the substance in the interface layer.*

The accumulation of the intermediate substance at the interface, resulting in the formation of a self-generating interfacial film for the most common model of extraction in the system of two semi-limited phases with successive reactions at the interface can be described according to the equation

$$m_2(t)/C_0 = A_1\sqrt{t} + A_2\left[\exp(\varphi^2 t) \cdot \operatorname{erfc}(\varphi\sqrt{t}) - 1\right] - A_3\exp(-k_{21}t) \cdot I(t) \quad (3)$$

where  $A_1, A_2, A_3$  - some constants,  $\alpha = \varphi^2 + k_{21}$ ;  $\varphi = k_{11}/\sqrt{D_1}$ ;

$$I(t) = \int_0^t \exp(\alpha\tau) \cdot \operatorname{erfc}(\varphi\sqrt{\tau}) \cdot d\tau$$

The calculation shows that accumulation of the intermediate substance is represented by a curve with a maximum (Fig.4a). If in the process of extraction, one of the extracted elements accumulates in the interfacial layer but the other does not, dynamic separation stipulated by this difference can be important (Fig.4b).

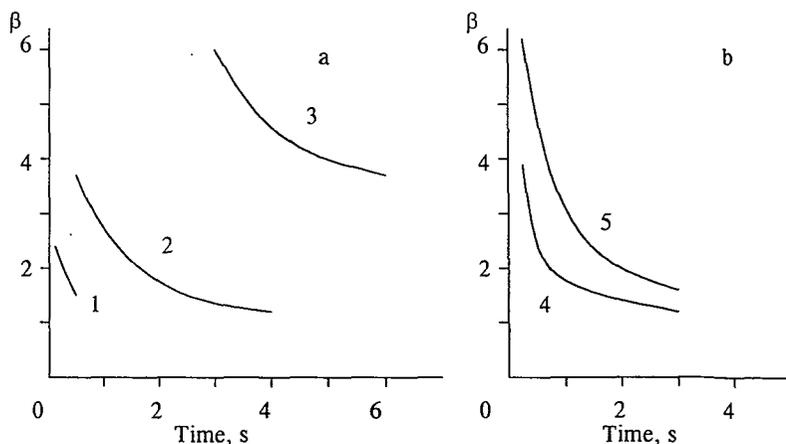


Fig. 2. The influence of the rate constant of the direct reaction (a) and the diffusion coefficient (b) of the extracted complex of the element in donor phase on the dependence of the separation coefficient with time. Calculated according to the equation (2) when  $k_{11}, s^{-1}$ : 10 - (1); 1 - (2); 0.1 - (3);  $D \cdot 10^5, cm^2/s$ : 2 - (4); 0.5 - (5).

### EXPERIMENTAL

HDEHP(grade"technic") was purified according to the method of Partridge and Jensen (1969). Toluene (grade"ch.c.") was used without additional purification. Metal salts (grade"c.") were purified by recrystallisation. The concentrations of Co(II) and Ni(II) were determined according to standard procedure by spectrophotometry or atomic absorption spectrometry using an AAS-1N. The concentrations Pr(III) and Nd(III) was determined by spectrophotometry. The experiments involving study of the dynamic separation were carried out with a Lewis-type cell and a differential a contactor, which gives a short contact time of laminar layers of aqueous and organic phases.

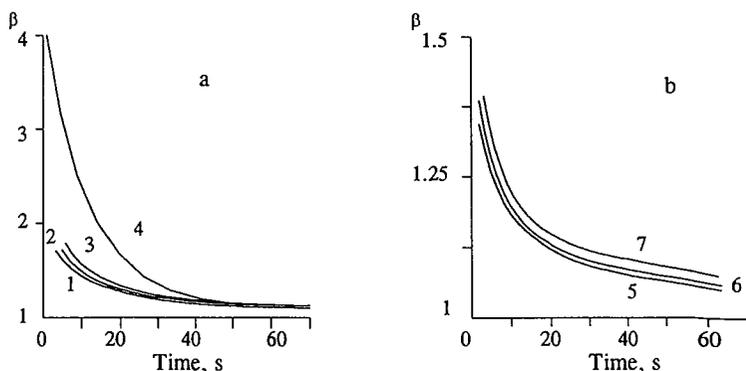


Fig. 3. The influence of the rate constants (a) and the diffusion coefficient (b) on the dependence of the dynamic separation coefficient with time. Calculated experiment. Values for the constants,  $k_1$ ,  $\text{dm}^3/(\text{mol}\cdot\text{s})$ :  $1\cdot 10^4$  - (1), (2); 1 - (3);  $k_2/k_1$ : 1 - (5-7); 5 - (1); 10 - (2); 100 - (3, 4);  $D_2/D_1$ : 2 - (5); 5 - (6); 10 - (7).

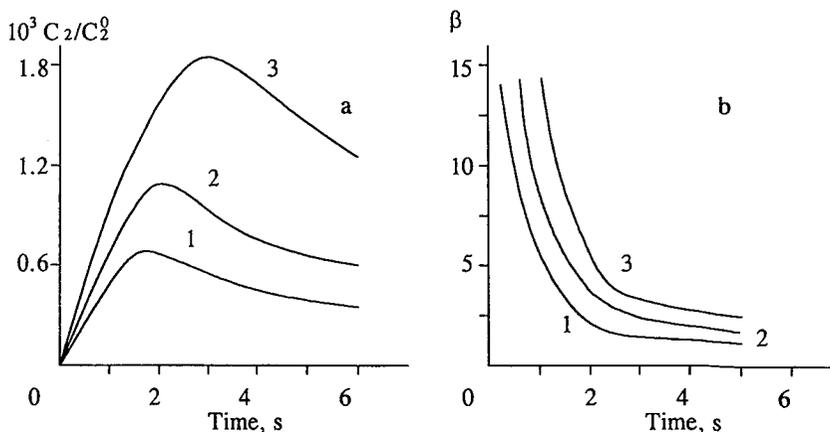


Fig. 4. Kinetics of the accumulation of the intermediate product (a) and the dependence of the dynamic separation coefficient on time (b). Calculated according to the equation (3) when  $k_{11}=3.16\cdot 10^{-3}$   $\text{cm}^2/\text{s}$ ;  $D_1=1\cdot 10^{-5}$   $\text{cm}^2/\text{s}$ ;  $k_{21}$ ,  $\text{s}^{-1}$ : 2-(1); 1 - (2); 0.5 - (3).

### RESULTS AND DISCUSSION

Investigations of the extraction kinetics for  $\text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$  by HDEHP dissolved in toluene showed that reducing the time of phase contact increases the difference in their rates of extraction, and was used for improvement of their separation. The efficiency of the dynamic separation was determined according to the extent of enrichment of the organic phase. The increase of the separation efficiency is determined by the decreasing of concentration  $\text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$  in the initial solution, and by increasing of extractant concentration (fig.5). Reduction of acidity decreases the separation effect.

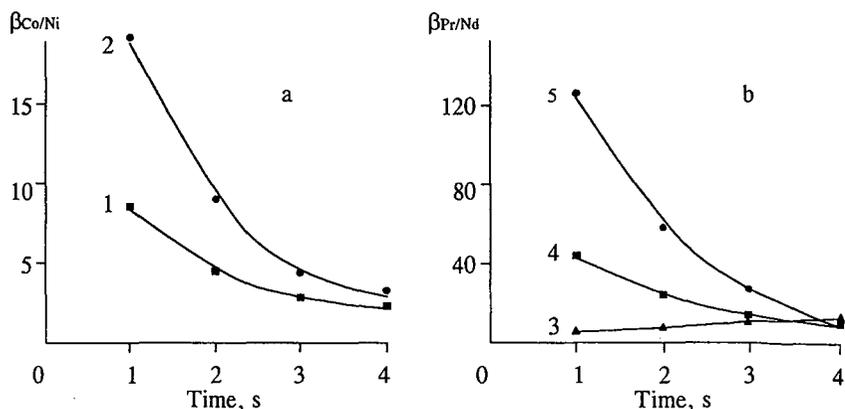


Fig. 5. The influence of the concentration of the metal salt (a) and the extractant (b) on the dynamic coefficient of separation.  $C_{Co(II)}$ ,  $C_{Ni(II)}$ , M: 0.09-(1); 0.18-(2);  $C_{HDEHP}$ , M: 0.3-(3); 0.6-(4); 1.2-(5).

When interpreting the effect of the dynamic separation we took into account the formation of the interfacial film and we came to the conclusion that the model with accumulation reflects best the observed effects. The reason for primary accumulation of Ni(II) in the interfacial layer is due of its high tendency to hydrolyse which is confirmed by us by the calculation of the ion forms according to Butler (1973). In the system Pr(III), Nd(III), HCl,  $H_2O/HDEHP$ , toluene for laminar fluidity of the layers of the aqueous and the organic phases the effect of dynamic separation is observed for the phase contact time of 1-5 s. Fig.5 gives the experimental data, obtained for the system at high extractant concentration. As it is seen, the dynamic separation coefficient can be 20-50 times higher than at equilibrium.

### NOMENCLATURE

erf(x) integral of calculus probability (-)  
 K equilibrium constant (-)  
 $\alpha$  local coefficient of distribution (-)

### SUPERSCRIPTS

o initial state  
 - another component

### SUBSCRIPTS

i ordinal component (phase)  
 n number of root

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## A NEW PROCESS FOR COPPER RECOVERY IN A Gold Refinery

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### ABSTRACT

A survey has been carried out to select a suitable hydroxyoxime reagent to extract copper from a leach solution of the calcine obtained from the sulphating roasting of gold containing sulphide ores. The behaviours of the extraction and stripping of copper, iron and other impurities in the leach solution have been investigated both at the bench scale and in counter-current experiments in mixer-settlers. An extraction-electrowinning process has been suggested, which ensures a better copper recovery and purity, and in particular ensures, no harm for the cyanidation of gold and silver in the copper leach residue.

### INTRODUCTION

Gold concentrates with a high content of chalcopyrite and pyrite are treated in a large gold refinery in east China by a process including sulphating roasting, leaching and cementation of copper with iron scraps from the calcine, and cyanidation of gold and silver from the copper leach residue. The discharged solution from the cementation usually contains 0.3g/L to 0.7g/L of copper and more than 10g/L of iron. Copper powder contains only about 70% of copper is produced and the powder is shipped to a copper refinery to refine. A solvent extraction-electrowinning process has been developed to recover copper from the leach solution to replace the cementation, and the results shows that new process has higher recovery for copper and better efficiency than the existing one. Selections of extractants and diluents, and optimisation of conditions for extraction and stripping have been carried out, and the difference between the process used in the gold refinery and the ordinary copper plant has been discussed.

### EXPERIMENTAL

The LIX reagents were kindly supplied by Henkel Corporation, and have been used as received. In bench experiments, aqueous solutions were prepared with A.R. reagents according to the composition of the leach solution in the gold refinery and partly with leach solution from the gold refinery. The concentrations of metals were determined by both chemical analysis and atomic absorption. Counter-current test was carried out in a battery of mixer-settler units with the calcine leach solution. The dimensions of the mixer was 60mmX60mmX70mm and the size of the settler was 2.5 times of that the mixer.

## RESULTS AND DISCUSSION

### Comparison of The Extractants

Although copper solvent extraction has been widely practised in the copper industry[Zhu,1986] its use in gold refinery requires taking into account some differences compared to the ordinary copper solvent extraction plant. In copper processes, the raffinate is usually recycled to leach copper from ores or other raw materials and to reuse the acid generated during solvent extraction. A litter contamination of the raffinate by the organic solvent usually does not cause a serious problem for copper leaching. In a gold refinery after leaching of copper, the residue is subjected to cyanidation of gold and silver. To avoid any risk of harming the cyanidation of gold and silver, the raffinate should discharge directly, instead of recycling to leach the calcine. Accordingly, in order to reduce the loss of copper, the concentration in the raffinate should be as low as possible.

The extraction abilities of LIX 860(5-dodecylsalicylaldoxime), LIX 84(2-hydroxy-5-nonylacetophenone) and LIX 622 (dodecylsalicylaldoxime and tridecyl alcohol) have been compared according to data offered by the producer. LIX 84 was the weakest extractant because of the weaker complexation ability with copper of the ketoxime compared to the aldoxime. On the other hand, copper is easier to strip from the loaded phase than from the other reagents and under the same stripping conditions, the copper remaining in the barren organic phase is much less, therefore, the net transfer of copper is higher in a extraction and stripping circuit.

### Mixture of The Reagents

When copper was extracted with a mixture of a total concentration of 20%(v/v) of LIX 84 and LIX 860 in different ratios, the extraction of copper was increased proportionally with the amount of LIX 860, the aldoxime, as shown by Curve 1 in Fig.1. It was demonstrated that there was no synergism between the two reagents upon extraction of copper, each one took part in the extraction reaction independently, and the total extraction was the sum of the contributions of the two reagents. On stripping copper from the loaded mixed solvents with a 150g/L sulphuric acid solution, the amount of stripped copper increased with the amount of LIX 84 in the mixture, as shown by Curve 2 in Fig.2. The mixed solvent also had good extraction and stripping kinetics and selectivity for copper over iron. The copper concentration in the calcine leach solution varied between 6g/L to 10g/L and there were quite high concentrations of iron, both ferrous and ferric, and minor amounts of zinc, lead, manganese, aluminium, magnesium, calcium and other impurities.

The concentration of copper in the discharged raffinate was designed to be lower than 0.1g/L, thus a reagent with a higher net transfer ability which could be stripped with a lower concentration of sulphuric acid was more suitable for the process. LIX 84 mixed with a little aldoxime LIX 860 was adopted, which has a high enough selectivity for copper over iron.

### Effect of Diluent

It has been reported that the effect of different diluents on the extraction of copper by hydroxyoxime has the following order[Van der Zecuw, 1975]:

branched chain alkane > n-alkane > cycloalkane > aromatic hydrocarbons

The extraction of copper with LIX 84 in different diluents has been compared. Under the same condition and taking the extraction ability of the extractant in sulphonating kerosine as 1.00, then in *n*-octane it was 0.995, in kerosine 0.984, in cyclohexane 0.958 and in xylene 0.835. Addition of xylene to kerosine had a negative effect on the extraction ability of LIX 84, the results of the investigation is shown in Table 1.

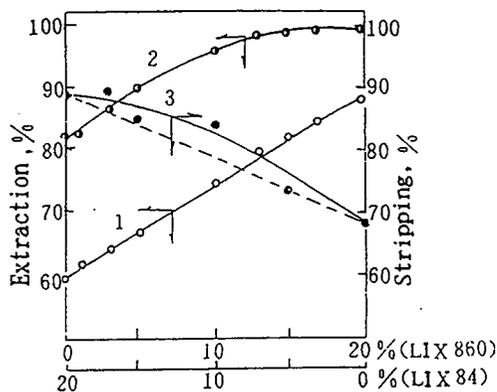


Fig. 1 Extraction of copper with mixture of hydroxyoximes  
 1 Cu = 12.14g/L, pH = 2.0  
 2 Cu = 6.21g/L, pH = 2.0  
 3 H<sub>2</sub>SO<sub>4</sub> = 150g/L

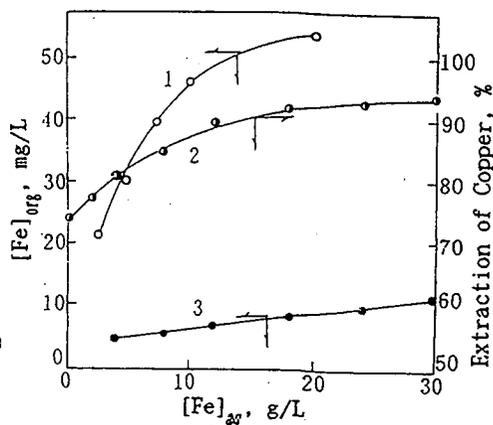


Fig. 2 Extraction of ferric iron and its effect on the extraction of copper  
 1 pH = 2.0  
 2, 3 Cu = 8.16g/L, pH = 2.0

Table 1  
 Effect of xylene on the extraction

Xylene, %	20	40	60	80	100
Extraction, %	75.8	72.4	71.0	66.9	64.3

Although xylene did not benefit the extraction, it favoured phase separation, which was also reported by other researchers [Yoshizuka 1990]. A 20%(v/v) solution of LIX 84 in kerosine containing a small amount of aromatic hydrocarbon was used in the following experiments. The extraction and stripping kinetics and phase separation speed were also satisfied for the process.

### Extraction of Copper

A hydroxyoxime can extract copper at low pH values (about 0.5), but during extraction two hydrogen ions are released into the aqueous solution. Since the initial concentration of copper in the feed solution in the present research was much higher than that in ordinary ore leach solutions in the copper industry, and a lower copper concentration in the raffinate was demanded, a lower acidity in the initial solution was necessary. The isotherm with the true calcine leach solution containing 7.25g/L of copper and 7.10g/L of iron at pH 1.5 was obtained, which revealed that the raffinate could be lower

than 0.1g/L of copper by using three stage of extraction with a phase ratio of 1/1, according to the McCabe-Thiele plot. The copper recovery was expected to be 3-5% higher than that of the iron cementation process currently used in the gold refinery.

### Behaviours of Impurities and Their Effect on The Copper Extraction

Table 2 is the typical composition of the leach solution in the gold refinery. Ferric iron is the main impurity which might interfere with the extraction of copper, Curve 1 in Fig. 2 shows the extraction of Fe(III) and only about 20mg/L of iron was extracted when the concentration Fe(III) was as high as 20 g/L in the aqueous solution.

The copper extraction increased with an increase of the concentration of ferric iron in the solution as shown by the Curve 2 in the figure. The extraction of copper was 75% when there was no Fe(III) in the solution and 94% when there was 30g/L of Fe(III). This might be caused by a "salting out effect". The copper loaded organic phase contained 5mg/L to 11mg/L of iron (Curve 3), which was much lower than that in the case of the aforesaid pure iron extraction.

**Table 2**  
Composition of the calcine leaching solution

Element	Cu	Fe	Zn	Mn	Si	Al	Ca	Mg	Pb	Cr
Conc..g/L	7.16	3.00	1.63	0.12	0.12	0.48	0.55	0.69	0.0087	0.0011

Ferrous iron had a weaker effect on the extraction of copper than ferric iron. When the feed solution contained 15g/L of ferrous iron and 6.75g/L of copper at pH 2 the extraction of copper was about 84%, and under the same conditions, without Fe(II), copper extraction was 82%. For solutions containing copper and both ferric and ferrous iron, when the concentration of ferrous iron was 9.3g/L, and copper was 5.93g/L and Fe(III) 5.81g/L, the extraction of copper was 93%, which was similar to that when there was no Fe(II) present. This fact again demonstrates that ferrous iron has no obvious influence upon the extraction of copper. The concentration of iron in the organic phase was from 10mg/L to 30mg/L, or in other words, the distribution coefficient of iron was at the order of  $10^{-3}$ , therefore the separation factor of copper over iron was greater than 2000. The coexistence of ferric and ferrous iron in the calcine leach solution would not cause any problem for the recovery of copper from the solution.

Zinc, calcium, magnesium and aluminium virtually were not extracted at pH 2. For example, for contacting solutions containing zinc from 0.5g/L to 15g/L with the same volume of the 20% of LIX 84 solvent only about 2mg/L of zinc was detected in the organic phase.

### Stripping of Copper

Stripping of copper from the loaded organic phase was almost proportional to the concentration of the acidity of the strip solution when the acidity was lower than 1mol/L (about 100g/L) of sulphuric acid, but it deviated as the acidity increased, as shown by Curve 1 in Fig.3.

As expected, the stripping of copper would be depressed by the copper in the strip solution, Line 2 in Fig.3 shows that stripping decreased with increase in the concentration of copper in the

aqueous strip solution. With a strip solution containing 20g/L to 30g/L of copper and 150g/L of sulphuric acid, the stripping of copper was 92% to 94%. In a solvent extraction-electrowinning process the barren electrolyte from the tank house usually contains 20g/L to 30g/L of copper. In this case a concentration of 170g/L to 190g/L of sulphuric acid is needed to strip about 99% of the copper from the loaded organic phase in one stage.

Fig.4 Curve 1 is the stripping isotherm which shows that with a solution containing 31g/L of copper and 150g/L of sulphuric acid with a suitable phase ratio, copper can be enriched to 50g/L in two stages. Curve 2 shows that copper in the barren organic phase can be lowered to 0.05g/L in three stages, which can surely lower the copper concentration in the raffinate to less than 0.1g/L.

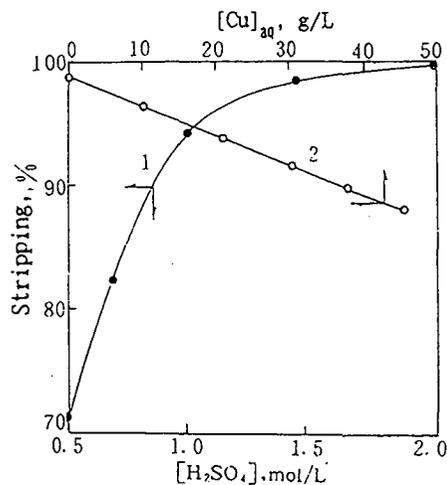


Fig.3 Effect of acidity and concentration of copper on stripping  
 organic phase: Cu = 6.20g/L  
 aqueous phase: 1 H<sub>2</sub>SO<sub>4</sub>, Cu = 0  
 2 H<sub>2</sub>SO<sub>4</sub> = 150g/L

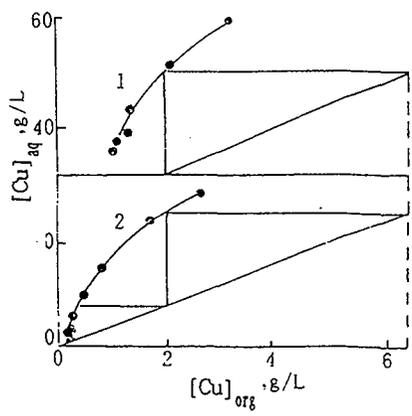


Fig.4 Isotherm of stripping  
 organic phase: Cu = 5.52g/L  
 aqueous phase: 1 Cu = 31.62g/L  
 H<sub>2</sub>SO<sub>4</sub> = 150g/L  
 2 H<sub>2</sub>SO<sub>4</sub> = 150g/L  
 Cu = 0g/L

**Counter-Current Test**

a counter-current test has been carried out in a battery of mixer-settler units with three stage extraction and two stage stripping. Calcine leach solutions containing different concentration of copper and iron were used as the feed and a 20% LIX 84/kerosine(v/v) solution as the organic phase. Adjusting the feed solution to about pH 2, copper could be lowered to 0.1g/L in the raffinate. Therefore, the recovery of copper was higher than 98%, and the separation factor of copper over iron was more than 1000 in all extraction runs. The stripping solution was a synthetic electrolyte containing 20g/L to 30g/L of copper and 180g/L of sulphuric acid and it resulted in a pregnant copper solution higher than 50g/L, which is suitable for electrowinning of copper. The accumulation of iron in the stripping solution was about 0.1g/L to 0.2g/L in every stripping run, which was much higher than that in the shaking

experiments and was caused by entrainment of the feed into the organic phase. It is necessary to bleed part of electrolyte to remove iron, thereby to ensure the quality of the cathode copper and the plating efficiency.

#### **ACKNOWLEDGMENTS**

This work was supported by Chinese National Foundation of Nature Sciences.

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## EQUILIBRIUM AND MODELLING FOR THE METAL EXTRACTION OF YTTERBIUM AND YTTRIUM INTO P507-KEROSENE FROM HYDROCHLORIC ACID SOLUTIONS

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### ABSTRACT

Mathematical models for the extraction of Yb(III), or Y(III) - HCl by P507(20%,v/v) in kerosene have been developed based on the equilibrium data using the double-variable form of

$$C_{org} = f(C_{aq}, [H^+])$$

Using the final model of

$$C_{org} = (A[H^+] + B) * C_{aq}^{C[H^+] + D}$$

to predict the metal concentration in the organic phase, the deviations between the experimental data and the predicted values are +4.6% for Yb and +4.0% for Y respectively

### INTRODUCTION

Modeling for metal extraction has been reported by many authors (refer to Table 1). The most important factors affecting the extraction equilibrium for an acidic extractant system are the metal concentration in aqueous phase,  $C_{aq}$ , and the aqueous acidity. The extractant concentration usually is in excess. The modeling in the form of  $C_{org} = f(C_{aq}, [H^+])$  for the system of Yb(III) - HCl- P507 -Kerosene and Y(III)-HCl-P507 -Kerosene is reported in this paper.

TABLE 1  
Modeling examples for metal extraction

function	equation	system
$y=f(x)$	$y=A_1A_2x/(1+A_2x)$ $y=A_3x^{A_4}$ $y=A_1A_2x/(1+A_2x)+A_3x^{A_4}$ notes: $A_1$ - $A_4$ , parameters; $x$ , metal aqueous concentration; $y$ , metal organic concentration.	$\text{Cu}^{2+}$ - $\text{H}_2\text{SO}_4$ -Lix64N, [4] $\text{CoSO}_4$ - $\text{Na}_2\text{SO}_4$ -Cyanex272 -kerosene $\text{NiSO}_4$ - $\text{Na}_2\text{SO}_4$ -Cyanex272 -kerosene [1,2]
$y=f(x_1, x_2)$	$D=A_1I^{A_2}Y_H^{A_3}$ notes: $I$ , ion strength; $Y_H$ , concentration fraction of HCl; $D$ , distribution ratio. $D^{-1}=(A_1e^{A_2[H]}-A_3)+(A_4+A_5[H])[M]$ $[H]$ , acidity of aqueous feed; $[M]$ , equilibrium metal concentration of aqueous phase	$\text{DyCl}_3$ -HCl-P204-kerosene [3] $\text{Er}(\text{or Tm})$ -HCl-P507 -kerosene [6]
$y=f(x_1, x_2, x_3)$	$y=A_1[M]A_2[H^+]^{A_3}(L_0-A_4y)^{A_5}$ $[M]$ , $y$ , metal concentration of aqueous and oil phase; $L_0$ , initial P204 concentration; $[H^+]$ , equilibrium acidity.	$\text{YCl}_3$ -HCl-P204-Amsco [5]

### EXPERIMENTAL

$\text{Yb}_2\text{O}_3$ , or  $\text{Y}_2\text{O}_3$ , with purity higher than 99%, was dissolved in HCl and diluted to a definite concentration.

P507, industrial extractant, supplied by Shanghai Institute of Organic Chemistry of Academia Sinica, containing (2-ethylhexyl) phosphonic acid mono-(2-ethylhexyl) ester about 95%, was dissolved in kerosene on a volume basis.

The metal concentration in the aqueous phase after equilibration (phase volume ratio 1:1) was analysed by EDTA titration. The organic concentration was calculated by difference.

## RESULTS AND DISCUSSION

### I. Extraction Isotherm

The extraction isotherms for the systems of P507( 20%, v/v) in kerosene - Yb(III) in HCl (0.1-2.0 mol/L) and P507(20%) - Y(III) in HCl(0.1-1.0 mol/L) at 298K in a phase volume ratio of 1:1 are shown in Fig.1 and 2 respectively.

Considering the following four semi-empirical models:

- 1). Langmuir absorption equation:  $y=A_1A_2x/(1+A_2x)$  (1)
- 2). Freundlich absorption equation:  $y=A_3x^{A_4}$  (2)
- 3). The combination of above two:  $y=A_1A_2x/(1+A_2x)+A_3x^{A_4}$  (3)
- 4). Redlich-Petterson equation:  $y=A_1A_2x/(1+A_2x^{A_3})$  (4)

We obtained the parameters listed in table 2 by a best fit least squares method for the extraction of Yb.

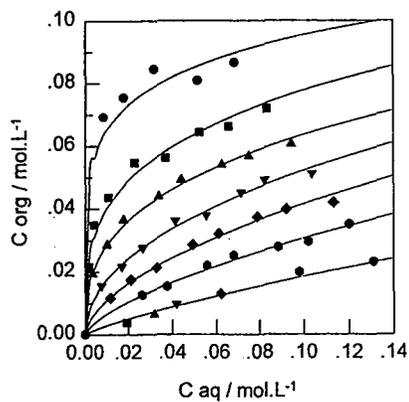


Fig.1. extraction isotherm of Yb(III)  
The lines, from the top to the bottom, [HCl] are 0.1, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0 mol/L respectively

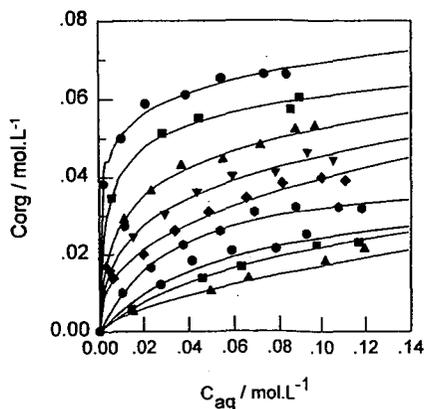


Fig.2. extraction isotherm of Y(III)  
The lines, from the top to the bottom, [HCl] are 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 mol/L respectively

TABLE 2

Parameters in the modeling equations for the system of Yb( III)  
in HCl(0.1-2.0 mol/L) - P507(20%) in kerosene

equation	[H <sup>+</sup> ]	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	SSR*
(1)	0.1	0.07455	2246			2.120e
	0.5	0.06611	270.9			5.417e
	0.75	0.05974	109.7			7.104e
	1.0	0.06073	36.75			5.888e
	1.25	0.06097	18.60			1.796e-3
	1.5	0.06614	8.500			2.025e-3
	2.0	0.06238	4.198			1.737e-2
(2)	0.1			0.1396	0.1654	3.607e-3
	0.5			0.1503	0.2869	5.215e-3
	0.75			0.1413	0.3477	5.956e-4
	1.0			0.1553	0.4749	1.044e-3
	1.25			0.1569	0.5786	1.206e-3
	1.5			0.1416	0.6664	1.955e-3
	2.0			0.1174	0.8050	1.650e-2
(3)	0.1	-0.2336	0.9673	0.1698	0.1943	2.962e-3
	0.5	3.344	-0.1147	0.2542	0.3714	3.350e-3
	0.75	8.347	0.7307	-7.507	1.151	4.292e-2
	1.0	0.4898	4.264	-1.575	1.196	1.754e-2
	1.25	0.06098	18.60	-9.480	19.19	1.796e-3
	1.5	0.06692	8.317	22.14	8.209	2.035e-2
	2.0	0.4299	0.8374	-0.2216	1.177	1.714e-2
(4)	0.1	0.1381		0.8377		3.599e-3
	0.5	0.1034	290.5	0.8494		1.540e-3
	0.75	0.1232	212.3	0.7123		2.306e-4
	1.0	0.1544	963.6	0.5288		1.041e-3
	1.25	0.1181	16.10	0.6423		4.278e-4
	1.5	0.1183	6.943	0.6117		1.868e-3
	2.0	0.1316	5.290	0.2787		1.654e-2

\* SSR=  $[(Y_{\text{cal}} - Y_{\text{exp}}) / Y_{\text{exp}}]^2 / N$ , where  $Y_{\text{exp}}$  is the experimental data of the metal concentration in organic phase,  $Y_{\text{cal}}$  is calculated value, and N is the number of the data point.

The result indicates that the models (3) and (4) are better than (1) and (2), see Fig.3.

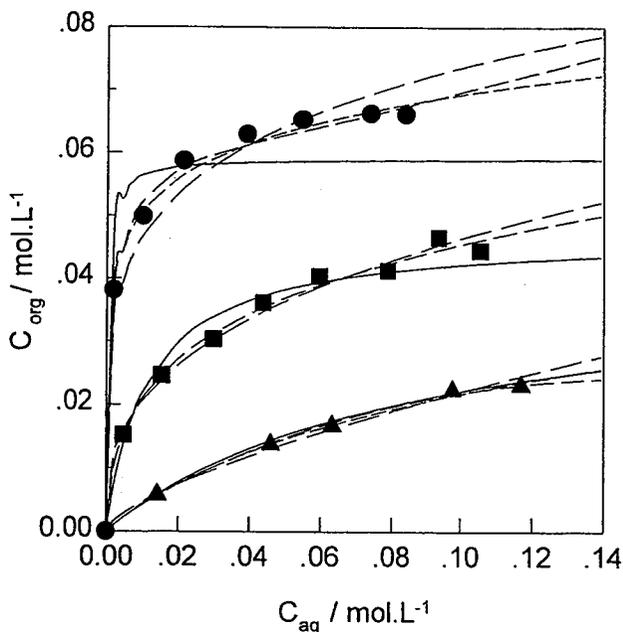


Fig.3. Comparison of the four models by fitting with the experimental data for the extraction of Y(III)  
 ●  $[H^+]=0.1\text{mol/L}$ , ■  $0.4\text{mol/L}$ , ▲  $0.8\text{mol/L}$   
 — eq.1, - - eq.2, - - - eq.3, - · - eq.4

## II. The Model of Two Variables

The model with two variables (metal concentration of aqueous phase and acidity) has an important practical value because it is difficult to keep the acidity constant in the extraction performance. It was found that there is a simple relationship between acidity and the parameters in equations (1) and (2) but not in (3) and (4) although they have a better fit.

The relationship has the following form for the two extraction systems respectively:

For the extraction of Y:  $A_1 = -0.03128[H^+] + 0.06159$  (5)

$\log A_2 = 3.251[H^+]^2 - 5.871[H^+] + 3.719$  (6)

$A_3 = -0.04747[H^+] + 0.1261$  (7)

$A_4 = 0.5981[H^+] + 0.1321$  (8)

For the extraction of Yb:  $A_1 = -0.006604[H^+] + 0.07031$  (9)

$\log A_2 = 0.4631[H^+]^2 - 2.453[H^+] + 3.581$  (10)

$A_3 = 0.005127[H^+] + 0.1431$  (11)

$A_4 = 0.3666[H^+] + 0.1084$  (12)

Comparing Langmuir and Freundlich absorption equations, the latter give the best result. The final models selected are:

For Yb:  $C_{org} = (0.005127[H^+] + 0.1431) \cdot C_{aq}^{0.3666[H^+] + 0.1084}$  (13)

For Y:  $C_{org} = (-0.04747[H^+] + 0.1261) \cdot C_{aq}^{0.5981[H^+] + 0.1321}$  (14)

The deviations between experimental data and predicted values are  $\sigma = 4.6\%$  for Yb and  $4.0\%$  for Y respectively.

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## EXTRACTION OF METALS WITH TETRAOCTYLALKYLENEDIAMINES

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### INTRODUCTION

It is known (Gibalo I. M., 1976) that alkylenediamines  $R_2N(CH_2)_nNR_2$  ( $n = 2, 4, 6$ ) substituted with lower alkyls have an affinity to form complexes with metal salts because of the presence of two donor nitrogen atoms in their molecules. Compounds of this type with longer hydrocarbon radicals have low solubility in water and good compatibility of their complexes with organic solvents which are necessary for extractants (Gibalo I.M., 1976; Semenov V.A., 1984). For example, extraction of Cu, Co and U with some tetraoctylenediamines from hydrochloric solutions has been studied (Breer J.G.H., 1984; 1985).

### RESULTS AND DISCUSSIONS

In the present paper, the results of indium, bismuth, zinc, iron and gold extraction with solutions of tetraoctylalkylenediamines  $(C_8H_{17})_2N(CH_2)_nN(C_8H_{17})_2$  where  $n = 2$  (tetraoctylethylenediamine -TOEDA),  $n = 4$  tetraoctylbutylenediamine-TOBDA) and  $n = 6$  (tetraoctylhexylenediamine - TOHDA) in benzene are reported.

The dependencies of indium distribution coefficients on the initial  $Cl^-$  ion concentration in the extraction with diamines and tri-n-octylamine (TOA) solutions in benzene from aqueous sulphate-chloride solutions at constant  $H_2SO_4$  and indium concentrations are shown in Fig. 1. As it is shown in Fig. 1, the largest values of the indium distribution coefficients take place for TOHDA as an extractant in which the nitrogen atoms are situated at the longest distance from each other. The extraction ability of diamines increases regularly in accordance with an increase in the number of methylene substituents between the nitrogen atoms. Moreover, when the  $Cl^-$  ion concentration in the aqueous phase is increased for a series of diamines placed according to their increasing extraction ability, TOEDA and TOBDA change their places. One can assume these effects may be caused by various mechanisms of indium extraction with the particular extractants. The number of amine molecules associated with the extracting compounds have been determined from the tangents of the slope for straight lines in  $\lg D - \lg C_{Am}$  plots and were equal to 2,0 for TOA and 1,0 for tetraoctylalkylenediamines.

The dependencies of zinc and iron distribution coefficients on the initial concentration of the  $Cl^-$  ion in extraction with a 5% diamine solution in benzene are shown in Fig. 2. For iron as well as for indium, maximum extraction takes place when TOHDA is used as an extractant and is minimal for TOEDA while zinc extraction follows the opposite order. In this case, zinc is extracted into the organic phase as complex compounds which contain two molecules of an extractant in extraction with TOEDA and one molecule with TOBDA and TOHDA. On the contrary, iron forms organic phase complex compounds with one extractant molecule for TOEDA and two molecules for TOBDA and TOHDA.

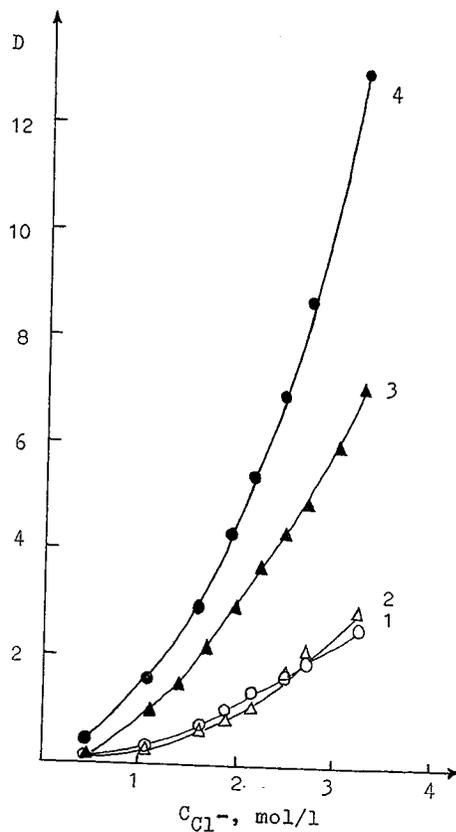


Figure 1. Indium distribution coefficient dependence on  $Cl^-$  ion concentration in extraction with 5% solutions: 1 - TOEDA, 2 - TOBDA, 3 - TOA, 4 - TOHDA in benzene.  $C_{H_2SO_4} = 0,5$  mole/l,  $C_{In} = 9 \cdot 10^{-3}$  mole/l.

Gold was extracted with diamines from chloride solutions containing thiourea (Thio). It was rather well extracted with all three tetraoctylalkylenediamines at low Thio concentrations that may be due to an anion - exchange mechanism involving the  $[AuCl_4]^-$  ion. At Thio concentrations  $> 0,05$  mole/l in aqueous solution, gold is reduced to the mono-valent state and is not practically extracted with TOBDA and TOEDA while TOHDA extracts gold into the organic phase in a marked degree. At low Thio concentrations, the distribution coefficients of gold (Fig. 3) increase for all the diamines with increase of the  $Cl^-$  ion concentration in the aqueous phase. Moreover, the  $\lg D_{Au}$  dependence on  $C_{Cl^-}$  has a different character in extraction with TOEDA than in systems with TOBDA and TOHDA. The dependencies of gold extraction into the organic phase on the extractant concentration at  $C_{Thio} = 0,05$  mole/l have an anomalous character. For TOBDA and

TOHDA, these dependencies are curves with a maximum while, in case of TOEDA, the extraction of gold increases at first and then remains at 100%. For this concentration of 0,3 mole/l in the initial aqueous solutions, the  $\lg D_{Au}$  dependency on

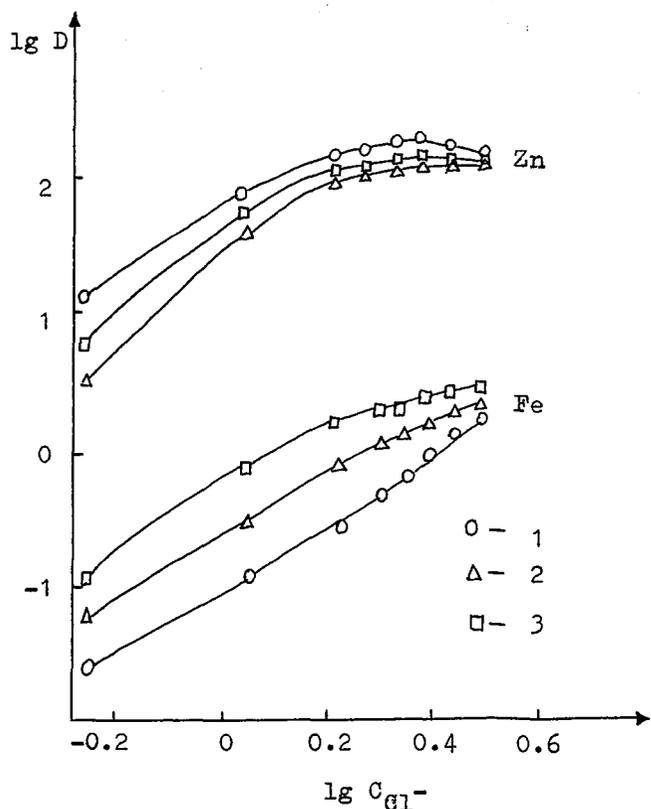


Figure 2. Zinc and iron distribution coefficients dependencies on  $Cl^-$  ion concentration in extraction with 5% solutions: 1 - TOEDA, 2 - TOBDA, 3 - TOHDA in benzene.  $C_{H_2SO_4} = 0,5$  mole/l,  $C_M = 1,5 \cdot 10^{-2}$  mole/l.

the extractant concentration in bilogarithm co-ordinates has a linear character. The slope for this dependency in the case of TOHDA approaches 2 while, in case of TOEDA and TOBDA, approaches 1.

In contrast to indium, zinc, iron and gold, the extraction of bismuth with diamines from chloride solutions is characterized by a decrease of the bismuth distribution coefficient with increase in the  $Cl^-$  ion concentration. All these facts show that metal extraction with diamines does not follow a common regular behaviour. One of the reasons may be that diamines have the ability to extract metal complex compounds of various compositions. In order to determine the composition of the metal complexes, IR - spectra of extracts containing indium, zinc and iron and the UV - spectra of bismuth, iron and gold extracts have been analysed.

The comparison of the IR - spectra of indium extracts with those for amine salt solutions allows us to conclude that, in the case of TOA and TOHDA,  $[InCl_4]^-$  anions

are present in the organic phase. This conclusion is based on the presence of absorption bands with a maximum at  $332\text{ cm}^{-1}$  and the peak at  $320\text{ cm}^{-1}$  corresponding to the valent vibration of In-Cl bonds in the slightly distorted octahedral  $[\text{InCl}_4]^-$  ion. These absorption bands are absent in the spectra of indium extracts with TOEDA and TOBDA. Nevertheless, the IR - spectra of indium extracts with TOEDA, TOBDA and TOHDA in contrast to the TOA extracts have absorption bands of valent vibrations associated with In - N and C - N bonds. These facts allow to suggest that TOEDA and TOBDA extract indium as the complex  $[\text{InCl}_3(\text{R}_2\text{NR}'\text{NR}_2)]$  while for

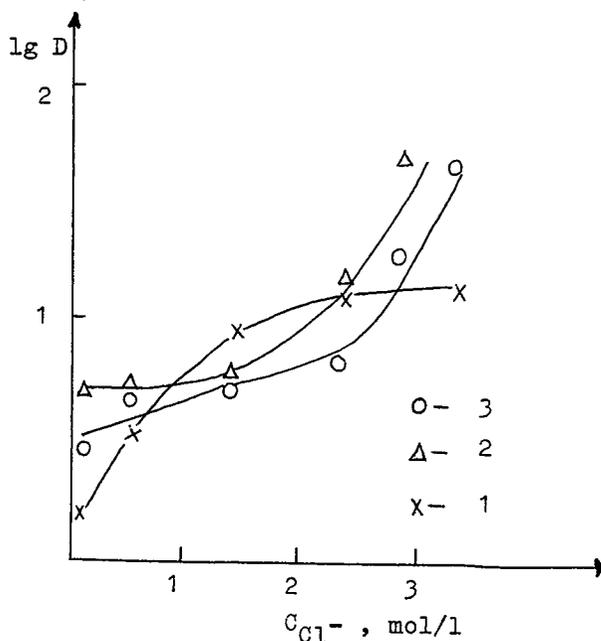


Figure 3. Gold distribution coefficient dependence on NaCl concentration in extraction with 5% solutions: 1 - TOEDA, 2 - TOBDA, 3 - TOHDA in benzene.  $C_{\text{Thio}} = 0,05$  mole/l,  $C_{\text{Au}} = 5 \cdot 10^{-3}$  mole/l.

TOHDA both indium complex compounds present in organic phase that may explain its maximum extraction.

Different extraction nature of TOBDA and TOA explains different modifier influence on metal extraction. In the system with TOA and methyl-hexylketone (RO)  $\lg D_{\text{In}}$  for  $C_{\text{RO}} < 2C_{\text{TOA}}$  increased linearly with  $\lg C_{\text{RO}}$  increase but for  $C_{\text{RO}} > 2C_{\text{TOA}}$  the indium distribution coefficient did not depend on the ketone concentration. In the system with TOBDA a different ketone influence on  $\lg D_{\text{In}}$  took place when  $C_{\text{RO}} = 4C_{\text{TOBDA}}$ . In the initial part of the dependence with  $C_{\text{RO}} < 4C_{\text{TOBDA}}$ , the distribution coefficient did not depend on the RO concentration while for  $C_{\text{RO}} > 4C_{\text{TOBDA}}$  it increased linearly with  $C_{\text{RO}}$  increase ( $C_{\text{TOA}}$ ,  $C_{\text{TOBDA}}$ ,  $C_{\text{RO}}$  - initial concentrations). IR- and UV- data show zinc, bismuth, gold and iron presence as  $[\text{ZnCl}_4]^{2-}$ ,  $[\text{BiCl}_5]^{2-}$ ,  $[\text{AuCl}_4]^-$  and  $[\text{FeCl}_4]^-$  anions in the organic phase in the extraction with diamines. As

for zinc and iron, the complexes  $[\text{ZnCl}_2\cdot\text{TOBDA}]$ ,  $[\text{ZnCl}_2\cdot\text{TOHDA}]$ ,  $[\text{FeCl}_3\cdot\text{TOBDA}]$  and  $[\text{FeCl}_3\cdot\text{TOHDA}]$  are formed as well.

Hence, depending on the hydrocarbon chain length between the nitrogen atoms, the diamines extract metal complex compounds with various ratios of extractant : metal that may explain the absence of a clear trend among TOEDA, TOBDA and TOHDA towards to various metals.

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## SYNERGISTIC EXTRACTION OF IRON(III) FROM AQUEOUS SULPHURIC ACID SOLUTIONS, A VIABLE ALTERNATIVE TO JAROSITE PRODUCTION

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### ABSTRACT

The extraction of iron(III) from sulphate solutions using alkyl phosphoric acids and a primary amine was studied.

The use of a two-level factorial design was helpful to define the solvent composition.

The experimental results show that the presence of the primary amine - Primene JMT (T alkyl primary amines) - in the solvent phase (DEHPA (di(2-ethylhexyl) phosphoric acid) or MEHPA (2-ethylhexyl acid phosphate) and 2-octanol in Shellsol T) promotes the stripping process. The best results concerning the recovery of iron were obtained with the mixture DEHPA and JMT. The isotherm curves equilibrium reveal that the increase in the acid concentration in the range studied (9-30g/l H<sub>2</sub>SO<sub>4</sub>) drastically decreases the efficiency of the extraction.

The single drop method was used in order to evaluate the extraction kinetics. The experiments were carried out with a mixture of DEHPA and JMT. The temperatures range studied was 298-333 K. The results indicate that the kinetics of the process depends very much on the temperature and the process is kinetically controlled, the activation energy being about 83 kJ/mol.

### INTRODUCTION

Nowadays, most of the hydrometallurgical zinc producers use the Jarosite process (Dutrizac,1980; Pammenter,1981) to remove iron from leach solutions. The predominance of this process over the goethite (Boxal,1986) or hematite (Ropenack,1986) process is related to its lower operational costs. The main drawback in the use of precipitating techniques is associated with the co-precipitation of other metal ions (Dutrizac,1984) (Zn, Ag, Ga, Ge, etc.) present in the solutions. The production of contaminated residues that are difficult to recover, is a major complication.

The use of solvent extraction techniques has been pointed out as an alternative to the precipitation process. The most promising iron extractants are included in the class of organophosphorus (Demopoulos,1984,1989,1993) and Versatic (Agatzini,1986; Stefanakis,1987) acids. An extensive number of studies involving these extractants have been published. The common problem in the use of these solvents is related to difficulties in the stripping process (Demopoulos,1984,1989; Collier 1986; Majima1985). Demopoulos(1984) noticed that the recovery of iron from loaded DEHPA could only be accomplished with a 6 M hydrochloric acid medium. However, due to a degradation problem the solvent can not be in contact with this solution over a long period. The recovery of ferric iron has also difficult when the extractant used was MEHPA (Demopoulos,1989). The best results (60% Fe(III) stripped) were obtained using 6 M hydrochloric acid containing 0.25 M of Na<sub>2</sub>SO<sub>4</sub>. The hydrolytic stripping (Demopoulos,1989) of MEHPA was also tried. The precipitated iron compound is not of pigment quality and cannot be used as such. Agatzini(1986) and Stefanakis (1987) have extensively studied the iron extraction using Versatic acids. Several techniques sulphuric acid stripping(Collier,1986), hydrolytic stripping(Thorsen,1980; Teixeira,1983; Monhemius,1983; Doyle-Garner,1985), precipitation stripping(Collier,1986; Thorsen,1980; Doyle-Garner,1985) have been proposed to recover the ferric ion from the loaded solvent phase. However, none of these have proven to be satisfactory.

More recently, Chen(1992) proposed to use mixed solvents to overcome the stripping problems. The mixtures tested (Amine with DEHPA, DEHPA with trialkyl phosphine oxide, amine with monoalkylphosphoric acid) allow the use of less concentrated stripping solutions (0.5M H<sub>2</sub>SO<sub>4</sub>). This paper presents equilibrium and kinetic studies for iron extraction using the mixture of DEHPA and the primary amine - Primene JMT.

### EXPERIMENTAL

#### Reagents

The extractants used were DEHPA (di(2-ethylhexyl) phosphoric acid), MEHPA - IONQUEST 2EHAPO<sub>4</sub> (2-ethylhexyl acid phosphate) (Albright, Wilson) and a primary amine - Primene JMT (T alkyl primary amines) (Rohm and Haas). The modifier used was 2-octanol and the diluent was ShellSol T (Shell). The aqueous solutions were prepared using analytical grade chemical reagents.

#### Procedure

The equilibrium experiments were carried out at a controlled temperature (298 K) using a mechanical shaker to mix the aqueous and the organic phases during 24 hours in separatory funnels. The concentrations of iron (III) in both the organic and aqueous phases were directly analysed using atomic absorption spectrophotometry. The acid solutions were titrated with NaOH using Mg-EDTA as complexing agent for iron (Rolia, 1984).

Kinetic studies were carried out using the single drop method (Whewell, 1975).

### RESULTS AND DISCUSSION

The equilibrium experiments were designed by the aid of a two level factorial method. The parameters studied were the concentrations of DEHPA, Primene JMT and 2-octanol and the response analysed was the iron recovered from the loaded organic phase, which was determined by:

$$\frac{\text{loading capacity of solvent (g/l)}}{\text{residual iron after stripping (g/l)}}$$

The stripping step was carried out at 298 K using a solution with 50 g/l of H<sub>2</sub>SO<sub>4</sub> and a phase ratio (A(aqueous)/O(organic)) of two. Other experimental conditions are presented in table 2.

Table 2 - Range of variables for factorial design

	Range
a - [PRIMENE JMT]	2 - 18 % (v/v)
b - [DEHPA]	5 - 35 % (v/v)
c - [2-Octanol]	5 - 35 % (v/v)

Table 3 - Results of factorial experiments

Fact. design code	capacity of solvent phase [Fe] (g/l)	iron recovered from organic phase (g/l)
1	5.38	5.12
a	14.1	11.4
b	28.8	12.1
ab	37.5	18.8
c	3.67	3.67
ac	13.8	13.2
bc	27.4	20.7
abc	31.6	19.4

The statistical analysis of the results obtained shows that the significant effects (>95% confidence level) are:

- 1 - [DEHPA] - positive
- 2 - [JMT] - positive
- 3 - Interaction DEHPA - JMT - negative
- 4 - Interaction JMT - 2-Octanol - positive

The optimum concentration of reagents ( DEHPA - 40.5% , JMT- 27.5 % , 2 -octanol - 22%) was achieved using the steepest slope method. The latter composition leads to recovery of 21.9 g/l of iron from the organic phase. When the mixture has a composition in the middle range (20% DEHPA, 10% JMT and 20 % 2-octanol) the iron removed decreases to 17.5 g/l. Despite the benefits for extraction by increasing the parameters, the values of the viscosities of the organic phase became prohibitive. This physical constraint leads to the use of a solvent with medium composition.

#### Influence of acid concentration

The extraction of iron (III) from aqueous solutions was realised at different concentrations of sulphuric acid with DEHPA and JMT at 298 K. The results are shown in Figure 1. It can be observed that the extraction of iron decreases with the increase in the acid concentration.

Liberation of acid was noticed during experiments. This fact, in addition to the existence of sulphate complexes which are predominant Magini(1979) in sulphate media, suggest the following reaction of extraction:

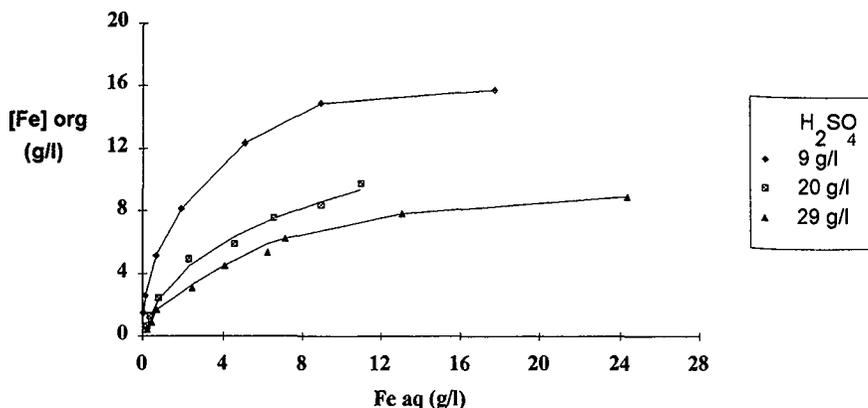
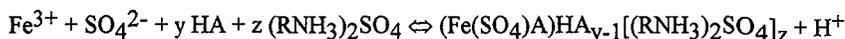


Fig. 1 - Equilibrium isotherm curves at different sulphuric acid concentration. Organic phase - 20% DEHPA, 10% JMT, 20% 2-Octanol in Shellsol, T=298 K.

#### Comparative study between the use of DEHPA and MEHPA

The promising results obtained with the mixture of DEHPA and JMT led us to test another alkyl phosphoric acid - MEHPA. The equilibrium isotherm curves (extraction and stripping) for both mixtures are presented in figures 2-3. The results obtained show that the mixture of MEHPA and JMT has a higher loading capacity than the mixture of DEHPA and JMT. However the stripping of

Fe (III) from the loaded organic phase - MEHPA and JMT with sulphuric acid (50 g/l) is not satisfactory. Despite the presence of the amine favouring the stripping step, the iron content is not reduced below ~5.5 g/l. The substitution of MEHPA by DEHPA favours this process (Fig. 3).

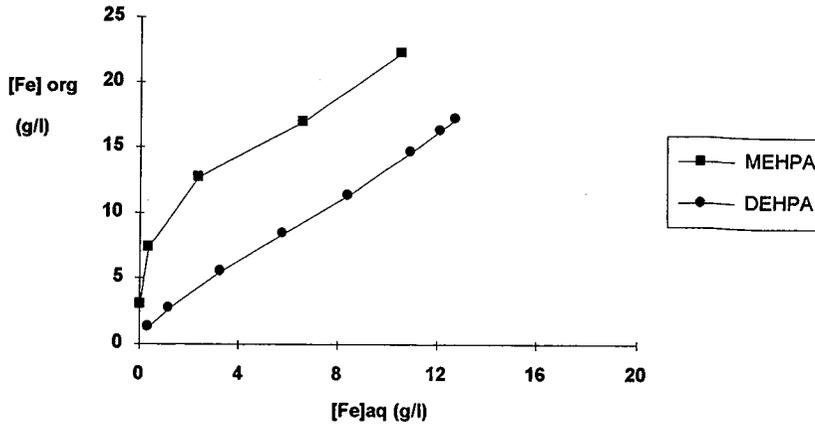


Fig. 2 - Equilibrium isotherm curves for iron (III) extraction. Organic phase - 20% DEHPA or MEHPA, 10% JMT and 20% 2-Octanol in Shellsol T. Aqueous phase -  $Fe^{3+}=13.9$  g/l, pH=1.35. T=298 K

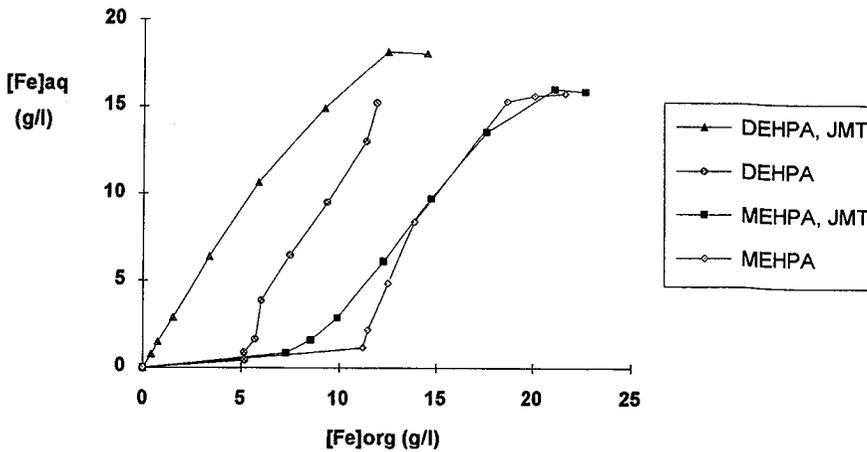


Fig. 3 - Equilibrium isotherm curves for iron (III) stripping. Effect of addition of amine on Fe(III) stripping by sulphuric acid solution (50 g/l). Organic phase - 20% DEHPA or MEHPA, 0% or 10% JMT and 20% 2-Octanol in Shellsol T. T=298 K

### Kinetic studies

A set of experiments, using the mixed tank method, were carried out to analyse the influence of 2-octanol on the kinetics of extraction and stripping of iron using 20%DEHPA-10%JMT in Shellsol T Ismael (1994). It was concluded that the presence of this modifier makes the kinetics of extraction process more difficult, but improves significantly the kinetics of the stripping process. These facts led us to conclude that the amount of 2-octanol must be optimised according to the equilibrium and kinetic studies.

In this work, we decided to proceed with a mixture containing 20% of modifier. This concentration of alcohol allows to reach the equilibrium time for the stripping process within 5 minutes which makes the use of a column possible. However the extraction is very slow (equilibrium time > 30 min.) and should be carried out at higher temperatures (50°C) in mixer settlers.

The single drop method was used to determine the extraction rates of iron (III) with the mixture DEHPA and JMT over a temperature range of 298-343K. When the temperature studied was 298 K and the residence time was 15 s no mass transfer was detected. The results obtained at higher temperatures - 313-343 K - are presented in figure 4. It can be concluded that the rates of the extraction of iron depend very much on the temperature. This dependence is expressed by the Arrhenius equation  $V_o = K'_o e^{-E/RT}$ . The activation energy (E) calculated for iron extraction assumes the value of 83 kJ/mol, which is a characteristic value for a chemical controlled process.

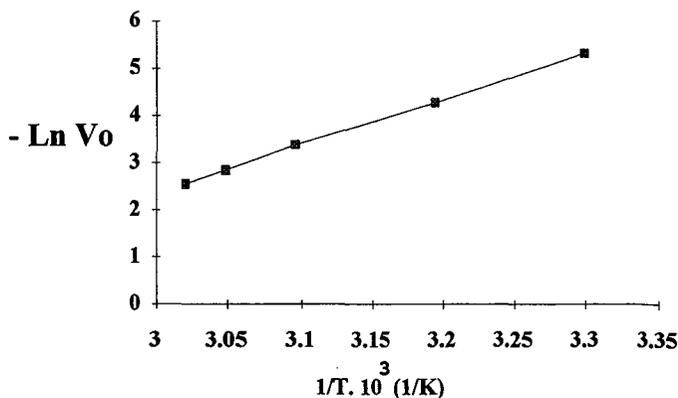


Fig. 4 - Influence of temperature on initial rate for the extraction of iron. Organic phase : 20% DEHPA , 10% JMT and 20% 2-Octanol in Shellsol T. Aqueous phase -  $Fe^{3+}$ - 13.9 g/l, pH=1.35

### CONCLUSION

This work demonstrates that is possible to use the synergistic mixture - DEHPA and PRIMENE JMT - to recover iron from leach solutions. The results obtained show that is possible to use a solution containing 50 g/l of sulphuric acid to strip the loaded organic phase. The results previously published in the literature pointed toward the use of an 500g/l of  $H_2SO_4$  to recover the ferric ion from loaded DEHPA.

The kinetic studies for the extraction of iron with the mixture DEHPA-JMT shows that this process is very dependent on the temperature. The activation energy associated with iron extraction is

83kJ/mol. From this value it can be concluded that the chemical reaction is the controlling step of the extraction process.

#### ACKNOWLEDGEMENTS

The authors would like to acknowledge the help of Shell (Portugal), Rohm and Haas (France) and Albright & Wilson (U.S.A.), for kindly supplying us respectively Shellsol T, Primene JMT and DEHPA-MEHPA.

Thanks are due to Engs. Margarida Colaço, Nuno Mantas and Remigio Machado for their valuable help in carrying out part of the experimental program.

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## SOLVENT EXTRACTION OF TETRAVALENT TERBIUM Tb(IV) AND OTHER TRIVALENT RARE EARTHS WITH QUATERNARY AMINE

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### ABSTRACT

The differences between the solvent extraction of Tb(IV) and trivalent rare earth periodate complexes with quaternary ammonium compound were studied. The effects of extractant concentration, form of the anion in the extractant, diluent, phase volume ratio and pH of the aqueous phase on the extraction of Tb(IV) and Tb(III) were investigated. Distribution ratios and separation factors were calculated. Separation and preconcentration of terbium from mixture of terbium and yttrium using oxidation and solvent extraction method are reported.

### INTRODUCTION

No work has yet been reported on the solvent extraction of tetravalent terbium (IV) from aqueous solution, because of the high standard reduction potential of the Tb(IV) (+3.1v. vs. normal hydrogen electrode) as it can easily be reduced in aqueous solution. Nevertheless, we recently found that the potential can be lowered to +0.68v. (vs. NHE) in  $\text{KIO}_4$  - KOH alkaline complex solution. Tb(IV) can be formed by oxidation of Tb(III) periodate complex with  $\text{O}_3$ ,  $\text{K}_2\text{S}_2\text{O}_8$  or irradiating under ultraviolet ray at wavelength of 366nm [Su Qiang(1989)]. The Tb(IV) formed by method of oxidation is greater than 98%, and is rather stable in this alkaline media. It can be extracted by quaternary ammonium salt  $\text{R}_3\text{CH}_3\text{NX}$  where R is a mixed alkyl group containing  $\text{C}_8$  -  $\text{C}_{10}$  carbons and X is an anion in different form ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  or  $\text{OH}^-$ ).

In general, complexation ability and extractibility of cation of higher valency state are higher than its lower valency state as it is well known that tetravalent Ce(IV) can easily be separated from other trivalent rare earths by solvent extraction. In this paper, it was also found that the extractibility of Tb(IV) is higher than other trivalent rare earth metals. The experimental data and conditions for the extraction of the Tb(IV) periodate complex are reported.

### EXPERIMENTAL

#### Preparation of the Rare Earth(RE) Complex Solutions

The RE periodate complex solutions were prepared by adding RE nitrate solution to a  $\text{KIO}_4$ -KOH solution and mixing under vigorous stirring.  $\text{Ce}^{3+}$  can be oxidized into tetravalent Ce(IV) by  $\text{KIO}_4$ -KOH during preparation.

The complex solution containing Tb(IV) was prepared by oxidizing the Tb(III) periodate with  $\text{O}_3$  with constant stirring at room temperature. The percent of Tb(IV) obtained was about 98% and a red-brown solution was obtained.

### Extractant

A quaternary ammonium salt  $N_{263}$  ( $R_3CH_3NCl$ , tricaprylmethylammonium chloride, corresponding to Aliquat 336) produced from Dalian Chemical Plant (Dalian, China) was selected as the extractant. Sulphonated kerosene, cyclohexane, heptane and octane were used as diluent. In order to improve the solubility of  $N_{263}$  in the diluent, 5% (vol.%) 1-octanol was added.

To convert the chloride form of the extractant  $N_{263}(Cl)$  into other form, it was treated with an equal volume of an aqueous salt solution containing anion in the other form.

### Extraction Procedures

Except for the phase volume ratio experiments, 20 ml organic phase and 20 ml aqueous phase of pH 13 were added to a separatory funnel. It was shaken mechanically at temperature between 10-15°C. The experimental results showed that the extraction equilibration was reached within 10 minutes. The shaker was then stopped and two phases were allowed to settle. A portion of the aqueous phase was removed and analyzed.

### Analytical Methods

The RE concentration in aqueous phase was analyzed by complexometric titration with EDTA. Before titration the periodate must be decomposed with  $NH_2OH \cdot HCl$  and  $H_2O_2$  successively and the  $I_2$  was removed by evaporation.

The content of periodate and the degree of oxidation of the terbium were analyzed with iodimetry.

## RESULTS AND DISCUSSION

### Comparison of the Extraction Yield(E%) of Tetravalent $Ce^{4+}$ and $Tb^{4+}$ with Trivalent RE

In these experiments, the concentration of RE and  $KIO_4$  in the starting aqueous phase at pH 13.0-13.1 were  $4 \times 10^{-3}$  M and 0.06 M, respectively. The molar ratio between periodate and terbium ( $C_I/C_{Tb}$ ) is 15. The extractant used is in the carbonate form: 25%  $N_{263}(CO_3)$ -8% 1-octanol-kerosene. The variation of %E with atomic number of RE and the comparison of %E of tetravalent  $Ce^{4+}$  and  $Tb^{4+}$  with trivalent RE and  $Y^{3+}$  are shown in Fig. 1.

It can be seen that 100% of  $Ce^{4+}$  and 93.2% of  $Tb^{4+}$  are extracted in this system. But the %E of  $Y^{3+}$  and  $Dy^{3+}$  are only 33.2% and 40.2%, respectively. The difference in the extraction yield(%E) between tetravalent and trivalent RE is quite large, so, this extraction system can be used to separate  $Ce^{4+}$  or  $Tb^{4+}$  from other trivalent RE.

From this result, it was decided to use the complex solutions of Tb(III) and Tb(IV) as the aqueous phase to study the extraction conditions in more detail.

### Effect of Extractant Concentration

In these experiments, the concentrations of Tb(III) and Tb(IV) in the aqueous phase are  $6 \times 10^{-3}$  M.

$C_I/C_{Tb} = 15.2$ .  $pH=12.9$ . The extractant used is in the  $OH^-$  form:  $N_{263} (OH)^-$ -- 5% 1-octanol--sulphonated kerosene. The results of extraction yield (%E), distribution ratio ( $D=C_{Tb(org.)}/C_{Tb(aq.)}$ ) and separation factor  $\beta (=D_{Tb(IV)}/D_{Tb(III)})$  between tetravalent and trivalent terbium are listed in Table 1. As the degree of oxidation is slightly less than 100%, the values of %E and D in b columns are smaller than the real values of pure Tb(IV). This is because included in the values are not only the contribution of Tb(IV), but also of Tb(III) which had not been oxidized and coexists with Tb(IV) in the complex solution. The listed separation factor  $\beta$  is slightly less than the real separation factor between Tb(IV) and Tb(III).

When the concentration of extractant used is higher than 25%, it takes a longer time to separate the phases into two layers. Therefore, an extractant concentration of 25% was chosen for the experiments described in the following sections.

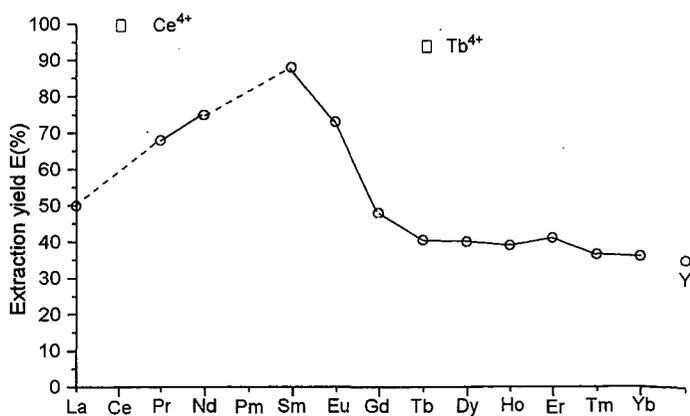


Figure 1. Comparison of the extraction yield(E%) of tetravalent  $Ce^{4+}$  and  $Tb^{4+}$  with trivalent rare earths and Y

TABLE 1  
Effect of extractant concentration on extraction of Tb  
(a) before oxidation and (b) after oxidation

Extractant concentration(vol%)	E(%)		D		$\beta$
	a	b	a	b	
20	43.6	71.7	0.773	2.53	3.27
25	47.9	74.3	0.919	2.89	3.14
30	56.4	82.1	1.29	4.59	3.56
35	60.2	86.2	1.51	6.25	4.14
40	72.5	95.1	2.64	19.4	7.35

#### Effect of Phase Volume Ratio

The extractant used was in the  $OH^-$  form: 25%  $N_{263} (OH)^-$ --5% 1-octanol--sulphonated kerosene.

The aqueous phase a and b used were the same as those shown in the previous section.

The results were listed in Table 2. When the phase ratio is 0.25, the aqueous phase turns slightly cloudy after extraction. With increasing phase ratio, the separation factor gradually increases.

#### Effect of The pH Value of The Aqueous Phase

The  $\text{OH}^-$  form extractant used was the same as that in the previous section. The concentrations of Tb in the aqueous phase (a) and (b) were  $6.08 \times 10^{-3}$  M and  $6.15 \times 10^{-3}$  M, respectively.  $C_I/C_{Tb} = 15.6$ .

As shown from the results listed in Table 3, %E, D and  $\beta$  all decrease with increasing pH value of the aqueous phase.

**Table 2**  
Effect of phase volume ratio on extraction of Tb  
(a) before oxidation (b) after oxidation

Phase volume ratio	E(%)		D		$\beta$
	a	b	a	b	
0.25	32.1	43.6	1.89	3.09	1.63
0.50	35.0	52.3	1.08	2.19	2.03
1	47.9	74.3	0.92	2.89	3.14
2	71.9	98.2	1.28	27.3	21.3

**TABLE 3**  
Effect of pH value of the aqueous phase on extraction of Tb  
(a) before oxidation (b) after oxidation

pH		E(%)		D		$\beta$
a	b	a	b	a	b	
13.2	13.2	55.1	69.5	1.23	2.28	1.85
13.56	13.51	48.4	62.7	0.94	1.68	1.79
13.85	13.85	42.4	45.9	0.74	0.85	1.15

#### Effect of The Diluent

Different diluents were used to prepare the  $\text{OH}^-$  form extractants: 25%  $\text{N}_{263}(\text{OH})$ --5% 1-octanol--diluent. The concentrations of Tb in the aqueous phase (a) and (b) were  $6 \times 10^{-3}$  M, pH=12.9,  $C_I/C_{Tb} = 14.9$ . The results are listed in Table 4.

Toluene and xylene can not be used as diluents because they may reduced the Tb(IV). For cyclohexane and heptane, the time needed for clean phase separation is too long, its takes more than 40 minutes. Sulphonated kerosene is the best diluent, because it has higher separation factor and the time needed for clean phase separation is less than 5 minutes.

**TABLE 4**  
Effect of the diluent on extraction of Tb  
(a) before oxidation (b) after oxidation

Diluent	E(%)		D		$\beta$
	a	b	a	b	
Cyclohexane	45.9	75.0	0.85	3.00	3.54
Heptane	51.9	65.0	1.08	1.86	1.72
Octane	54.7	68.3	1.21	2.15	1.78
Kerosene (sulphonated)	47.9	74.3	0.92	2.89	3.14

**Effect of The Different Form of Extractant**

Seven forms of the extractants [25%  $N_{263}$  (X)--5% 1-octanol--sulphonated kerosene] shown in Table 5 were used. The concentration of Tb in the aqueous phase (a) and (b) were  $6 \times 10^{-3}$  M, pH = 12.9,  $C_T/C_{Tb} = 14.9$ .

As shown in Table 5, distribution ratios (D) of both tri- and tetra- valent terbium increase with the extractant form in the order of  $NO_3^- < Cl^- < SO_4^{2-}$ . This indicates that the replacement of these anions by Tb complex anion becomes easier in that order.

**TABLE 5**  
Effect of the extractant form on extraction of Tb  
(a) before oxidation (b) after oxidation

Extraction from X	E(%)		D		$\beta$
	a	b	a	b	
$IO_4^-$	51.7	74.7	1.07	2.95	2.76
$OH^-$	47.9	74.3	0.92	2.89	3.14
$SO_4^{2-}$	23.3	43.6	0.30	0.77	2.54
$CO_3^{2-}$	15.5	50.5	0.18	1.02	5.54
$HCO_3^-$	10.5	46.5	0.12	0.87	7.43
$Cl^-$	2.39	11.7	0.024	0.13	5.54
$NO_3^-$	0.34	1.19	0.004	0.012	3.00

This result is in line with the fact that the affinity of these anions(X) for the extractant decreases in the order of  $NO_3^- > Cl^- > SO_4^{2-}$ .

The stability of the Tb(IV) complex anion in the various forms of extractants is different. Tb(IV) complex anion can maintain its tetravalent state in red brown color for about 40 minutes in the periodate form of the extractant, but for about 20 min. in the  $OH^-$  and  $CO_3^{2-}$  form of the extractants, and less than 10 min. in the other four forms of the extractants.

For the periodate and  $OH^-$  form of the extractants, the extraction yields are higher, but the

separation factors are lower. For the  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  form of the extractants, the separation factors are higher, and the extraction yields are high. Tb(IV) complex however, can maintain its tetravalent state in the  $\text{CO}_3^{2-}$  form of the extractant for a longer time than in the  $\text{HCO}_3^-$  form of the extractant. Therefore, from the separation point of view, the  $\text{CO}_3^{2-}$  form of the extractant is probably the best choice.

### Separation of Tb and Y

As shown in Fig.1, the extraction yield of  $\text{Y}^{3+}$  is similar to other trivalent yttrium group ions ( $\text{Tb}^{3+}$  --  $\text{Yb}^{3+}$ ), therefore, we chose  $\text{Y}^{3+}$  as a representative of yttrium group to prepare the feeds. The feeds containing 0.09 M  $\text{KIO}_4$  and various mole percentage of Y and Tb were oxidized by ozone at pH 13.0. And then they were extracted by the carbonate form of the extractant: 25%  $\text{N}_{263}(\text{CO}_3^{2-})$ --8% 1-octanol--sulphonated kerosene with phase volume ratio(o/a) of 1:1. After extraction, the RE in the extract can be easily stripped by 0.5 N HCl in phase volume ratio(o/a) of 1:1. The results obtained are shown in Table 6. It can be concluded from this that terbium can be separated and concentrated by this oxidation and extraction method.

**TABLE 6**  
Separation of Tb by solvent extraction with quaternary amine

No.	Feed			Extract	E(%)	
	$C_{\text{Tb}}$ ( $\times 10^{-3}\text{M}$ )	$C_{\text{Y}}$	Tb (mol%)	Tb (mol%)	Tb	Y
1	0.62	5.42	10.2	23.0	61.3	23.4
2	1.24	4.82	20.4	44.0	64.5	21.2
3	3.09	3.01	50.6	81.7	70.9	16.3
4	4.94	1.21	80.4	96.7	59.5	8.3

### CONCLUSION

Terbium can be oxidized into tetravalent state in the  $\text{KIO}_4$  -  $\text{KOH}$  alkaline media with ozone at room temperature. When the molar ratio of periodate to RE ( $C_{\text{I}}/C_{\text{RE}}$ ) is 15 and the pH value is 13, tetravalent terbium, cerium and trivalent RE and Y can be extracted by quaternary ammonium salt  $\text{N}_{263}$  in  $\text{IO}_4^-$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$  form. The extractibilities of Tb(IV) and Ce(IV) are higher than those of other trivalent RE. Using 25%  $\text{N}_{263}(\text{CO}_3^{2-})$ --8% 1-octanol--sulphonated kerosene system, Tb can be separated and concentrated from yttrium group.

### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China.

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## SEPARATION OF STRONTIUM IONS FROM OTHER ALKALINE EARTH METAL IONS USING MASKING REAGENT

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### ABSTRACT

$\text{Cs}^+$  and  $\text{Sr}^{2+}$  have been well known as serious elements in high level radioactive waste. Separation of  $\text{Cs}^+$  has already been successful when using an ion-exchange method from solution in the presence of other alkali metal ions. The separation of  $\text{Sr}^{2+}$  is, however, not so easy by any known separation method such as solvent-extraction and ion-exchange methods. This is because  $\text{Sr}^{2+}$  is in the middle of the selectivity series, which is  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$  for the solvent-extraction method and  $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$  for the ion-exchange method.

In the present study, separation of strontium from other alkaline earth metal ions was studied by a combined use of three types of separation methods at 298 K: the solvent-extraction method was applied for the first separation, in which thenoyltrifluoroacetone (TTA, extractant) and trioctylphosphine oxide (TOPO, adduct forming ligand) were used for the organic phase of the system. The separation factors for each combination of four alkaline earth metal ions were determined by the values of the distribution ratio. The  $\text{Mg}^{2+}$  was well separated from  $\text{Sr}^{2+}$  by the TTA-TOPO system. However, the separation of the combinations of  $\text{Ca}^{2+}$ - $\text{Sr}^{2+}$  and  $\text{Sr}^{2+}$ - $\text{Ba}^{2+}$  was not complete by the above solvent-extraction system. The second separation method, an ion-exchange method was applied using dihydrogen tetratitanate hydrate fibers ( $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$ ) as an ion exchanger to separate  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . The separation factors for each combination of four alkaline earth metal ions were calculated by the values of the distribution coefficients.  $\text{Ba}^{2+}$  was well separated from  $\text{Sr}^{2+}$  by the ion-exchange method. To separate  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ , however, a modified solvent-extraction method was finally used in which  $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$  was used as a masking reagent of  $\text{Sr}^{2+}$ . After the dihydrogen tetratitanate hydrate fibers were contacted with the aqueous solution containing  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ , the organic solution containing TTA and TOPO was added to the liquid-solid system. Only  $\text{Ca}^{2+}$  was successfully moved to the organic solution and, thus,  $\text{Sr}^{2+}$  was completely separated in the solid phase.

### INTRODUCTION

Ion-exchange and solvent-extraction reactions of each alkaline earth metal ion have been studied using various separation reagents. For example, these metal ions were ion exchanged on antimonate -Abe(1985)-, zirconium phosphate and dihydrogen tetratitanate hydrate -Komatsu(1984). These metal ions were also extracted into the organic solution by solvent

extraction with extractant, such as TTA, TBP(tributyl phosphate), and IPT(isopropyl tropolone) -Poluektov (1970), Hasegawa (1967,1970), Sekine (1975), Lapitskaya (1967), Komatsu (1992). In the present study, the complete separation of  $\text{Sr}^{2+}$  has been investigated for an aqueous solution containing  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  ions by solvent-extraction, ion-exchange methods and the solvent-extraction method using masking reagent. As background data, a time dependence of the solvent-extraction reaction is measured for the system between the aqueous solution and the organic solution containing TTA and TOPO. To ascertain the required experimental conditions, the values of  $\text{pH}_{1/2}$  and the separation factors of those metal ions at 298 K are determined using the solvent-extraction data. These data are compared with those obtained by an ion-exchange method on crystalline dihydrogen tetratitanate hydrate fibers. Finally, these three separation methods (the solvent-extraction, the ion-exchange and the combined method) are applied for the separation of  $\text{Sr}^{2+}$  from for an aqueous solution containing the four alkaline earth metal ions at 298 K.

## EXPERIMENTAL

The TTA and TOPO were obtained from Dojindo Laboratories. Potassium tetratitanate fibers,  $\text{K}_2\text{Ti}_4\text{O}_9$  have been synthesized by the method reported previously -Fujiki (1980). The fibers of about 10 g was filled to a glass column and converted to the protonated form,  $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$  (dihydrogen tetratitanate hydrate fibers), by passing through 1 mol  $\text{dm}^{-3}$  hydrochloric acid solution until no potassium ion was detected in the effluent (using an atomic absorption method). Distilled and deionized water was used throughout. —All the other reagents were of a reagent grade. The phase transport experiment of alkaline earth metal ions were carried out in a thermostated room at 298 K.

### (1) SOLVENT-EXTRACTION SEPARATION

Stoppered glass tubes were used to contact an aqueous solution (10 mL) and the organic solution (10 mL, benzene containing TTA and TOPO). The aqueous solution contained an alkaline earth metal ion in the form of chloride with the concentration of 0.1 mM and acetate buffer of 5 mM. The pH of the aqueous solution was adjusted with perchloric acid or sodium hydroxide solution. The pH of the aqueous phase was measured after establishing the equilibrium. The tubes were shaken by a mechanical shaker which was placed in a thermostated room at 298 K.

In order to know the time dependence of the extraction reaction and to ascertain the equilibrium, series of experiments were carried out for different duration of shaking time. The ionic strength of the aqueous phase was controlled at 0.1 M with sodium perchlorate. The metal content in the aqueous phase was determined by atomic absorption spectrophotometry method (Hitachi 180-80 Polarized Zeeman Spectrophotometer) or an inductively coupled plasma spectrophotometry (Daini Seikosha, SPS 1100). From the analytical data, the distribution equilibria of the alkaline earth metal ions were determined at 298 K. The pH of the solution was measured by a pH meter (model TOA, HM 60s).

### (2) ION-EXCHANGE SEPARATION

Stoppered glass tubes of 20 mL were used to equilibrate the ion-exchange reaction of

alkaline earth metal ions between solid (0.1 g) and aqueous solution (10mL). The initial metal chloride concentration was  $1 \times 10^{-4} \text{ mol dm}^{-3}$  and the pH was adjusted with hydrochloric acid solution. The content of the tubes was agitated 100 times a day by hand for 15 days. The equilibrium of the ion-exchange reaction was attained within this period. After standing the tubes for one day, the materials were separated by aid of a centrifugation for twenty minutes at 4000 r.p.m. The metal content in the supernatant and the pH were measured with the same methods for the solvent-extraction experiment. The metal content in the solid phase was calculated from the initial and equilibrium concentrations in the aqueous solution.

### (3) SOLVENT-EXTRACTION SEPARATION USING MASKING REAGENT

As the ion-exchange reaction takes a long time to reach the equilibrium, aqueous solution containing alkaline earth metal ions was firstly contacted with dihydrogen tetratitanate hydrate fibers as a masking reagent. The organic solution was added to the solid-liquid system at 10 days after the contact. The three phase mixture, aqueous-organic-solid, was slowly agitated for 5 days to achieve the equilibration. Other experimental procedures were the same as those described above.

## RESULTS AND DISCUSSION

The solvent extraction of the alkaline earth metal ions is expressed in terms of the distribution ratio, D:

$$D = C_{M(o)}/C_M \quad (1)$$

where C represents the total concentration and the subscript "o" denotes the organic phase. Figure 1 gives the log D values as a function of pH in the aqueous phase. The log D is proportional to the pH of the aqueous solution under a substantially constant concentration of the hydrogen-ion in the organic phase. As the slopes of the linear relations shown in Fig. 1 were close to +2 and the two TOPO were attached to one metal ion by the previous results (Komatsu, 1992), this indicates that solvent-extraction reaction of alkaline earth metal ions can be written as the following reaction.



where HA denotes TTA and the subscript "o" denotes the chemical species in the organic phase.

As is shown in Fig. 1, in the solvent-extraction system order of extraction is  $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ . This order is reverse of that given by the ion-exchange method, that is,  $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$  -Komatsu (1984). This order is explained in term of the solvation effect or steric effect in forming the chelating ring for the first order, while the second selectivity series is due to the hydration energy of the alkaline earth metal ions in the aqueous solutions. This reversed relationship is dependence on the ionic radii. The  $pH_{1/2}$

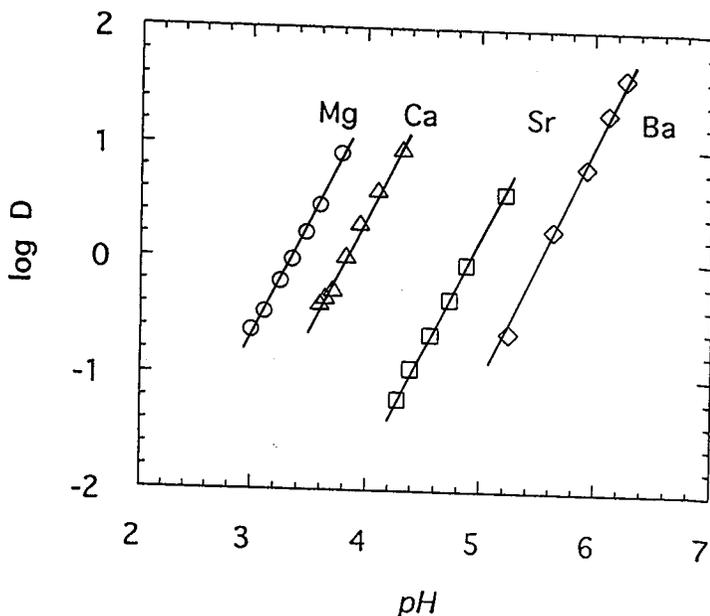


Fig.1 Distribution ratio of alkaline earth metal ions as a function of pH in the aqueous solutions at 298 K.

Aqueous solution: 0.1 M (Na,H)ClO<sub>4</sub> containing 1 x 10<sup>-4</sup> M alkaline earth metal ions and 5 x 10<sup>-3</sup> M of acetate buffer.

Organic solution: Benzene containing 0.1 M TTA and 0.1 M TOPO.

metal ions in the aqueous solutions. These are inverse relationship in the dependence on ionic radii. The pH<sub>1/2</sub> values defined as pH at 50% solvent-extraction or ion exchange states of alkaline earth metal ions are listed in Table 1 (A). These values are used for the calculation of separation factors listed in Table 1 (B).

It is obvious in Table 1(B) that the separation factor between magnesium and strontium by solvent-extraction method is enough large to separate each other. The value between strontium and barium by ion-exchange method is also large for the separation but that between calcium and strontium difficult.

To separate calcium and strontium, the ion exchanger was used as a masking reagent for strontium. Figure 2 gives the distribution ratio in the solvent-extraction system with masking reagent as a function of pH in the aqueous solution:

**TABLE 1**

Summary of  $pH_{1/2}$  values and separation factors given by the solvent extraction into benzene with TTA-TOPO (without masking reagent) and the ion exchange on dihydrogen tetratitanate hydrate fibers at 298 K.

A  $pH_{1/2}$  values

	Mg	Ca	Sr	Ba
solvent extraction	3.35	3.80	4.80	5.50
ion exchange	4.62	3.50	3.14	2.02

## B Separation factors

	Mg-Sr	Ca-Sr	Sr-Ba
solvent extraction	795	100	25.1
ion exchange	913	5.25	174

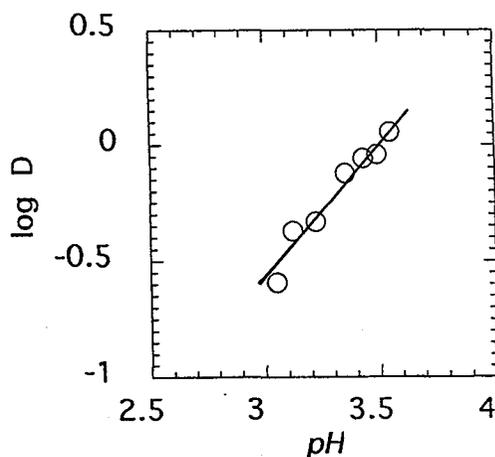


Fig.2 Distribution ratio of calcium ions as a function of pH.  
 Organic phase: Benzene containing 0.2 M TTA and 0.2 M TOPO.  
 Aqueous solution:  $1 \times 10^{-4}$  M alkaline earth metal ions.  
 Solid phase:  $H_2Ti_4O_9 \cdot nH_2O$ .

$$D = C_{(o)}/(C_{(a)} \text{ containing } C_{(s)}) \quad (3)$$

where C represents the total concentration and the subscript "o" denotes the organic phase, "aq" denotes aqueous phase and "s" denotes solid phase. As part of the calcium ions was transferred to the ion exchanger, the slope of the log D of calcium in Fig.2 decreased to below 2. On the other hand, strontium ions were not extracted in this experimental condition and calcium ions were moved to the organic solution, then the separation of these two metal ions is established completely.

### CONCLUSIONS

- i) The separation factors of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  were determined for the solvent extraction and the ion-exchange reactions.
- ii)  $Mg^{2+}$  can easily be separated from  $Sr^{2+}$  by the solvent-extraction method using TTA as a extractant and TOPO as an adduct forming ligand.
- iii)  $Ba^{2+}$  can also be separated from  $Sr^{2+}$  by the ion-exchange method using dihydrogen tetratitanate hydrate fibers.
- iv)  $Ca^{2+}$  which can not be separated by the solvent extraction and the ion-exchange methods, can be separated by the present technique of the solvent extraction method using a masking reagent that had been used as ion exchanger.

### ACKNOWLEDGEMENT

The author is very grateful to Drs. Yoshinori Fujiki, Takashi Akahane, Takayoshi Sasaki and Mr. Shuichi Shimomura of National Institute for Research in Inorganic Materials (NIRIM) for their experimental aid. The author is also very grateful to Professor Henry Freiser of University of Arizona, Professor Tatsuya Sekine of Science University of Tokyo and Dr. Hiromoto Nakazawa of NIRIM for their useful discussion.

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## Modelling of Solvent Extraction Equilibria Including the Nonideality of the Aqueous and Organic Phases in the System Zinc Sulfate/D2EHPA

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### ABSTRACT

Extraction equilibria at 25°C have been investigated to estimate the influence of the nonideal behaviour of the organic and the aqueous phase. The test-system for reactive extraction of the European Federation of Chemical Engineering- Zinc sulfate/bis-(2-ethylhexyl)-phosphoric acid (D2EHPA) in heptane - has been taken as an example for modelling the phase equilibrium. Various analytical methods such as Karl-Fischer titration, FT-IR, AAS and complexometric titration have been employed to study this system. A model of the extraction equilibrium of this system has been developed by means of the computer program SXLSQA making use of the method of Pitzer for calculating the aqueous activity coefficients and of the Hildebrand/Scott theory to account for the nonideality of the organic phase. The model proposed has fitted well with the experimental results over a wide concentration range both for the aqueous zinc/sulfuric acid phase and for the organic D2EHPA phase. The Zinc/D2EHPA complexes have been studied by FT-IR spectroscopy and compared with other complexes, such as, Ni/D2EHPA. In contrast to the nickel complex, there is no water solubilized in the aggregates formed by zinc in the organic phase.

### INTRODUCTION

The equilibrium study of the present system has been investigated several times in the literature - Kunzman (1992), Sastre (1984), Bart (1992). The modelling was performed on the basis of the mass action law neglecting activity effects or using an empirical formula for the activity coefficients. This led to very complex models with many species in the organic and aqueous phases. The lower distribution coefficient in the zinc sulfate system compared to the perchlorate system was explained in terms of the formation of zinc mono- to tri-sulfate complexes in the aqueous phase.

In contrast to these earlier works, we considered the nonideality of both phases using more fundamental thermodynamic theories. The activity coefficients in the aqueous electrolyte solutions are calculated by the method of Pitzer, while the organic nonideal behaviour is taken into account by the Hildebrand/Scott treatment. For the estimation of the equilibrium constants, the computer program SXLSQA (Oak Ridge National Laboratory) has been used. It allows the variation and optimization of the equilibrium constants, the Pitzer parameters and the solubility parameters  $\delta$ . The program was slightly modified to introduce the ionic strength dependence of the third virial coefficient  $C^\phi$  of the Pitzer equation proposed by Archer (1992).

### EXPERIMENTAL

High purity solvents have been used in all extraction and analytical studies. Chemicals in the aqueous phase were of high purity analytical grade and the Zn(II) sulfate solutions were prepared in freshly distilled deionized water. D2EHPA (Merck, 96%) was purified by a modification, Sainz-Diaz (1995) of the copper salt method described by Partridge (1969), obtaining a purity of 99%, with 0.5% of the mono 2-ethylhexyl-phosphoric acid (M2EHPA). The purity of this reagent was determined by an acid-base titration method, Sainz-Diaz (1995), with a Vit90 Radiometer titrator.

The organic phase water content was determined using Karl-Fischer titration with a VIT90 Radiometer titrimeter. The low range of zinc concentration in the aqueous phase was analysed by Atomic Absorption Spectrometry (AAS) with a Video 22 Instrumentation Laboratory spectrometer at 213.9 nm, and the high range of zinc concentration was determined by semi-automatic complexometric titration with EDTA (Titriplex III, Merck). The organic zinc content was measured by titration after reextraction or, in case of very low concentrations, directly in the organic media by AAS. Density measurements were carried out using a vibration tube densitometer. Sulfuric acid concentration was determined by acid-basic titration. FT-IR measurements of the organic phase of this extraction system were performed with a Mattson 3000 FT-IR spectrometer in a KBr demountable cell. FT-IR spectra were recorded at  $2\text{ cm}^{-1}$  resolution. The extraction studies were performed in shaking funnels thermostated at  $25^\circ\text{C}$ , with a low shaking rate in order to minimize disturbing the interphase at least for 20 h. The phases were separated after 1 h of settling.

Data were fitted by SXLSQA according to a least squares procedure. The criterion for the ability of a proposed model to describe the given set of data is the agreement factor  $\sigma$ -Baes (1990). This factor becomes unity for a perfectly fitting model. The observed experimental quantity was, in our case, the distribution coefficient or the total zinc content of the organic phase. The experimental error of these quantities was assumed to be 5%.

## RESULTS AND DISCUSSION

### FT-IR Studies

Figure 1a shows the FT-IR spectrum of a highly zinc loaded organic phase (90.4%). In contrast to nickel (figure 1b), it becomes clear that no water is extracted into the organic zinc complexes, because in the case of zinc, the broad absorption band of water at  $3400\text{ cm}^{-1}$  is absent.

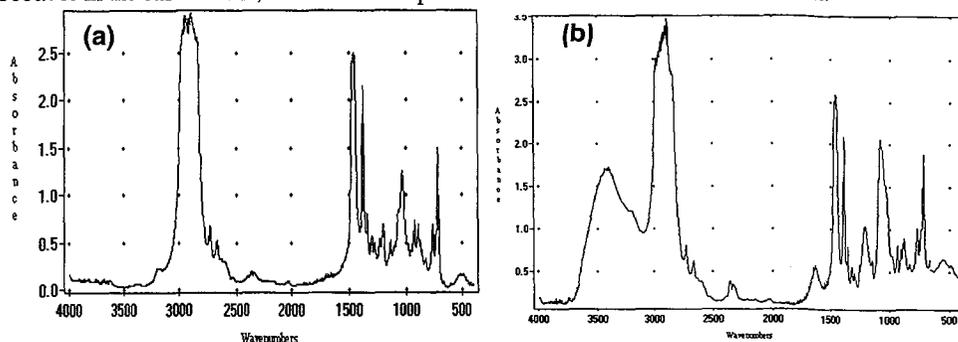


Figure 1. FT-IR spectra of the organic phase for the system D2EHPA/n-heptane/M(II) sulfate solution: a) M=Zn, initial  $[\text{Zn}]=0.3\text{ M}$ ,  $[\text{D2EHPA}]=0.15\text{ M}$ , b) M=Ni, initial  $[\text{Ni}]=0.2\text{ M}$ ,  $[\text{D2EHPA}]=0.15\text{ M}$ .

The determination of the water content of the different loaded organic samples by Karl Fisher titration confirms this fact. Experiments were performed with  $0.09\text{ M}$  D2EHPA and zinc concentrations in the organic phase ranging from 1 to 25 mM. The water content was constant and very low at about  $6 \pm 1.5\text{ mM}$ . Thus for the computer modelling it is not necessary to include organic species containing water in the formulae.

### Extraction Experiments

A series of experiments of the extraction of zinc sulfate with D2EHPA in n-heptane has been performed under different conditions of pH and D2EHPA and Zn concentrations. The results are

shown in figures 2-4.

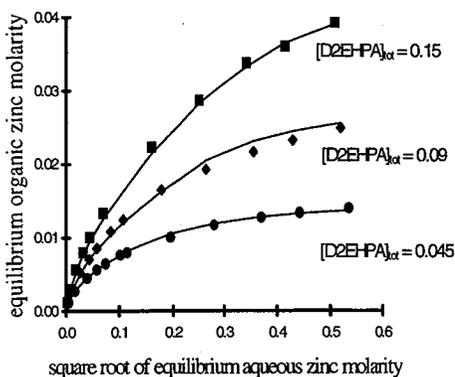


Figure 2. Organic zinc content vs. square root of aqueous zinc concentration at 25°C.  $[\text{H}_2\text{SO}_4]_{\text{ini}} = 0.117 \text{ mM}$ ; solid lines = model 2.

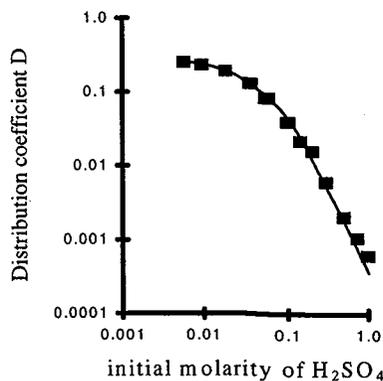


Figure 3. Distribution coefficient vs. initial sulfuric acid concentration.  $[\text{D2EHPA}]_{\text{tot}}$  and  $[\text{Zn}]_{\text{ini}} = 0.1\text{M}$ ; solid line = model 2.

#### Slope Analysis

Five experiments with different total zinc concentration from 0.17mM to 1.02 mM were performed ( $[\text{D2EHPA}]_{\text{tot}} = 0.09 \text{ M}$ ;  $[\text{H}_2\text{SO}_4]_{\text{ini}} = 11.1 \text{ mM}$ ). The distribution coefficient proved to be constant. This leads to the conclusion that no polynuclear zinc complexes are formed in the organic phase in this low range of concentration.

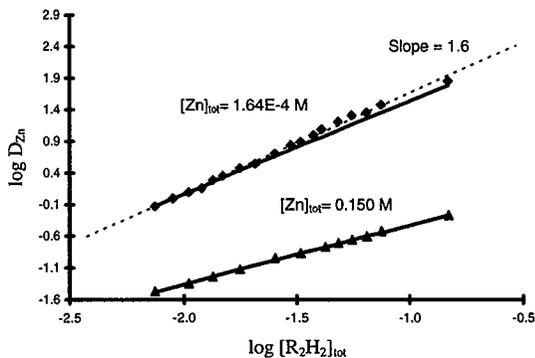


Figure 4. Log. distribution coefficient vs. log. concentration of the dimeric D2EHPA for low ( $[\text{H}_2\text{SO}_4]_{\text{ini}} = 4.968 \text{ mM}$ ) and high zinc concentration ( $[\text{H}_2\text{SO}_4]_{\text{ini}} = 0.117 \text{ mM}$ ) at 25°C; dotted line = linear regression; solid lines = model 2.

In figure 4, the equilibrium zinc distribution coefficient is represented as a function of the total D2EHPA (free and complexed) concentration in the organic phase. The slope analysis of these results shows that the dimeric extractant/Zn stoichiometric ratio is 1.6. This means that more than one species are formed. The extraction can be represented by the following equation -Sastre (1984),

Kunzman (1992):



$a$  is one as long as the zinc concentration is low enough. Therefore  $b$  should adopt the values 3 and 4 to account for the slope of 1.6.

### Nonideality of Aqueous Phase

The zinc sulfate system has been studied by Pitzer (1974). Awakura (1984) determined isopiestic data for the  $\text{ZnSO}_4/\text{H}_2\text{SO}_4$  system. We added this author's water activity data (8 points, error  $\pm 0.0003$ ) to the data set used by Pitzer to refit the Pitzer interaction parameter for  $\text{Zn}^{2+}\text{-SO}_4^{2-}$ . We assigned an error of  $\pm 0.008$  to the osmotic coefficient data obtained by Brown (1956) from melting point depression experiments and  $\pm 0.002$  to that of Robinson (1965). The parameters to be estimated are  $\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $\beta^{(2)}$  and  $C^{\phi(0)}$  with  $\alpha_1 = 1.4$  and  $\alpha_2 = 12$ .

The agreement factor  $\sigma$  becomes slightly lower (from 1.453 to 1.333) when the ionic strength dependence of the third virial coefficient is included ( $C^{\phi(1)}$ ). The best fit is obtained with  $\omega$  set to 3.3. The results can be observed in table 1. Fitted parameters are marked with an asterisk.

**TABLE 1**  
Pitzer parameters for the  $\text{ZnSO}_4/\text{H}_2\text{SO}_4$  system for 25°C

Interaction	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{\phi(0)}$	$C^{\phi(1)}$	$\alpha_1$	$\alpha_2$	$\omega$
$\text{Zn}^{2+}\text{-SO}_4^{2-}$	0.16724 *	3.49906 *	-40.5911 *	0.036746 *	-12.9451 *	1.4	12	3.3
$\text{Zn}^{2+}\text{-HSO}_4^-$	0.56879 *	2.61593 *		-0.046724 *		2.0		
$\text{H}^+\text{-SO}_4^{2-}$	0.06421	0.225902		0.031126		2.0		
$\text{H}^+\text{-HSO}_4^-$	0.22297	0.460016		-0.002660		2.0		
$\text{Zn}^{2+}\text{-H}^+$		0						
$\text{Zn}^{2+}\text{-H}^+\text{-SO}_4^{2-}$		0						
$\text{Zn}^{2+}\text{-H}^+\text{-HSO}_4^-$		0						
$\text{HSO}_4^-\text{-SO}_4^{2-}$		-0.135342						
$\text{HSO}_4^-\text{-SO}_4^{2-}\text{-Zn}^{2+}$		0.0731378 *						
$\text{HSO}_4^-\text{-SO}_4^{2-}\text{-H}^+$		0.0278059						

To get the parameters for the zinc-hydrogen sulfate interaction, the 65 data sets of Awakura (1984) for  $\text{ZnSO}_4/\text{H}_2\text{SO}_4$  mixtures have been used. The unsymmetrical mixing term resulting from the interactions of ions with different charges -Pitzer (1975)- was included. The constant for the formation of hydrogen sulfate from sulfate was taken from Pitzer (1979) and Clegg (1994) ( $\log_{10} K_{\text{HSO}_4} = 1.9788$ ). The parameters of the Pitzer equation for the sulfuric acid system can be found in the literature -Clegg (1994), Pitzer (1979), Hovey (1993). We tried out these three sets and found that the parameters obtained by Hovey from the fit of the  $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$  system gave by far the best results. The parameter  $C^{\phi(1)}$  of the  $\text{Zn}^{2+}\text{-HSO}_4^-$  interaction did not improve the fit and was omitted. The triple ion interaction parameter  $\psi$  for  $\text{HSO}_4^-\text{-SO}_4^{2-}\text{-Zn}^{2+}$  influences significantly the goodness of the results and was therefore also estimated together with  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^{\phi(0)}$  for  $\text{Zn}^{2+}\text{-HSO}_4^-$ . The agreement factor was 1.214 when the same uncertainty for the water activity data is used as for the fit of the  $\text{ZnSO}_4$  system. Results are summarized in table 1.

### Fit of Equilibrium Data

SXLSQA needs the single ion Mason volume parameters in order to convert from the molarity to molality scale necessary for the calculation of activity coefficients in the aqueous phase. Additivity of these coefficients is assumed. The listed values of the apparent molar volume  $\phi_{v,i}^0$  at infinite dilution and the proportionality constant  $S_{v,i}$  (table 2) are based on the arbitrary convention of

$\phi_{v,i}^0 = 0$  and  $S_{v,i} = 0$  for  $H^+$ . The values for sulfate and hydrogen sulfate were taken from Moyer (1993). The parameters for the zinc ion were calculated from density data for  $ZnSO_4$  at 25°C measured in our laboratory.

**TABLE 2**  
Volume parameters at 25°C

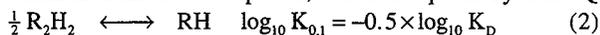
species	MW [g/mol]	$\phi_{v,i}^0$ [cm <sup>3</sup> /mol]	$S_{v,i}$	$V_{org}$ [cm <sup>3</sup> /mol]
H <sup>+</sup>	1.0079	0	0	
Zn <sup>2+</sup>	65.38	-22.27	4.66	-4.2
SO <sub>4</sub> <sup>2-</sup>	96.0636	13.98	8.64	
HSO <sub>4</sub> <sup>-</sup>	97.0715	37.88	2.18	

SXLSQA assumes additivity of molar volumes in the organic phase. The molar volumes  $V_{org}$  of the solvent, extractant and extractable ions have to be supplied. The molar volume of zinc in the organic phase was determined from density measurements of the zinc loaded organic phase.  $V_{org}$  of heptane and D2EHPA were obtained from their measured densities at 25°C. The Hildebrand/Scott solubility parameter  $\delta$  for heptane can be found in literature -Barton (1983), Hildebrand (1964). A group contribution method -Barton (1983)- was applied to get the solubility parameter for the monomeric extractant. These parameters are summarized in tables 2 and 3.

**TABLE 3**  
Parameters of organic species and solvent at 25°C

	$V_{org}$ [cm <sup>3</sup> /mol]	Model 1: $\sigma = 1.648$		Model 2: $\sigma = 1.585$	
		$\log_{10} K$	$\delta$ [cal <sup>1/2</sup> cm <sup>-3/2</sup> ]	$\log_{10} K$	$\delta$ [cal <sup>1/2</sup> cm <sup>-3/2</sup> ]
Heptane	147.44		7.45		7.45
RH	332.61		----	-2.4	8.56
ZnR <sub>2</sub> (RH)		-0.9439±0.009 *	9.085±0.2 *	-0.9133±0.008 *	7.45
Zn <sub>3</sub> R <sub>6</sub> (RH) <sub>2</sub>		----	----	-1.2865±0.134 *	7.45
R <sub>2</sub> H <sub>2</sub>		----	7.45		8.1 *

The equilibrium constant for the dimerization of D2EHPA ( $\log K_D = 4.8 \pm 0.15$  in octane, Kolarik (1982)) is very high and does not strongly affect the calculations with SXLSQA, if the reaction equations are given in terms of the dimeric D2EHPA. From the dimerization constant follows the constant for the dissociation of the dimeric species, which is required by SXLSQA:



As a starting point for fitting our 88 data points, only one mononuclear zinc complex in the organic phase was assumed. The dissociation of the dimeric D2EHPA was neglected. The solubility parameter of the dimeric extractant was set equal to that of the solvent, since aggregation processes in nonpolar solvents can be described in terms of a matching of the solubility parameter of the aggregate with that of the diluent -Little (1964). Initially, the solubility parameter of the organic zinc species was also set equal to that of heptane. It was found that the organic zinc complex ZnR<sub>2</sub>(RH) gives a good description of the equilibrium ( $\sigma = 1.766$ ). The goodness of the fit can significantly be improved when  $\delta$  of this complex is also allowed to vary ( $\sigma = 1.648$ ). Table 3 shows the estimated parameters of model 1, marked with an asterisk. No improvement could be achieved by adding a second mononuclear zinc complex ZnR<sub>2</sub>(RH)<sub>2</sub> to the first one.

A second, slightly more complicated approach was carried out. The dissociation of the dimeric extractant is taken into account by equation 2,  $\log K_{0,1}$  being -2.4. In addition to the mononuclear ZnR<sub>2</sub>(RH)<sub>2</sub> complex, polynuclear complexes with a stoichiometric factor  $a$  (equation 1) of zinc

from 2 up to 5 and  $b$  ranging from 4 to 15 were systematically tested. The lowest agreement factor was received with  $Zn_3R_6(RH)_2$  giving a coordination number of 4 to zinc. When the solubility parameter of the two organic product species and the dimeric D2EHPA were assigned the same value as heptane, an agreement factor of 1.599 was reached. Increasing the solubility parameter of one of the two organic products made a worse fitting, while adjusting the solubility parameter of the dimeric extractant to 8.1 lowered  $\sigma$  a little bit ( $\sigma = 1.585$ ). Estimated parameters of this model (model 2) are given in table 3.

### CONCLUSIONS

The extraction equilibrium of the system zinc sulfate/D2EHPA in heptane has been studied over a wide concentration range of zinc (0.0001 to 0.3 M), sulfuric acid (0 to 1 M) and extractant (0.015-0.3 M). Two models for the extraction equilibrium have been developed by means of the computer program SXLSQA making use of the Pitzer method for calculating aqueous activity coefficients and the Hildebrand/Scott theory for the organic ones. Although the first model is very simple the quantitative description of the equilibrium is surprisingly good. The second more complicated model gives a very good picture of the behaviour of this equilibrium. The complexes zinc/D2EHPA have been studied by FT-IR spectroscopy and compared with other complexes, such as, nickel/D2EHPA. The water content in the zinc/D2EHPA complex has been found to be negligible.

### ACKNOWLEDGEMENTS

The authors are grateful to the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung" and the EC/HCM program for supporting this work. The authors wish also to thank Prof. Awakura of the Kyoto University for providing his isopiestic data on the zinc/sulfuric acid system.

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## Highly Selective Extraction-Separation System Utilizing Macrocyclic Ionophores as Masking Reagents

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### ABSTRACT

Highly selective extraction-separation can be achieved in the extraction of alkaline earths with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and tri-*n*-octylphosphine oxide, and of lanthanides with di(2-ethylhexyl)phosphoric acid. In both cases, by adding a macrocyclic ionophore such as 18-crown-6 or cryptand[2.2.2] to the aqueous phase as an ion-size selective masking reagent, the larger the ionic radius is, the the higher the pH region the extraction moved to. Consequently, the separation among the metal ions was enhanced.

### INTRODUCTION

Application of a masking effect to the solvent extraction method is an effective means for a selective separation of metal ions. Generally, the extractability of metal ions with the conventional chelating reagents such as  $\beta$ -diketones is governed by the stability of the metal complexes. In the solvent extraction of alkali, alkaline earth and lanthanide metal ions with the chelating reagents, metal ions having smaller ionic radii exhibit higher extractability. On the other hand, the stability of the complex formation between the macrocyclic ionophores such as crown ethers and the above mentioned metal ions exhibits a quite different tendency. Thus, a solvent extraction system of high selectivity could possibly be developed by the combination of the chelating reagents and the macrocyclic ionophores. 18-Crown-6 (Umetani(1993)) and Cryptand[2.2.2] (Sasaki(1994)) have been shown to be useful ion-size selective masking reagents in the synergistic extraction of alkaline earths into cyclohexane with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone(HPMBP) and tri-*n*-octylphosphine oxide(TOPO).

Macrocyclic ionophores have been used alone as extractants or as synergists with the chelating extractants. In the present work, a novel macrocycle application has been proposed.

### RESULTS AND DISCUSSION

#### (A) Extraction of alkaline earths in the presence of 18-crown-6

The results for the extraction of alkaline earths with 0.05 M HPMBP and 0.01 M TOPO into cyclohexane in the absence (blank symbols) and presence (solid symbols) of 18-crown-6 (0.03 M) are shown in Figure 1. Alkaline earths were extracted in the order, Mg>Ca>Sr>Ba, which is the same order that the ionic radius decreases. When 0.03 M 18-crown-6 was added to the aqueous phase, the extractions were made in the higher pH region. The larger the ionic radius is, the higher pH region the extraction moved to. As a result, the separation among

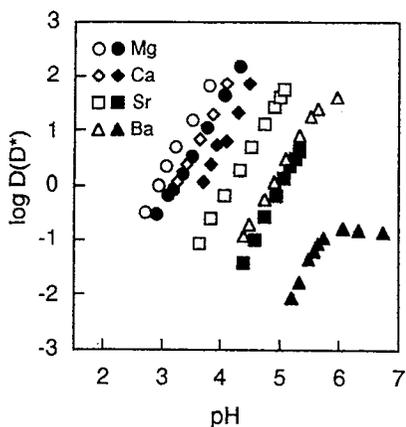


Figure 1. Extraction of alkaline earths in the absence and presence of 18-crown-6.

alkaline earths especially for Ca-Sr and Sr-Ba has been improved. It is clear that 18-crown-6 works as an ion-size selective masking reagent in the aqueous phase. The distribution ratio of 18-crown-6 between cyclohexane and water is reported to be  $10^{-2.91 \pm 0.05}$ , indicating that the concentration of 18-crown-6 in the cyclohexane phase is negligible.

In the synergistic extraction of alkaline earths ( $M^{2+}$ ) with HPMBP (HA) and TOPO (L), the extraction equilibrium and the extraction constant,  $K_{ex,L}$ , can be written as follows;



$$K_{ex,L} = \frac{[MA_2L_{s,o}][H^+]^2}{[M^{2+}][HA]_o^2[L]_o^s} = D \frac{[H^+]^2}{[HA]_o^2[L]_o^s} \quad (2)$$

where subscript o denotes the species in the organic phase and D is defined as  $[MA_2L_{s,o}]/[M^{2+}]$ . The number of TOPO units in the adduct is two per metal for Mg, Ca and Sr, and three for Ba. The  $\log K_{ex,L}$  values were obtained from Fig.1 using eq (2) on the basis of the known s values and are summarized in Table 1.

The distribution ratio in the presence of 18-crown-6 (CE),  $D^*$ , can be expressed in eq (3).

$$D^* = \frac{[MA_2L_{s,o}]}{([M^{2+}] + [M(CE)^{2+}])} \\ = K_{ex,L} \frac{[HA]_o^2 [L]_o^s}{[H^+]^2} \{1 + \beta [CE]\} \quad (3)$$

where  $\beta$  is the complex formation constant between alkaline earths and 18-crown-6 in the aqueous phase defined as  $[M(CE)^{2+}]/[M^{2+}][CE]$ . Dividing D by  $D^*$  gives eq (4).

$$D/D^* = 1 + \beta [CE] \quad (4)$$

The  $\log \beta$  values are summarized in Table 1. The separation factor, SF, between two metal ions, M1 and M2, is defined as the difference of the logarithmic value of the respective distribution ratio.

$$SF = \log(D_{M1}/D_{M2}) = \log(K_{ex,L,M1}/K_{ex,L,M2}) \quad (5)$$

The separation factor in the presence of crown ether,  $SF^*$ , is written in eq (6) when  $s_1$  and  $s_2$  are the same and [CE] is high enough.

$$SF^* = \log(D_{M1}^*/D_{M2}^*) = \log(K_{ex,L,M1}/K_{ex,L,M2}) (\beta_{M2}/\beta_{M1}) \quad (6)$$

TABLE 1  
Extraction parameters for alkaline earths

	$\log K_{ex,L}$	s	$\log \beta$	SF	SF*
Mg	0.80	2	2.25		
Ca	0.16	2	2.30	0.64	0.69
Sr	-1.74	2	3.06	1.90	2.66
Ba	-1.16	3	3.82	1.42	2.18

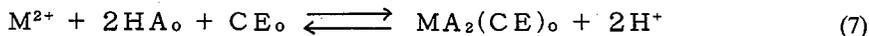
Comparing eqs 5 and 6, the separation factor can be improved as much as  $\beta_{M2}/\beta_{M1}$ . Separation factors in the presence and absence of crown ether are summarized in Table 1. Since the separation factor for Sr-Ba

depends on  $[TOPO]_o$ , they were obtained under the condition,  $[TOPO]_o = 0.01$  M.

On the other hand, as reported previously, benzene as an organic solvent is superior to cyclohexane for the selective extraction of alkaline earths. Application of 18-crown-6 to the benzene system has been examined. Figure 2 shows the results for the extraction of alkaline earths with HPMBP and TOPO into benzene in the presence of 18-crown-6. As seen in Fig.2, the selectivity for Mg/Ca was slightly lower and those for Ca/Sr and Sr/Ba were higher than those in the cyclohexane system. The slopes of the straight portions in Fig.2 are found to be 2. The extraction constants,  $K_{ex,L}$ , were obtained from eq(2) on the basis of the known s values.

The  $pH_{L/2}$  values are 4.12, 4.39, 5.62 and 6.44 in the absence of 18-crown-6 and 4.43, 4.55, 6.15, and 6.63 in the presence of 18-crown-6 for Mg, Ca, Sr, and Ba, respectively. Alkaline earths were extractable into benzene with HPMBP and 18-crown-6 in the absence of TOPO, as shown in Fig.3. The preliminary experiments show that the extraction into cyclohexane with HPMBP and 18-crown-6 in the absence of TOPO is very low. The distribution ratio of 18-crown-6 between benzene and water is reported to be  $10^{-1.31 \pm 0.06}$ , much larger than that for cyclohexane-water. The concentration of 18-crown-6 in the benzene phase is not negligible. Considering that alkaline earths are not extractable with HPMBP alone, it is clear that 18-crown-6 works as a synergistic reagent like TOPO in the benzene phase as well as a masking reagent in the aqueous phase.

In the synergistic extraction of alkaline earths with HPMBP and 18-crown-6, the extraction equilibrium and the extraction constant,  $K_{ex,CE}$ , can be expressed as follows;



$$K_{ex,CE} = \frac{[MA_2(CE)]_o [H^+]^2}{[M^{2+}] [HA]_o^2 [CE]_o}$$

$$= D [H^+]^2 / [HA]_o^2 [CE]_o \quad (8)$$

where D is  $[MA_2(CE)]_o / [M^{2+}]$ . Actually, the masking effect takes place at the same time. The distribution ratio of metal ion is expressed in eq(9). When eq(8) is substituted in eq(9),

$$D^* = \frac{[MA_2(CE)]_o}{\{[M^{2+}] + [M(CE)^{2+}]\}} \quad (9)$$

eq(10) is obtained. When  $\beta[CE]$  is large enough as compared to 1,

$$D^* = D / (1 + \beta[CE])$$

$$= K_{ex,CE} [HA]_0^2 [CE]_0 / [H^+]^2 (1 + \beta[CE]) \quad (10)$$

$$D^* = K_{ex,CE} ([HA]_0^2 / [H^+]^2) (P / \beta) \quad (11)$$

where P is the partition constant of 18-crown-6 between benzene and water, defined as  $[CE]_0/[CE]$ . The extraction constants,  $K_{ex,CE}$ , were obtained from eq(10).

In the extraction of alkaline earths into benzene with HPMBP and TOPO in presence of 18-crown-6, the synergistic extraction with 18-crown-6 as well as with TOPO and the masking reaction in the aqueous phase take place simultaneously. The extraction behaviors in Fig.2 could be well reproduced by the combination of  $K_{ex,L}$ ,  $K_{ex,CE}$  and the masking effect in the aqueous phase. The separation factors in the presence of 18-crown-6 were read from Fig.2. The separation for Ca/Sr was much improved. The SF value of 3.20 is the best one given in the present work. In contrast, the separation for Sr/Ba became much poorer. The extraction into the benzene phase in the presence of crown ether is the sum of the synergistic extractions by HPMBP/TOPO and HPMBP/18-crown-6, subject to the masking effect.

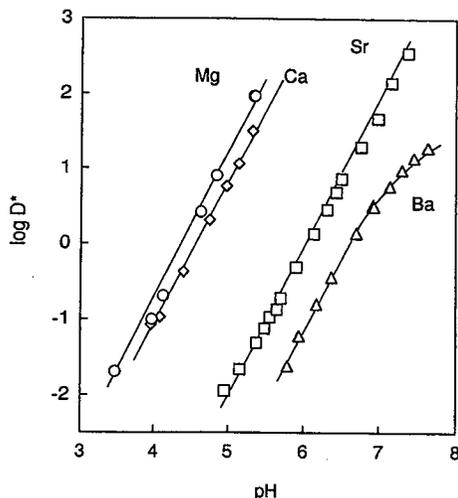


Figure 2. Extraction of alkaline earths with HPMBP and TOPO into benzene in the presence of 18-crown-6.

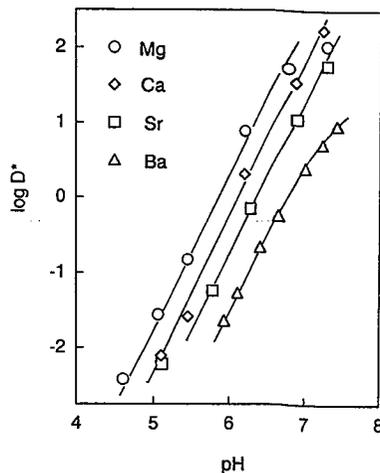


Figure 3. Extraction of alkaline earths with HPMBP and 18-crown-6 into benzene in the absence of TOPO.

### (B) Extraction of alkaline earths in the presence of cryptand [2.2.2].

Diazapolyoxabicyclic ligands (cryptands) exhibit a prominent selectivity for alkali and alkaline earth metals. They are soluble in water and their stability in complexation is large enough for using as a practical masking reagent. Incorporating nitrogens as an element constituting the ring structure, the masking effect of cryptands depends on pH unlike crown

ethers such as 18-crown-6. Cryptand [2.2.2] should be the most suitable masking reagent for separating Ca and Sr in the series of alkaline earths. Figure 4 shows the results for the extraction with 0.01 M HPMBP and 0.01 M TOPO into cyclohexane in the absence (blank symbols) and presence (solid symbols) of 0.01 M cryptand [2.2.2]. The extraction behaviors for Mg and Ca in the presence of cryptand [2.2.2] are quite similar to those in the absence of cryptand [2.2.2]. The log D values for Sr in the presence of cryptand [2.2.2] increase as the pH increases similarly to those in the absence of cryptand [2.2.2], then begin to decrease over pH 5.

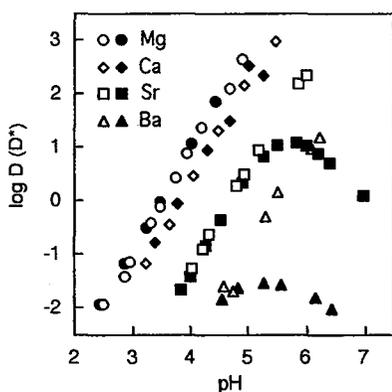


Figure 4. Extraction of alkaline earths in the absence and presence of cryptand[2.2.2].

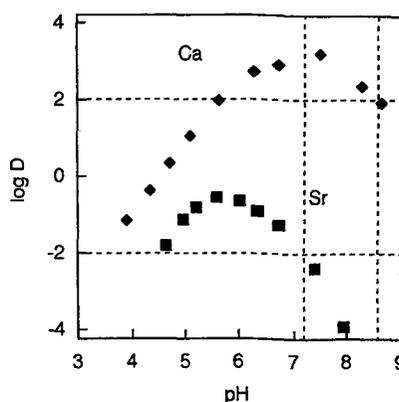


Figure 5. Quantitative extraction-separation of calcium from strontium.

The log D values for Ba in the presence of cryptand [2.2.2] deviate from those in the absence of cryptand [2.2.2] over pH 4.5.

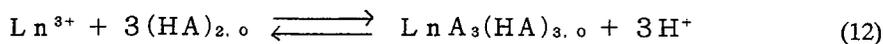
The results obtained indicate that the masking effect by cryptand depends on the stability in complexation and on the pH. The extraction behaviors in the presence and absence of cryptand can be predicted by taking the above equilibrium and the concentrations of the reagents into consideration. In order to establish the quantitative extraction-separation system for Ca and Sr, the extraction was made reducing the concentrations of HPMBP and TOPO to  $4 \times 10^{-3}$  M keeping the initial concentration of cryptand at  $1 \times 10^{-2}$  M. As shown in Fig.5, the distribution ratio of Sr decreases rapidly over pH 5.6 as expected, while that of Ca still increases by pH 7.5. Ca can be separated from Sr quantitatively in the pH range 7.2 to 8.6 where more than 99% of Ca ( $\log D > 2$ ) is extracted into cyclohexane, while more than 99% of Sr ( $\log D < -2$ ) remains in the aqueous phase at the same time. A careful control of pH at 7.8 could lead to the best separation; 99% extraction of Ca ( $\log D > 3$ ) leaving 99% of the Sr ( $\log D < -3$ ) in the aqueous phase.

### (C) Extraction of lanthanides into cyclohexane in the presence of 18-crown-6.

The application of 18-crown-6 to the solvent extraction of lanthanides into cyclohexane has been examined (Tsurubou(1995)). While the  $pH_{1/2}$  values for the heavy lanthanides, Dy, Ho

and Yb, did not change on adding 0.1 M 18-crown-6 into the aqueous phase, those for light lanthanides, La, Nd, Sm and Eu, increased. The differences of the  $pH_{1/2}$  values in the presence and absence of 18-crown-6,  $\Delta pH_{1/2}$ , increase linearly as the ionic radius increases.

In the extraction of lanthanides ( $Ln^{3+}$ ) with DEHPA (HA), the extraction equilibrium and the extraction constant,  $K_{ex}$ , can be written as follows;



$$K_{ex} = \frac{[LnA_3(HA)_{3.o}][H^+]^3}{[Ln^{3+}][(HA)_{2.o}]^3} \quad (13)$$

TABLE 2

Extraction parameters for lanthanides

	$\log K_{ex}$	$\Delta pH_{1/2}^a$	$\log \beta$	SF	SF*
La	0.57	0.32	1.91	0.33	0.75
Nd	0.90	0.18	1.39	0.66	0.81
Sm	1.56	0.13	1.16	0.72	0.78
Eu	2.28	0.11	1.06	1.35	1.68
Dy	3.63	-	-	0.15	0.15
Ho	3.78	-	-	0.36	0.36
Yb	4.14	-	-		

<sup>a</sup>  $[DEHPA]_O = 0.01$  M in cyclohexane,  $[18C6] = 0.1$  M.

been known to be very difficult due to the similar nature of the metal cations. The SF for lanthanum-dysprosium increased from 3.06 to 4.02. This improvement is significant. 18-Crown-6 has been found to be an effective masking reagent for light lanthanides.

Reagents which are quite soluble in water, with high selectivity and with high stability are required to extend the applicability of the present system. Macrocyclic ligands having negatively charged moiety may possibly satisfy the above mentioned requirements. Highly water-soluble reagents do not distribute into organic solvents. Synthesis and application of such macrocyclic ligands are now under study.

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The  $\log K_{ex}$  values were

obtained on the basis of eq 8

and are summarized in Table 2.

The  $\log \beta$  values were obtained by substituting the  $D/D^*$  values read from the figure in eq 4 and they are summarized in Table 2 together with the SF and SF\* values. Owing to the small  $\beta$  values, a high concentration of 18-crown-6 was required.

However, it is obvious that an addition of a size-selective masking reagent decidedly

improves the separation of lanthanides whose separation has



## SOLVENT EXTRACTION OF GOLD IN THIOSULFATE SOLUTIONS

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The solvent extraction of gold from aqueous thiosulfate solutions with neutral organo-phosphorus esters, the primary amine  $N_{1923}$  and their mixture was studied, respectively. It was found that only in alkaline thiosulfate solutions could gold be extracted with alkyl phosphorus esters. A combination of the primary amine and the neutral donor reagents, such as alkyl phosphorus esters, was found to be the most effective solvent for the extraction of gold from thiosulfate solutions. The composition of the extracted gold species with mixed solvents was studied and proposed. The effects of the primary amine and tributyl phosphate(TBP) on the extraction of gold are different under different aqueous pH conditions. It may be proposed that with an equilibrium  $\text{pH} < 9$ , the primary amine  $N_{1923}$  is the main extractant with TBP as a synergistic extractant, while with an equilibrium  $\text{pH} > 9$ , the primary amine shows a synergistic effect on the extraction of gold with TBP.

### INTRODUCTION

From the point of view of environmental protection, several non-cyanide leaching processes of gold have been studied and developed in recent years (Udupa, 1990). The process of leaching with thiosulfate solution can be considered, in many cases, as the most promising one to replace cyanide leaching. Thiosulfate leaching, based on our experimental results, is the only process which can be used directly to treat certain gold-containing sulfide ores without a pretreatment step such as roasting, high pressure oxidation or bacteria leaching and also without consumption of large amounts of a high cost or toxic leaching reagent such as chlorine. It is expected the thiosulfate process could be developed initially for heap leaching of gold associated with low grade sulfide ores (Zhu, 1993). There is not much work reported on the recovery of gold from thiosulfate solutions. Work has been started on the recovery of gold from thiosulfate solutions by cementation and adsorption on carbon with a number of problems still to be solved (Hu, 1989).

The extraction of gold from cyanide solutions with neutral organo-phosphorus esters, primary amines and mixtures of primary amine with neutral esters as solvent was studied by Miller and Caravaca (Caravaca, 1994; Mooiman, 1986) respectively. In our laboratory, primary, secondary and tertiary amines have been tested for the extraction of gold from thiosulfate solutions. Organo-phosphorus esters and their mixtures with primary amines have also been studied. The present paper reports our experimental results on the separation of gold from thiosulfate solu-

tion with a primary amine and neutral extractants as solvent. The composition of the extracted gold species has also been proposed.

## EXPERIMENTAL

The primary amine  $N_{1923}$  with formula  $RR'CHNH_2$  (with a total of 19~23 carbon atoms) and TRPO with formula  $R_3PO$  (R with  $C_6 \sim C_9$ ) were supplied by the Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai. The secondary amine 7201 with formula  $(R_2CH)_2NH$  (R with  $C_7 \sim C_9$ ) and di-iso-amyl cyclohexyl phosphonate (DiAChP) were supplied by the Institute of Uranium Ore Processing, Beijing. The tertiary amine tri-n-octyl amine (TOA) with formula  $(C_8H_{17})_3N$  was chemically pure. Kerosene was used without further purification. The other reagents were analytical grade.

Metallic gold was first dissolved in aqua regia. Alkaline thiosulfate solution was added to convert the gold to  $Au(S_2O_3)_2^{3-}$ . The equilibrium distribution of gold(I) between the organic and aqueous phases was determined by mixing the two phases using a magnetic stirrer. The pH was adjusted by addition of a very small volume of dilute  $H_2SO_4$  or  $NaOH$  solution under agitation to prevent the precipitation of elemental sulfur. An equal amount of the organic phase was added to maintain a fixed phase ratio of 1:1. When equilibrium was reached, stirring was stopped. The gold content in the aqueous phase was determined using a Perkin-Elmer 4000 Atomic Absorption Spectrophotometer.

## RESULTS AND DISCUSSION

### Gold Extraction with Neutral Organo-Phosphorus Esters

The extraction of gold from thiosulfate solutions with alkyl phosphorus esters was studied and the results are shown in Fig.1. It can be seen that only in alkaline thiosulfate solutions

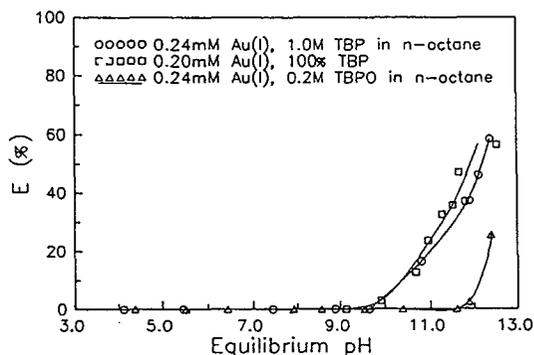


Figure 1. Percent extraction of Au(I) versus equilibrium pH for extraction with alkyl phosphorus esters from 0.8M  $Na_2S_2O_3$  solutions. Phase ratio (R)=1, 24 °C, contact time (t)=10min

can the gold be extracted with alkyl phosphorus esters. Further studies show that the gold in the organic phase can be expressed as  $\text{Na}_i\text{Au}_2(\text{S}_2\text{O}_3)_j(\text{OH})\cdot m\text{TBP}$ , where  $i$  varies with  $j$ , and the TBP coefficient  $m$  is in the range of 1.5~2.5 (Zhao, 1995).

#### Gold Extraction with the Primary Amine $\text{N}_{1923}$

Fig.2 shows the effect of the concentration of the primary amine  $\text{N}_{1923}$  on gold extraction from 0.8M  $\text{Na}_2\text{S}_2\text{O}_3$  solutions. The extraction increases with an increase in  $\text{N}_{1923}$  concentration as seen from a shift in the equilibrium pH to higher values. Our experimental results propose the gold complex extracted with the primary amine  $\text{N}_{1923}$  from thiosulfate media without ammonia is  $(\text{RNH}_2)_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 3\text{RNH}_2$ , which involves the solvation of the complex formed in the organic phase by three amine molecules.

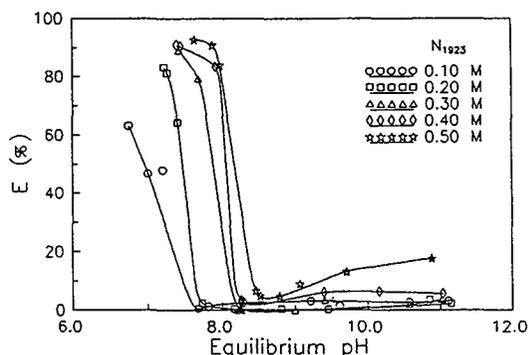


Figure 2. Effect of  $\text{N}_{1923}$  concentration in n-octane on the extraction of Au(I) from 0.8M  $\text{Na}_2\text{S}_2\text{O}_3$  solutions.  
0.24mM Au(I),  $R=1$ ,  $20^\circ\text{C}$ ,  $t=10\text{min}$

#### Gold Extraction with Mixed Solvents

The extraction of gold from thiosulfate solutions was carried out with a mixture of the primary amine  $\text{N}_{1923}$  and different neutral extractants and the results are shown in Fig.3. It is found that the enhancement effect by the neutral reagents studied on the extraction of gold with the primary amine  $\text{N}_{1923}$  is decreased in the order, electron donor reagents, reagents with electron donor and acceptor elements to electron acceptor reagents. Only by addition of neutral donor reagents the extraction of gold is increased and a synergistic effect observed.

Fig.4 shows the influence of the primary amine  $\text{N}_{1923}$  concentration on gold extraction in the presence of TBP. The extraction curves are shifted to the right, which means the extraction increases with an increase in  $\text{N}_{1923}$  concentration. It is noticed that in strongly alkaline thiosulfate solutions (equilibrium pH > 9), an increase in the  $\text{N}_{1923}$  concentration has very little effect on the gold extraction. It can be considered that the primary amine  $\text{N}_{1923}$  in the mixed solvents of  $\text{N}_{1923}$  and TBP is the main extractant only with an aqueous pH < 9.

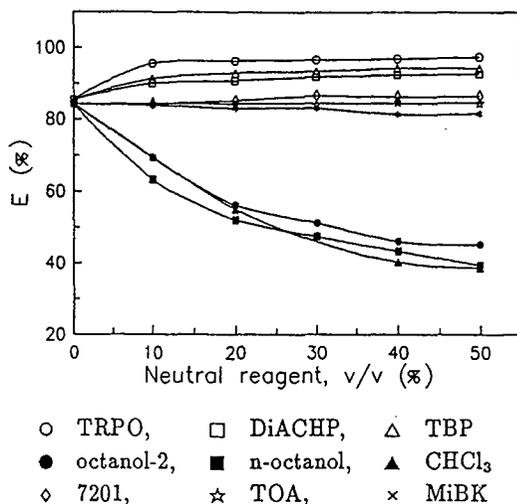


Figure 3. Effect of neutral reagents on the extraction of Au(I) with 0.5M  $N_{1923}$  in kerosene from 0.8M  $Na_2S_2O_3$  solutions. 0.21mM Au(I), pH 8.3, R=1, 18 °C , t=15min

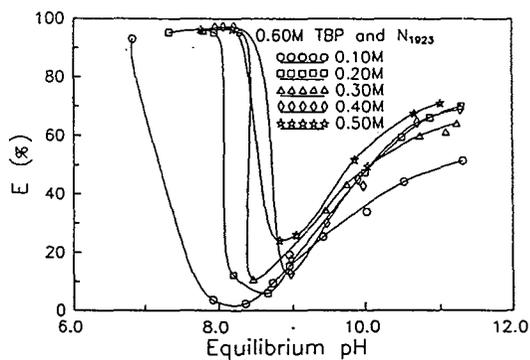


Figure 4. Effect of addition of different amounts of  $N_{1923}$  on the extraction of Au(I) by 0.60M TBP in n-octane from 0.8M  $Na_2S_2O_3$  solutions. 0.24mM Au(I), R=1, 18 °C , t=10min

In Fig.5, the extraction curves are also shifted to higher pH values with an increase in the TBP concentration, the percentage of gold extraction increases especially for pH values > 9. It may be considered that TBP in the mixed solvents is the main extractant for pH > 9.

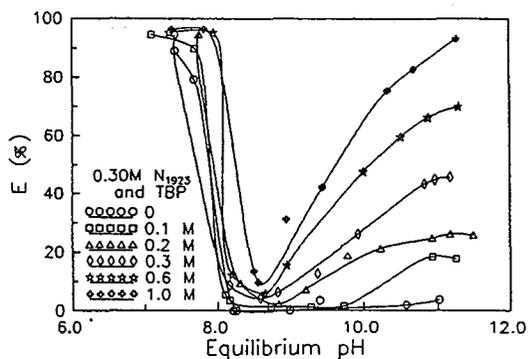


Figure 5. Effect of addition of different amounts of TBP on the extraction of Au(I) by 0.30M  $N_{1923}$  in n-octane from 0.8M  $Na_2S_2O_3$  solutions. 0.24mM Au(I),  $R=1$ ,  $25^\circ C$ ,  $t=10min$

The synergistic factors for gold extraction with mixed  $N_{1923}$  and TBP solvents have been calculated and the results are shown in Table 1. It can be seen that the factors are about ten, with either TBP as a synergistic extractant in weakly alkaline thiosulfate solutions ( $pH < 9$ ) or  $N_{1923}$  as a synergistic extractant in strongly alkaline thiosulfate solutions ( $pH > 9$ ).

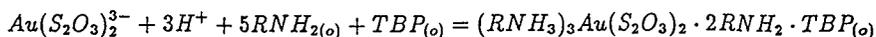
TABLE 1

The synergistic factor  $\beta$  for gold extraction with a mixture of  $N_{1923}$  and TBP in n-octane. ( 0.24mM Au(I) in 0.8M  $Na_2S_2O_3$  )

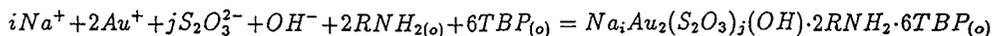
0.30M $N_{1923}$ with TBP TBP concentration	(pH 8.0) $\beta$	0.60M TBP with $N_{1923}$ $N_{1923}$ concentration	(pH 10.5) $\beta$
0.1 M	1.4	0.1 M	5.7
0.2 M	6.4	0.2 M	9.7
0.3 M	2.6	0.3 M	10.2
0.6 M	10.3	0.4 M	8.8
1.0 M	13.0	0.5 M	5.9

Using slope analysis, the compositions of the gold extraction species in mixed organic solvents were investigated and proposed:

When the equilibrium  $pH < 9$ , the primary amine  $N_{1923}$  in the mixed solvents should be the main extractant:



When the equilibrium  $pH > 9$ , TBP in the mixed solvents should be the main extractant:



Aqueous ammonia solution is always added when leaching gold-containing ores with thio-sulfate solutions to form the copper/ammonia complex as a catalyst for the leaching process. The mixed solvent of  $N_{1923}$  and TBP was used in the extraction of gold from ammoniacal thio-sulfate solutions and the results are shown in Fig.6. It can be seen that gold can be separated from the other metals present in the leach solutions for gold recovery.

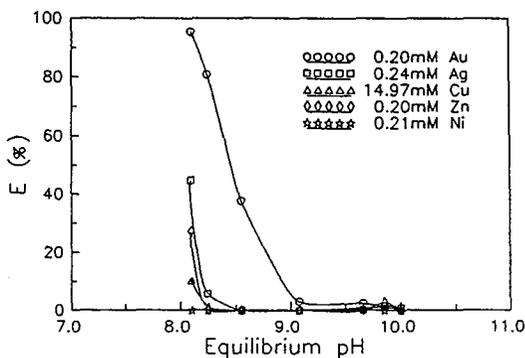


Figure 6. Percent extraction versus equilibrium pH for extraction of Au, Ag, Cu, Zn and Ni with 0.5M  $N_{1923}$  and 0.6M TBP in n-octane from 0.8M  $(NH_4)_2S_2O_3$  solution.  
 $R=1$ ,  $20\text{ }^\circ\text{C}$ ,  $t=10\text{min}$

#### ACKNOWLEDGEMENTS

The author would like to thank the National Natural Science Foundation of China for its financial support of this work.

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# STRUCTURAL STUDIES ON LANTHANIDE(III) COMPLEXES WITH DIPHOSPHINE DIOXIDE (DPDO) by NMR SPECTROSCOPY

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## ABSTRACT

Nuclear Magnetic Resonance spectra for lanthanide (III) - Diphosphine dioxide (DPDO) complexes were measured for the extraction system with DPDO from nitric acid solution. The obtained lanthanide induced shifts (LIS) for  $^{31}\text{P}$ NMR mainly consist of Fermi contact, dipolar, complex formation shifts, and were theoretically separated into these three components, so that it was found that there were two series of magnetic interactions in these complexes. This would be because 3 or 4 DPDO molecules are coordinated to the lanthanides in this extraction system. The hyperfine coupling constants, calculated by a series of Fermi contact shifts, indicated that the electron in the heavy lanthanide (Eu ~ Yb) -DPDO complexes delocalized and/or phosphorus s orbital overlapped directly with the next atom's orbital rather than was case for the light lanthanides (Ce ~ Sm). The bond angles between the phosphorus and the lanthanides to the principle axis of symmetry of the complex calculated by dipolar shift values were about  $54.7^\circ$  for the light lanthanides and  $54.7^\circ \sim 125.3^\circ$  for the heavy ones.

## INTRODUCTION

Diphosphine dioxides (DPDO), bidentate organophosphorus compounds are well known as extractants for the tri-valent lanthanides. Studies on the liquid-liquid extraction of the lanthanide-DPDO complexes have been performed by many researchers-Myasoedov et al (1986), Rozen et al (1986), (1976). From these studies, one of the most interesting features is the so-called "anomalous aryl effect" (AA effect). This is as follows: against the rule known for monodentate analogs<sup>4)</sup>, the extractive power of DPDO increases essentially when replacing aryl radicals at the phosphorus atoms by more electronegative aryl ones. Though it is not clear, this AA effect may be caused by strengthening of the complex by delocalization of electron density from the phenyl rings into the ring formed with a metal and by formation of a system of conjugated bonds in the ring. However, direct information available regarding the nature of the complex formed between the metal ion and the extractant compound has not been found so far. Information with respect to the electron structure of the extracted complex is very important to discuss concerning the extractability of such a bidentate complex. From the above point of view, in this study, nuclear magnetic resonance (NMR) spectra were measured to clarify a conformation and spin structure of lanthanide-DPDO complexes.

## EXPERIMENTAL

### Reagent

The extractant used was Tetra(p)tolylmethylene diphosphine dioxide purchased from Vernadsky Institute of geochemistry and analytical chemistry in Russia. The purity of this reagent was more than 99%, confirmed by melting point, analysis of the elements, NMR and thin-layer chromatography data. Therefore, we used this reagent without further purification.

### General procedure

Distribution ratios of the lanthanides were determined by ICP-MS ( Inductively Coupled Plasma - Mass Spectrometry ). Sample solutions containing 1ppm each of 14 lanthanides were prepared by dilution of the standard lanthanide solutions.  $1 \times 10^{-3} \text{ dm}^3$  of sample solution and the same volume of DPDO solution were shaken for 30 min. and centrifuged for 10 min. at 298 K.

The  $^{31}\text{P}$ NMR spectra were measured using  $\text{CDCl}_3$  solutions of the lanthanide-DPDO complexes at 300K by the Fourier transform mode at 161.9MHz with a Varian Unity 400 plus spectrometer (  $H_0 = 9.4 \text{ T}$  ). The extracted complexes were prepared by the usual extraction method.

### LANTHANIDE INDUCED SHIFT (LIS) SEPARATION THEORY

Nuclei of ligands in paramagnetic complexes are coupled to electronic spin of the central ion by the electron-nuclear hyperfine interaction. One of the consequences of this interaction is a large chemical shift in the NMR spectra of the ligands. This chemical shift is generally expressed as follows:

$$\Delta_{\text{LIS}} = \Delta_{\text{con}} + \Delta_{\text{dip}} + \Delta_{\text{cfs}} \quad \text{----- (1)}$$

Thus, the net LIS,  $\Delta_{\text{LIS}}$ , can be expressed as a sum of three contributions: the contact shift,  $\Delta_{\text{con}}$ , the dipolar shift,  $\Delta_{\text{dip}}$ , and the complex formation shift,  $\Delta_{\text{cfs}}$ .

The contact interaction results from a finite probability of finding an unpaired electronic spin on an atomic s orbital, and is referred to as spin polarization in contrast to delocalization or direct overlap. Therefore, this can be expressed as

$$\Delta_{\text{con}} = A \langle S_z \rangle \quad \text{----- (2)}$$

where A is the hyperfine coupling constant and  $\langle S_z \rangle$  is the projection of the total electron spin magnetization of the lanthanide on the direction of the external magnetic field. In this study, the  $\langle S_z \rangle$  values calculated by Golding and Halton(1972) were adopted.

The dipolar interaction takes place through space and causes a shift only if the magnetic susceptibility of the central ion is anisotropic.

$$\Delta_{\text{dip.}} = -\frac{1}{3r^3} \left\{ \left[ \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) \right] (3\cos^2\theta - 1) + \frac{3}{2}(\chi_{xx} - \chi_{yy}) \sin^2\theta \cos 2\phi \right\} \text{----- (3)}$$

If the complex is axially symmetric or has an effective axial symmetry because of the ligand atoms, equation (3) reduces to:

$$\Delta_{\text{dip.}} = \frac{K_{\text{CF}} C_m^{\text{D}}}{I^2} \left\langle \frac{3\cos^2\theta - 1}{I_2^3} \right\rangle = G_n C_m^{\text{D}} \text{----- (4)}$$

where  $C_m^{\text{D}}$  is a lanthanide ion dependent parameter calculated by Golding and Pyyko(1973).

The complex formation shift, attributed in part to changes in the ligand electron density caused by the presence of a diamagnetic shift reagents, or both. In that case, the complex formation shift is given by

$$\Delta_{\text{cf.}} = [\Delta^{\text{L}^{\text{a}}} + \Delta^{\text{L}^{\text{a}}}] / 2 \text{----- (5)}$$

From equation (2), (4) and (5), equation (1) is expressed by

$$\Delta_{\text{LIS}} = A \langle S_z \rangle + G_n C_m^{\text{D}} + K_n \text{----- (6)}$$

Furthermore, equation (6) can be modified to solve graphically as the following equation

$$\frac{\Delta_{\text{LIS}} - K_n}{C_m^{\text{D}}} = A \left( \frac{\langle S_z \rangle}{C_m^{\text{D}}} \right) + G_n \text{----- (7)}$$

Therefore, when a plot of the relationship between  $\left( \frac{\langle S_z \rangle}{C_m^{\text{D}}} \right)$  and  $\frac{\Delta_{\text{LIS}} - K_n}{C_m^{\text{D}}}$  is done, the

hyperfine coupling constant, A, and parameter,  $G_n$ , can be obtained, so that the spin density of the observed nucleus and bond angle between the lanthanide and the observed nucleus can be calculated.

## RESULTS AND DISCUSSION

### *Extraction properties*

Figure 1 shows the distribution ratios of the lanthanides with DPDO from nitric acid solution. Distribution ratios of the lanthanides in the nitric acid concentration range from 1 to 3 mol dm<sup>-3</sup> decreased with atomic number. It was an unexpected result from the point of view of complexation between hard cations and hard ligand. Because the lanthanide ionic radius decreases with atomic number due to the lanthanide contraction, the charge density of the lanthanide elements increases. Therefore, it is considered as a general pattern that distribution ratios increase with atomic number. Superimposed on this trend is the tetrad effect which is evident in three points (z=60~61, 64, 67~68). However, in this study, the minor dip at the 3/4 point is not clearly found. Jørgensen(1970) reported that the tetrad effect in the distribution coefficient of Ln<sup>3+</sup> has been regarded as an example of the nephelauxetic effect, with the interaction repulsion parameters decreasing with increasing covalency of the metal-ligand bonding.

Therefore, the tetrad effect in this study suggested that the bonding in Ln-DPDO extracted complexes would be classified into two types.

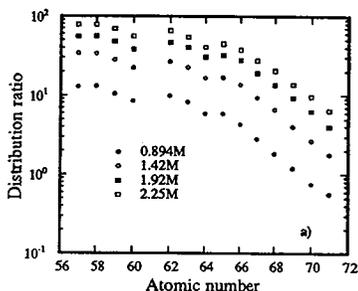


Fig. 1a) Distribution ratios of lanthanides with DPDO from nitric acid solution ( $[\text{HNO}_3]=0.894\sim 2.25 \text{ mol dm}^{-3}$ ).

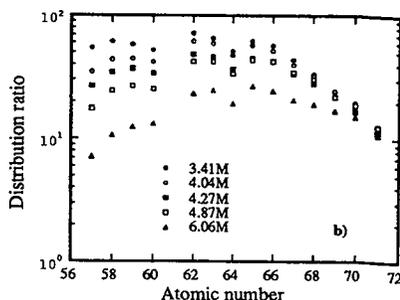


Fig. 1b) Distribution ratios of lanthanides with DPDO from nitric acid solution ( $[\text{HNO}_3]=3.41\sim 6.06 \text{ mol dm}^{-3}$ ).

#### NMR spectroscopy and LIS separation

The representative  $^{31}\text{P}$ NMR spectrum is shown in Fig. 2. These two peaks were attributed to a free peak ( $\delta=28$ ) and a complexed peak ( $\delta=34$ ), respectively, comparing with the simple DPDO peak ( $\delta=28$ ). The shift values of all the lanthanide elements, i.e.,  $\Delta_{\text{LIS}} = (34 - 28) \times 161.9 \text{ Hz}$ , were substituted into equation (7), and the plotted diagram of  $\langle S_z \rangle / C_m^{\text{D}}$  vs.  $(\Delta_{\text{LIS}} - K_n) / C_m^{\text{D}}$  is shown in Fig. 3. There are two linear relationships in this figure. This linearity means an axial symmetry justified by molecular symmetry and an apparent axial symmetry by motional averaging for the magnetic susceptibility. Furthermore, the structures of the lanthanide complexes could be classified into two groups, the light lanthanides (Ce ~ Sm) and the heavy lanthanides (Eu ~ Yb). The calculated shift values are listed in Table 1. These calculated total shift values agreed with the observed total values. Furthermore, the obtained  $A$  and  $G_n$  values, and the calculated spin density ( $\rho$ ) and bond angle between the lanthanide elements and the observed phosphorus atom to the principal magnetic  $Z$  axis of this system are listed in Table 2. From the results for the spin densities, the phosphorus atoms for the light lanthanides were found to have more unpaired electronic spin on an atomic  $s$  orbital, compared with that for the heavy ones. This means that delocalization or orbital direct overlap in light lanthanide complexes is less than that in the heavy ones. According to the AA effect model, these complexes are stabilized with electron delocalization. Therefore, this indicates that the heavy lanthanides are complexed and stabilized more highly than the light lanthanides.

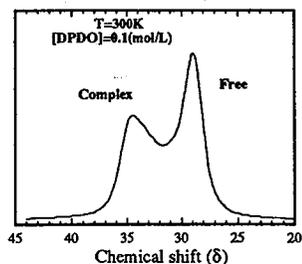


Fig. 2  $^{31}\text{P}$ NMR spectrum of La-DPDO complex in  $\text{CDCl}_3$  at 300K.

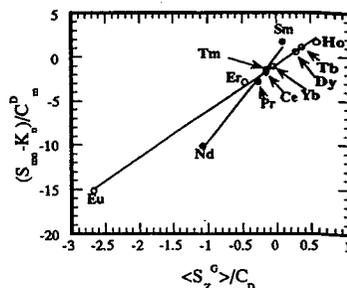


Fig. 3 Separation method applied to the  $^{31}\text{P}$ NMR LIS for Ln-DPDO coplexes.

Table 1 Calculated Fermi contact and dipolar  $^{31}\text{P}$  shifts for lanthanides- DPDO complexes.

Ln	Contact shift / ppm	Dipolar shift / ppm	LIS total	
			Calc.	Obs.
Ce	9.64	-1.18	18.1	20.9
Pr	29.3	-2.06	36.8	41.1
Nd	44.2	-0.786	53.0	52.2
Sm	-0.621	-0.131	8.85	8.46
Eu	-56.2	-3.32	-49.9	-50.9
Tb	-167	71.4	-86.0	-79.8
Dy	-150	83.1	-57.3	-46.8
Ho	-116	32.4	-74.0	-54.8
Er	-78.9	-27.4	-96.7	-86.8
Tm	-43.2	-44.0	-77.6	-68.8
Yb	-13.6	-18.3	-22.3	-12.4

These results agree with the decrease in distribution ratio of the light lanthanides in greater than 3M nitric acid (Fig. 1b). From the tetrad effect results, it was considered that the heavy lanthanides would complex more covalently with DPDO than the light ones. The spin density of DPDO also supports this idea, because this delocalization and orbital overlap are considered as evidence for bonding covalently.

**Table 2 Spin densities of the phosphorus atom and the bond angle between the lanthanides and the phosphorus.**

Compound(Ln <sup>3+</sup> )	Spin density ( $\rho$ )	Bond angle (degree)
DPDO(Ce ~ Sm)*	$2.2 \times 10^{-5}$	54.7
DPDO(Eu ~ Yb)*	$1.2 \times 10^{-5}$	54.7 ~ 125.3
CMPO(Ce ~ Sm)	$2.2 \times 10^{-5}$	57.5
CMPO(Eu ~ Yb)	$1.2 \times 10^{-5}$	57.6
TBP(Ce ~ Sm)	$3.8 \times 10^{-5}$	N.D.
TBP(Eu ~ Yb)	$3.1 \times 10^{-5}$	N.D.

\* This work

Furthermore, the spin densities of phosphorus for DPDO were similar to that for CMPO, but smaller in value in comparison with that for TBP. Therefore, a bidentate extractant is bound more covalently to the lanthanides than monodentate ones.

The bond angle between the phosphorus and the lanthanides to the principle axis of symmetry of the complex calculated by dipolar shift values was about 54.7° for the light lanthanides and 54.7° ~ 125.3° for the heavy ones.

### CONCLUSION

The hyperfine coupling constants were calculated by a series of Fermi contact shifts, so that the spin densities on the phosphorus atom were obtained. These spin densities indicated that the electron in the heavy lanthanide(Eu ~ Yb)-DPDO complexes is delocalized and/or phosphorus s orbital overlapped directly with the next atom's orbital rather than for the light lanthanide(Ce ~ Sm) ones. Therefore, the heavy lanthanides complexed more covalently with DPDO than the light ones. The bond angle between the phosphorus and the lanthanides to the principle axis of symmetry of the complex were about 54.7° for the light lanthanides and 54.7° ~ 125.3° for the heavy ones.

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## Liquid-Liquid EXTRACTION of METAL IONS with POLYTHIOETHER DERIVATIVES

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### ABSTRACT

Several kinds of new polythioether derivatives were successfully synthesized. Reagents containing 2, 3 and 4 sulfur atoms were synthesized by the reaction of the dithiol ( ethanedithiol, 3-thiapentane-1,5-dithiol and 1,4,8,11-tetrathiatetradecane ) and the appropriate alkyl bromide. Liquid-liquid extraction of metal ions with these reagents were examined. Soft metal ions such as Ag(I), Cu(I), Hg(II) and Pd(II) ions were selectively extracted, and hard and intermediate metal ions were not extracted, with the exception of Cu(II) ion. The extraction behavior of Ag(I) was examined in detail.

### INTRODUCTION

Thiacrown ethers ( macrocyclic polythioethers ), in which some sulfur atoms are included as thioether groups, act as soft Lewis bases. These can selectively react with soft Lewis acids such as Cu(I), Ag(I), Pd(II) and Hg(II). As well as thiacycrown ethers, Acyclic polythioethers have a high selectivity for soft metal ions. Extraction capabilities can be superior to thiacycrown ethers, and the synthesis of acyclic compounds is simple and shorter than for thiacycrown ethers. Nevertheless, the development of the chemistry of acyclic polythioether derivatives is important as there are few studies examining the behavior of acyclic polythioethers as solvent extraction reagents for soft metal ions. In this study, 13 kinds of reagents were synthesized and their extraction behaviors of metal ions were examined and compared.

### EXPERIMENTAL

#### *Synthesis of reagents*

The commercially available dithiol, 1,2-ethanedithiol was used. Two compounds, 3-

thiapentane-1,5-dithiol and 1,4,8,11-tetrathiatetradecane were synthesized according to the methods described previously.[2] Acyclic thioether 3,6-dithiooctane was synthesized according to the following method : Under nitrogen, sodium ( 5.18g, 0.255mol ) was dissolved in 200ml of ethanol, and 1,2-ethanedithiol ( 10.0g, 0.106mol ) was added dropwise. To this solution, 60ml of benzene containing ethyl bromide ( 23.4g, 0.215mol ) was added. After stirring at room temperature for 1h, the mixture was filtered and evaporated in vacuo. The residue was dissolved in benzene ( 200ml ), washed with 0.1N NaOH solution and water, dried over magnesium sulfate and evaporated. The oily residue was purified by silica gel column chromatography (benzene as eluent ). The other polythioethers were synthesized similarly according to the method described above. The products were purified by silica gel column chromatography, and recrystallized twice if the compounds were solid at room temperature. The purity was verified using NMR, IR and MS.

#### ***Other reagents and Apparatus***

Reagents used for liquid-liquid extraction were of analytical reagent grade except 1,2-dichloroethane. The extraction solvent 1,2-dichloroethane, was shaken three times with 2M potassium hydroxide solution followed by shaking three times with water, dried over calcium chloride, and distilled. Extraction was carried out in a Taiyo M incubator. A Hitachi z-8000 atomic absorption spectrophotometer was used to determine the concentration of metal ions in the aqueous solutions. The pH of the aqueous solutions was measured with a Hitachi-Horiba M-7 pH meter.

#### ***Liquid-liquid extraction of metal ions***

An aliquot ( 10ml ) of aqueous solution containing the metal ion (  $5 \times 10^{-5}M$  ), picrate ion (  $1 \times 10^{-3}M$  ), and acetate buffer (  $1 \times 10^{-2}M$  ) was adjusted to an ionic strength of 0.1 with sodium sulfate. This solution and 10ml of the di-, tri- or tetra-thioether derivative solution in 1,2-dichloroethane in a stoppered cylindrical tube were shaken (180 strokes  $\text{min}^{-1}$ ) for 30 min at  $25 \pm 0.1$  °C . The mixture was then centrifuged for 5 min at 2000 rpm. After the two phases were separated, the pH of the aqueous phase was measured and the concentration of the metal ion in the aqueous phase and in the organic phase were determined by atomic absorption spectrometry.

## RESULTS AND DISCUSSION

Thirteen thioether derivatives were successfully synthesized. The synthetic routes were simple and the yields were high ( 50-99% except 6-2Ph-2S of 16.4% ). On the other hand, in the case of the synthesis of macrocyclic polythioethers, preparation time is lengthy

Table 1 The extraction of various metal ions with dithioether derivatives  
 (  $\alpha$  : parameter of softness)

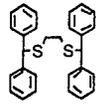
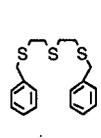
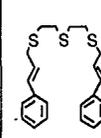
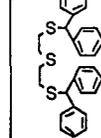
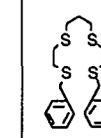
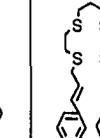
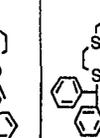
metal	class	$\alpha$ value	 8-2S		 12-2S		 6-2cH-2S		 6-2Ph-2S		 10-2Ph-2S		 6-2Sty-2S		 6-4Ph-2S	
			pH	E%	pH	E%	pH	E%	pH	E%	pH	E%	pH	E%		
Mn(II)	ab	1.04	4.8	0	4.8	0	4.9	0	4.8	0	4.7	0	4.8	0	4.8	0
Zn(II)	ab	1.25	4.8	0	4.9	0	4.9	0	4.8	0	4.8	0	4.8	0	4.8	0
Co(II)	ab	1.39	4.8	0	4.8	0	4.9	0	4.8	0	4.8	0	4.8	0	4.8	0
Ni(II)	ab	1.41	4.8	0	4.9	0	4.9	0	4.8	0	4.9	0	4.8	0	4.8	0
Cu(II)	ab	1.64	4.7	0	4.7	0	4.8	3	4.7	1	4.8	0	4.8	1	4.7	1
Cd(II)	b	1.65	4.8	0	4.8	0	4.8	0	4.8	0	4.9	0	4.8	0	4.8	0
Ag(I)	b	3.60	4.8	99	4.8	99	4.8	99	4.9	99	4.8	99	4.8	99	4.8	99
Cu(I)	b	3.92	4.6	100	4.5	70	4.7	93	4.7	96	4.5	63	4.5	59	4.5	63
Pd(II)	b	5.33	5.0	67	5.0	72	5.0	53	4.9	51	4.8	29	5.0	70	4.9	40
Hg(II)	b	5.83	3.2	84	3.2	99	3.2	99	3.2	92	3.2	97	3.2	95	3.2	99

Table 2 The extraction of various metal ions with tri- and tetrathioether derivatives

( $\alpha$  : parameter of softness)

metal	class	$\alpha$ value												
			pH	E%	pH	E%	pH	E%	pH	E%	pH	E%	pH	E%
Mn(II)	ab	1.04	4.8	0	4.8	0	4.8	0	4.8	0	4.8	0	4.8	0
Zn(II)	ab	1.25	4.9	0	4.9	0	4.9	0	4.9	0	4.9	0	4.9	0
Co(II)	ab	1.39	4.8	0	4.8	0	4.8	0	4.8	0	4.8	0	4.8	0
Ni(II)	ab	1.41	4.8	0	4.8	0	4.8	0	4.8	0	4.8	0	4.8	0
Cu(II)	ab	1.64	4.8	1	4.8	5	4.8	1	4.8	1	4.8	8	4.8	1
Cd(II)	b	1.65	4.8	0	4.8	0	4.8	0	4.8	0	4.8	0	4.8	0
Ag(I)	b	3.60	4.9	99	4.8	99	4.8	99	4.8	99	4.8	99	4.8	99
Cu(I)	b	3.92	4.8	29	4.9	38	4.9	40	4.9	47	4.9	70	4.9	65
Pd(II)	b	5.33	5.1	32	4.9	46	4.9	17	4.9	32	5.1	46	5.1	21
Hg(II)	b	5.83	3.4	97	3.1	98	3.1	98	3.3	99	3.4	99	3.3	99

and a large amount of solvent is required for the high dilution method. The percent extraction of metal ions after shaking for 30 min are shown in Tables 1 and 2. As well as the thiocrown ethers, each of the acyclic thioether derivatives extracted soft metal ions (class *b* metal ions) selectively. On the other hand, hard and intermediate (class *a* and *ab*) metal ions were not extracted at all, with the exception of Cu(II). Greater than 99% extraction of Ag(I) was achieved with each reagent. For the thioether compound with two terminal ethyl groups (8-2S) greater than 99% extraction of Cu(I) was also achieved. Low extraction efficiencies were obtained with the reagents containing lipophilic groups and three sulfur atoms. In the case of 3S and 4S ligands, 2 hours were required to reach the extraction equilibrium. Then, after shaking for 2 hours, all reagents extracted more than 99% Cu(I). Palladium (II) ion extraction required more than 2h to reach equilibrium for the 3S-ligands, 3h for the 4S-ligands and 5h for the 2S-ligands. At equilibrium, Pd(II) was extracted greater than 90% with each reagent. In the case of the Hg(II) ion, the 3S and 4S reagents extracted more than 99%.

#### *Extraction behavior of the silver ion*

The extraction behavior of the silver (I) ion with the thioether derivatives was examined in detail. Fifteen minutes was required to reach the extraction equilibrium in the case of the 3S and 4S-reagents, and a few minutes for the 2S-reagents. Figure 1 shows the plots of the percent extraction vs. pH of the aqueous phase in the case of the 2S-reagents. At a pH less than 4.0, the extraction efficiency begins to decrease, perhaps due to the proton dissociation of the picrate ion. Alternatively, greater than 99% extraction efficiency was achieved for the 3S and the 4S-reagents at a pH of less than 2.0. The compositions of the extracted species were obtained by the molar ratio method or by slope analysis. As shown in Fig.2, in the case of the 2S-reagents, the molar ratio of Ag:L (reagent) is 1:2. The composition of extracted species is Ag:L:Pic = 1:2:1 for the 2S-reagents (6-2Ph-2S, 6-2Sty-2S and 6-4Ph-2S), and for the 3S-reagents (9-2Ph-3S, 9-2Sty-3S and 9-4Ph-3S). For the 4S-reagents (13-2Ph-4S, 13-2Sty-4S and 13-4Ph-4S), the composition 1:1:1 was obtained. It is interesting that increasing the lipophilicity of the terminal groups causes a decrease in the percent extraction of the silver ion. The percent extraction of monovalent class *b* metal ions, including Cu(I), by the reagents which have lipophilic terminal groups is lower than that with the reagents which have ethyl-terminal groups. On the other hand, in the case of divalent metal ions such as Pd(II) and Hg(II), the percent extraction with a lipophilic reagent is higher than that for reagents with ethyl terminal groups. The percent extraction of Ag increases with an increasing number of sulfur atoms. It is believed that the silver ion takes on a tetrahedral configuration in the case of the 2-S and 4-S reagents, and on octahedral configuration

in the case of the 3-S reagents.

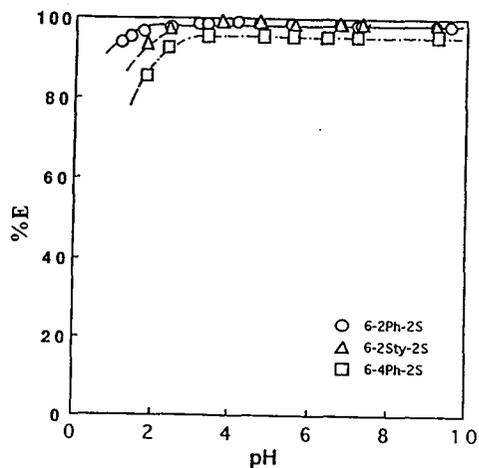


Fig. 1 Plots of %E vs. pH for the extraction of Ag(I) with dithioether derivatives.

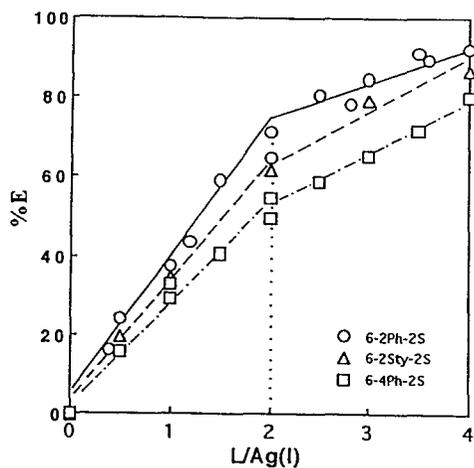


Fig 2. Plots of %E vs. the concentration ratio of dithioether derivatives and Ag(I)

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## Liquid-Liquid EXTRACTION of METAL IONS from MIXED Hydrochloric Acid-Sulphuric Acid Media by TBP

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### ABSTRACT

Tri-n-butyl phosphate (TBP) has been extensively studied in its performance for the extraction of metal ions from aqueous solutions. Numerous papers deal with the extractive properties of TBP from HCl with or without an additional electrolyte. In many of the systems studied a single anion is used. However, the extraction of metals from HCl/H<sub>2</sub>SO<sub>4</sub> media has been little considered. So, in this work the extraction behaviour of Cd(II), Cu(II), Co(II), Fe(III), Ni(II) and Zn(II) from HCl/H<sub>2</sub>SO<sub>4</sub> media by TBP has been studied systematically at 25°C. In addition, the diluent effect on the extraction by TBP has been also studied. It has been found that sulphuric acid causes, generally, a rise in the percentage of extraction (salting-out effect). Nevertheless, in the case of copper extraction, the presence of sulphuric acid does not remarkably influence the distribution curves of this metal ion. The results are treated in terms of thermodynamic activities in the aqueous phase, to determine the composition of the extracted complexes and to discuss the extraction mechanism. The activities of HCl and H<sub>2</sub>SO<sub>4</sub> are determined on the basis of Zdanovskii's rule and Mikulin's relationship, with the computer programme CALCACT (developed in this laboratory).

### INTRODUCTION

In the metallurgical industry, the separation and purification processes play a very important role in the production of a given metal. Thanks to this, separation techniques, such as liquid-liquid extraction, have been developed, and have been easily implemented in hydrometallurgical production lines. The development of commercial extractants has been of great importance in this process. Tri-n-butyl phosphate (TBP) is one of the commercial extractants most completely studied in the extractions of metal ions. Due to its chemical stability in highly acidic solutions and its low cost, TBP can be used in various hydrometallurgical processes, in the separation or recovery of metal ions by liquid-liquid extraction. A great number of studies deal with the extractive properties of TBP, for different metal ions from HCl solutions, with or without an additional electrolyte (Irving and Edgington (1959), Morris and Short (1962), Sato (1972), Mühl et al. (1980), Chang et al. (1986)). In most of these studies a single anion is used. However the extraction of metal ions from mixed HCl/H<sub>2</sub>SO<sub>4</sub> media, although commonly found in industry, has been little considered. Given the importance of efficient separation processes at an industrial level, it is necessary to develop separation methods that may be easily applied under different practical conditions. Thus in this paper, results obtained in the study of the extractive properties of TBP for different metal ions (Cd(II), Co(II), Fe(III), Ni(II) and Zn(II)) from mixed HCl/H<sub>2</sub>SO<sub>4</sub> media are presented.

## EXPERIMENTAL

All the reagents used were analytical grade. The tri-n-butyl phosphate was kindly supplied by the Daihachi Chemical Industry Co, LTD. The organic phase consists of concentrated TBP or TBP diluted to 25% with kerosene, xylene or toluene. The aqueous phase consists of the metal ion to be extracted and HCl and H<sub>2</sub>SO<sub>4</sub>. Given that TBP is capable of extracting water, it is necessary to equilibrate it previously with an aqueous phase, which contains HCl and H<sub>2</sub>SO<sub>4</sub> only, for 20 min. The extraction of the metal ions is carried out in the same acidic conditions. The phases are separated and the organic phase treated in this way is used to obtain the distribution curves of the different metal ions. The ratio of volumes of the organic phase ( $v_{org}$ ) and aqueous phase ( $v_{aq}$ ) was in every case equal to one ( $v_{aq} = v_{org} = 10$  ml). The solutions (aqueous phase /organic phase) are shaken with a (Colé Palmer 51502) ping-pong shaker at 150 rpm at 25 °C for 20 min, which is enough time to reach equilibrium. Once equilibrium is attained, the phases are separated and the concentration of the metal ion in the aqueous phase is determined with a (Perkin-Elmer 3110) atomic absorption spectrometer. Concentrations of metal in the organic phase are calculated by mass balance. The concentrations of HCl and H<sub>2</sub>SO<sub>4</sub> extracted by the TBP were determined by potentiometric titration (Titrimo 716 Metrohm) with NaOH 0.1 M.

The values of the activity of water ( $a_{H_2O}$ ) in HCl and H<sub>2</sub>SO<sub>4</sub> are those reported by Hamer and Wu (1972) and Staples (1981), respectively. In the case of the mixed HCl/H<sub>2</sub>SO<sub>4</sub> media, the values of  $a_{H_2O}$  were calculated using the CALCACT programme. This programme was written in Quick Basic. It allows us to obtain the activity coefficients (based on Mikulin's relationship) of the different electrolytes of a solution and the activity of water (based on Zadonvskii's rule) for the same solution.

## RESULTS AND DISCUSSION

**Distribution curves of Cd(II), Cu(II), Co(II), Fe(III), Ni(II) and Zn(II) in the TBP/HCl/H<sub>2</sub>O and TBP/HCl/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O systems.**

The results obtained in the study of the extraction of metal ions Cd(II), Cu(II), Co(II), Fe(III), Ni(II) and Zn(II) by concentrated TBP from solutions of hydrochloric acid (1-9 M) indicate, that the TBP has a different affinity for each of the metal ions under study. In the case of Cd(II), Fe(III) and Ni(II) the percentage of extraction (%E) is about 90%, 99% and 80% respectively, when the HCl concentration varies between 2 and 9 M. Zn(II) also showed high %E (95%) with concentrations of HCl around 2 M. These begin to decrease when the concentration of HCl is 4 M. At 9 M HCl concentration, the percentage of extraction for this metal ion is 65%. In the case of Cu(II) and Co(II), the %E obtained were low in comparison with the other ions studied. The maximum %E obtained was about 50% for Cu(II) ([HCl] = 7 M) and 60% for Co(II) ([HCl] = 9 M).

In the case of the mixed HCl/H<sub>2</sub>SO<sub>4</sub> media, the results obtained indicate that H<sub>2</sub>SO<sub>4</sub> has an important influence on the extraction process. The most notable effect of the presence of sulphuric acid is observed in the extraction of Ni(II). Indeed, in the absence of the acid, extraction efficiency levels of around 80% are achieved. On the other hand, in the presence of H<sub>2</sub>SO<sub>4</sub> (1 M) the levels of efficiency of extraction are less than 1%, in the whole range of concentrations of HCl studied (1-9 M).

The effect of the H<sub>2</sub>SO<sub>4</sub> concentration on the distribution curves of the metal ions Cd(II), Co(II), Cu(II) and Zn(II) are shown in figure 1. In this figure, the distribution coefficient is graphed as a function of the HCl concentration for different H<sub>2</sub>SO<sub>4</sub> concentrations (1, 2, 3 and 4 M).

A similar behaviour was recorded in the distribution curves for each one of the metal ions studied. That is, an increase is seen in the value of the distribution coefficient (D) with the concentration of hydrochloric acid, reaching a maximum and later decreasing. The influence of the sulphuric acid on the extraction process is observed by an increase in the maximum of D, and similarly by the displacement of the distribution curves towards lower HCl concentrations. The form of the distribution curves can be explained if one considers, on the one hand, the salting out effect and on

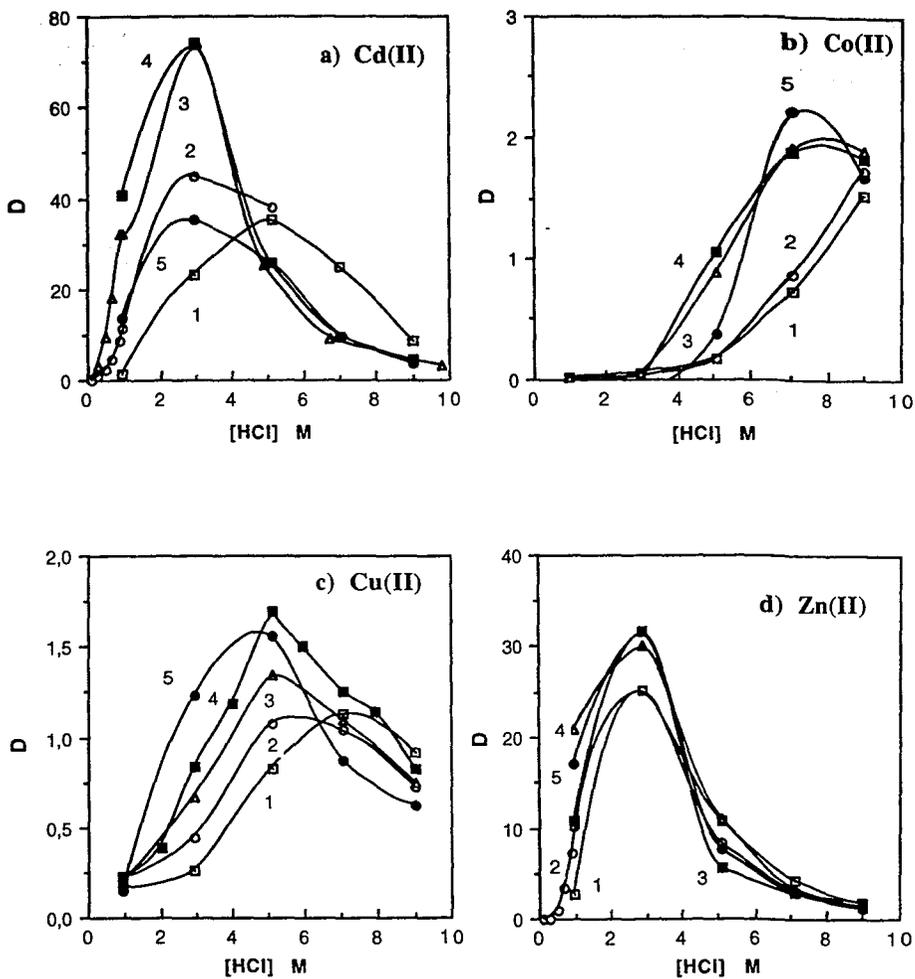


Figure 1.- Distribution Coefficient (D) of metal ions in the system TBP/HCl/ $H_2SO_4$ . a) Cd(II); b) Co(II); c) Cu(II); d) Zn(II). TBP concentrate.  $V_{org}/V_{aq} = 1$ .  $t_{ag} = 20$  min. [Metal ion] =  $1 \times 10^{-3}$  M. [ $H_2SO_4$ ] = 0 M (1); 1 M (2); 2 M (3); 3 M (4); 4 M (5).

the other hand, the extraction of the acid (HCl and H<sub>2</sub>SO<sub>4</sub>) by the TBP. In fact, the aqueous phase has an elevated concentration of electrolytes. Under these conditions the activity of water decreases and causes a variation in the activity coefficients of the different species in solution. The result of this phenomenon is an increase in the extraction of the metal ion by the TBP. The variation in the activity of water in different HCl concentrations, both in the absence and in the presence of sulphuric acid, is shown in table 1. The results shown in this table allow us to observe the differences in the activity of water caused by the presence of H<sub>2</sub>SO<sub>4</sub>.

**Table 1**

Values of the activity of water ( $a_{\text{H}_2\text{O}}$ ) in the absence and in the presence of sulphuric acid. The values in the mixed media were calculated with the assistance of the CALCACT programme.

[HCl] M	$a_{\text{H}_2\text{O}}$ In absence of H <sub>2</sub> SO <sub>4</sub>	$a_{\text{H}_2\text{O}}$ [H <sub>2</sub> SO <sub>4</sub> ] = 0,98 M
0.1	0.9966	0.9565
0.3	0.9897	0.9478
0.5	0.9823	0.9387
0.7	0.9747	0.9290
0.97	0.9637	0.9152
2.91	0.8592	0.7909

When the concentration of acids is very high, there exists a marked competition between these species and the metal ion for TBP. This causes a lowering in the extraction efficiency of that metal ion. For example, when the initial concentration of HCl is 0.1 M and of H<sub>2</sub>SO<sub>4</sub> 0.98 M, the total concentration of hydrogen ions in the organic phase is 0.062 M. At the same H<sub>2</sub>SO<sub>4</sub> concentration and with 9 M HCl, the total concentration of hydrogen ions in the organic phase is close to 2.8 M. Therefore, the concentration of acid in the aqueous phase increases, considerably, the total acidity in the organic phase.

On the other hand, it is interesting to note that the effect of the sulphuric acid on the extraction process varies from one metal ion to another. For example, in the case of Co(II), the presence of H<sub>2</sub>SO<sub>4</sub> has a favourable effect on the extraction yield. On the contrary, in the case of Ni(II), the opposite effect is observed. This has an application in the separation of these metal ions, which is difficult to carry out by other methods.

#### The diluent effect on the extraction of Cd(II) and Cu(II) by TBP

The study of the diluent effect was carried out in the case of the extraction of Cd(II) and Cu(II), using three diluents (kerosene, xylene and toluene), from HCl and mixed HCl/H<sub>2</sub>SO<sub>4</sub> media. The results show a marked decrease in the percentage extraction (%E) for both metal ions. The best extraction yields are obtained using kerosene as a diluent (figure 2).

The effect of sulphuric acid (0.98 M) on these extraction systems was more marked for Cd(II) than for Cu(II), whose extraction yields were about 25%. In the case of the extraction in presence of 2 M H<sub>2</sub>SO<sub>4</sub>, the percentage of extraction was similar in both cases.

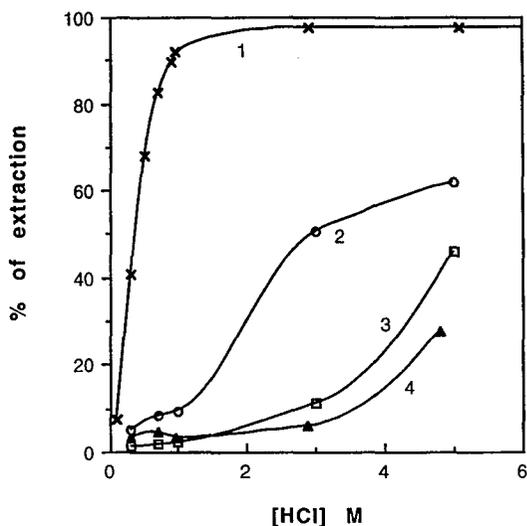


Figure 2. Diluent effect in the extraction of Cd(II) by TBP from HCl / H<sub>2</sub>SO<sub>4</sub> media. 1) TBP concentrated; TBP diluted in 2).- Kerosene; 3).- Toluene; 3).- Xylene.  $V_{org}/V_{aq} = 1$ . [Metal ion] =  $1 \times 10^{-3}$  M.

#### The nature of the species extracted in the organic phase

The determination of the nature of the extracted complex in the organic phase was carried out in the case of the extraction of zinc(II) by TBP in the mixed HCl/H<sub>2</sub>SO<sub>4</sub> media. According to the bibliography (Jörger and Kolarik (1993)), zinc(II) is extracted by TBP from the HCl medium in the form of the neutral molecule to which 2 or 3 molecules of TBP and 1 or 2 molecules of HCl are associated, depending on the conditions in which the extraction process is carried out. In the case of the extraction of Zn(II) from mixed HCl/H<sub>2</sub>SO<sub>4</sub> media, it is necessary to consider the role that sulphuric acid may play in the extraction process. On the one hand, this provides a salting out effect that causes a diminution in the activity of water in the medium, which brings as a result, an increase in the distribution coefficient of the metal ion. On the other hand, the sulphuric acid may directly contribute to the reaction of the extraction of the metal ion. The number of HCl and H<sub>2</sub>SO<sub>4</sub> molecules involved in the extraction process has been determined as follows. A simple model was developed on the basis of the HCl and H<sub>2</sub>SO<sub>4</sub> activities ( $a_{HCl}$  and  $a_{H_2SO_4}$  respectively). This model is applied for mixed HCl/H<sub>2</sub>SO<sub>4</sub> media at HCl concentrations of less than 1 M and 0.98 M H<sub>2</sub>SO<sub>4</sub>. Under these conditions, it is considered that there exists only one predominant complex both in the aqueous phase (ZnCl<sub>2</sub>) and in the organic phase; the activity of TBP (organic phase) is that of a pure solvent ( $a_{TBP} = 1$ ) and the variation of the activity of water is negligible. All the above were considered within the range of concentrations studied, resulting in the equation:

$$\log D = (\log K + b \log a_{H_2O}) + (c \log a_{HCl} + d \log a_{H_2SO_4})$$

Where b, c and d are the number of molecules of H<sub>2</sub>O, HCl and H<sub>2</sub>SO<sub>4</sub> involved in the extraction process of the metal ion.

The function  $\log D = f(c \log a_{HCl} + d \log a_{H_2SO_4})$  is the equation of a straight line with slope equal to 1. The coefficients c and d should be estimated so that experimental values of log D, fit on this straight line. This allows us to determine the number of molecules of HCl and H<sub>2</sub>SO<sub>4</sub> involved in the extraction process. The results obtained in this study are shown in figure 3.

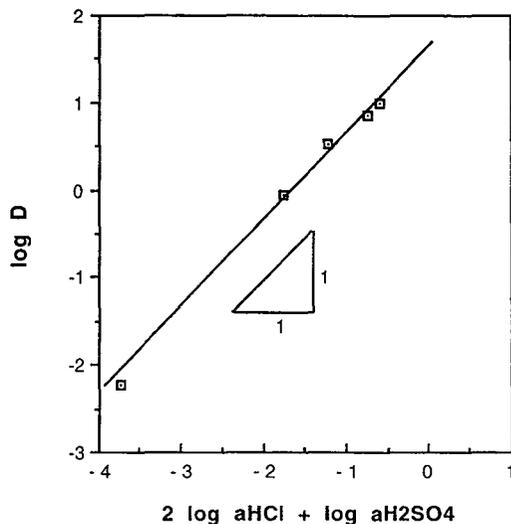


Figure 3.- Variation of  $\log D_{\text{Zn(II)}}$  as a function of  $2\log a_{\text{HCl}} + \log a_{\text{H}_2\text{SO}_4}$ .

It can be seen that the experimental data fits a straight line of slope 1, when the coefficients, c and d, are 2 and 1 respectively. This result suggests that the relationship between the metal ion and the acids in the extracted molecule is 1:2:1 ( $\text{Zn(II)}:\text{HCl}:\text{H}_2\text{SO}_4$ ). This indicates that the  $\text{H}_2\text{SO}_4$  directly contributes to the extraction reaction and does not only modify the characteristics of the medium.

### CONCLUSIONS

The extraction of metal ions by TBP in mixed  $\text{HCl}/\text{H}_2\text{SO}_4$  media is, generally, favoured by the presence of sulphuric acid. This phenomenon can be explained if we assume that the presence of sulphuric acid causes a decrease in the activity of water. As a result, there is better association between ions (cations and anions), to form neutral molecules or ion pairs easily extractable into organic phase. On the one hand, using the distribution curves obtained, it is possible to design a separation process for metal ions, such as in the case of  $\text{Ni(II)}/\text{Co(II)}$  whose separation is difficult to carry out. Also, due to the analysis of the nature of the extracted complex, in the case of the extraction of  $\text{Zn(II)}$  by TBP, it has been possible to determine that the  $\text{H}_2\text{SO}_4$ , as well as modifying the characteristics of the aqueous phase, also participates in the extraction reaction.

### ACKNOWLEDGMENTS

This study was financed by CONACYT as part of project 3177-A.

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# SELECTIVE RECOVERY OF GOLD FROM ELECTRONIC WASTE PRODUCTS BY SOLVENT EXTRACTION AND SURFACTANT LIQUID MEMBRANE EXTRACTION

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## INTRODUCTION

The electronic waste products containing gold are of various nature. Among them are conductors composed, for their metallic part, of a thin film of gold deposited on alloys in which the major component is often copper. A preliminary treatment leads to a hydrochloric acid solution of copper and traces of gold (Cu / Au ~ 100). The problem is therefore to recover the gold selectively.

Two processes were investigated from this point of view : solvent extraction and surfactant liquid membrane extraction ( SLM).

## SOLVENT EXTRACTION

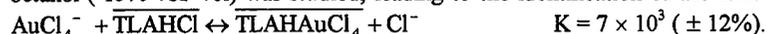
Extraction of gold (III) by tertiary amines was studied by many authors ( Alguacil et al, Sato et al, Villaescusa et al). The extracted species contains  $AuCl_4^-$ , but the extraction constant is rarely estimated. So it is relevant to investigate the Au extraction from this point of view and to determine the value of the equilibrium constant for this extraction. In addition, these extractants are known to extract gold from copper selectively ( Sato et al).

Two tertiary amines were selected: trilaurylamine or TLA and Hostarex A 327, in which the major component is trioctylamine. These amines were diluted in dodecane containing a small amount of octanol, which prevents the formation of a third phase.

The metal solutions contained hydrochloric acid, 0.05 to 0.1  $kg/m^3$  of gold and 5 to 10  $kg/m^3$  of copper.

## BATCH EXTRACTION OF GOLD (III)

Gold (III) is very stable in hydrochloric acid media;  $AuCl_4^-$  is the predominating species. The extraction of Au ( 0.05 to 0.7  $kg/m^3$ ) in HCl ( 2  $kmol/m^3$ ) by TLA ( 8.6  $mol/m^3$ ) in dodecane-octanol ( 15% vol/ vol) was studied, leading to the identification of the following mechanism:



Similar experiments were performed for Hostarex A 327 in the same diluent. The influence of the extractant concentrations was studied and the results are shown in figure 1, where log D ( distribution coefficient) is plotted versus log [Amine]. The slope of the straight line is approximately 1 which confirms the same extraction mechanism. The equilibrium constant is equal to  $3 \times 10^3 (\pm 10\%)$ .

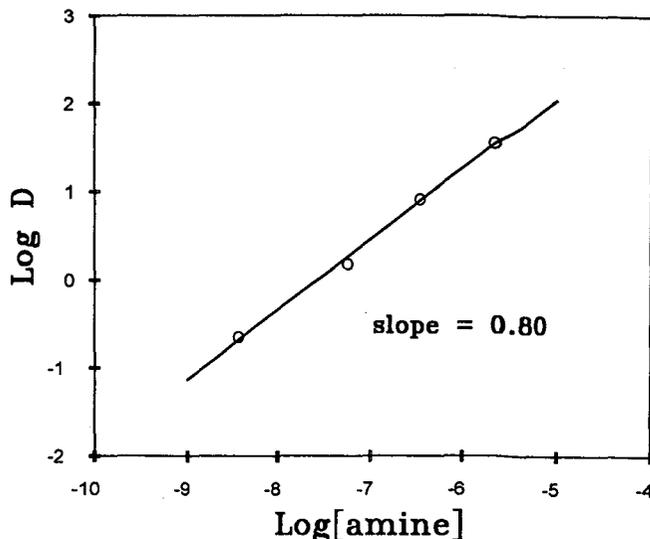
## BATCH STRIPPING OF GOLD

Several reagents were tested with the following conditions: equal volumes of the two phases, TLA ( 3.4 and 8.6  $mol/m^3$ ) in dodecane- octanol ( 15%) containing about 0.1  $kg/m^3$  Au. A mixture of  $NH_3$  or NaOH with NaCl or  $NH_4Cl$  gave precipitates of gold hydroxides.

The stripping efficiency of ammonium thiocyanate is poor ( 6%), but enhanced by the presence of NaOH ( 74% stripping). An efficiency of 100% was achieved with thiourea and sodium

sulfite ( 0.5 kmol/ m<sup>3</sup>). These latter reagents were tested on the solutions of gold in Hostarex A327 wich gave a 100% efficiency.

Figure 1: Extraction of gold by Hostarex A 327



#### BATCH EXTRACTION OF COPPER

Copper (II) was very poorly extracted in the same aqueous medium by both amines. Its distribution ratio was  $5.4 \times 10^{-3}$  for TLA ( 8.6 mol/m<sup>3</sup>) and  $2.5 \times 10^{-3}$  for Hostarex ( 4 mol/m<sup>3</sup>). The separation of the gold from copper was then possible.

#### CONTINUOUS EXPERIMENTS

They were performed in two different contactors: a packed column and a stage of mixer- settler. The column was packed with glass Raschig rings with a height of 0.87 m and an internal diameter of 0.024 m. The organic solution was the dispersed phase. In the stage of mixer-settler, the volumes of the mixer and the settler were respectively  $2 \cdot 10^{-4}$  and  $1.3 \cdot 10^{-3}$  m<sup>3</sup>. The organic solution consisted of Hostarex A 327 ( 7.5 mol/ m<sup>3</sup>) in dodecane- octanol ( 15% vol).

#### Extraction

The aqueous solution contained HCl ( 2 kmol/m<sup>3</sup>), Au ( 0.046 kg/m<sup>3</sup>) and Cu ( 4,5 kg/m<sup>3</sup>). Several total specific flowrates ( TSF) were studied along with different flowrate ratios ( ORG / AQ). As an example results are given for the following conditions:

TSF m <sup>3</sup> s <sup>-1</sup> m <sup>-2</sup>	ORG / AQ	[Au] <sub>raffinate</sub> kg/m <sup>3</sup>	[Au] <sub>org</sub> kg/m <sup>3</sup>	[Cu] <sub>org</sub> kg/m <sup>3</sup>
$1.4 \cdot 10^{-3}$	0.76	$2 \cdot 10^{-3}$	0.062	$6 \cdot 10^{-4}$

The extraction of copper was poor; but if a purity of 99.99% was desired, a scrubbing step would be necessary. These results show the feasibility of the extraction in a packed column; it appears that it was not possible to extract gold quantitatively and to concentrate it in the organic phase. An approximate calculation of the column height shows that in case of ORG/ AQ = 0.2, a

height of 4.5 m would be necessary to extract 99% of gold. The organic extract would then contain 0.23 kg/m<sup>3</sup> Au.

### Scrubbing

This step was tested in a stage of mixer settler with different flowrate ratios between the organic phase containing 0.08 kg/m<sup>3</sup> Au and 7×10<sup>-4</sup> kg/m<sup>3</sup> Cu and the scrubbing solution HCl ( 2 kmol/m<sup>3</sup>). The results were in good agreement with the measured distribution coefficients of the two metals. For example with the ORG / AQ ratio of 3, the concentrations of Au and Cu in the organic phase were 0.076 and 1×10<sup>-4</sup> kg/m<sup>3</sup> respectively . If high purity gold is needed, two scrubbing stages ought to be used.

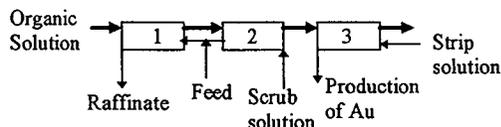
### Stripping

It was tested in both the stage of mixer- settler and in the packed column with thiourea ( 0.5 kmol/m<sup>3</sup>) and an organic solution containing 0.07 kg/m<sup>3</sup> of Au. The column was not very efficient because the stripping kinetics was rather slow. In the stage of mixer- settler the results were satisfactory. For example, with a ORG /AQ ratio of 2.4, the results were as follows: the stripping phase contained 0.136 kg/m<sup>3</sup> of Au and the organic phase 0.009 kg/m<sup>3</sup>.

The stripping was quantitative in these conditions and the stage efficiency was calculated to be equal to 87%, which is acceptable.

### CALCULATION OF THE FLOWSHEET

The previous studies confirmed the feasibility of such a separation. A process flowsheet is then proposed wich involves three steps: (1) extraction; (2) scrubbing; (3) stripping.



The organic phase contained 8 mol/m<sup>3</sup> Hostarex A 327 in dodecane- octanol ( 15%). The feed aqueous solution was HCl (2 kmol/m<sup>3</sup>) containing Au (0.05 kg/m<sup>3</sup>) and Cu ( 5 kg/m<sup>3</sup>). Table below shows an example of the conditions giving a high purity gold ( > 99.99%), a great recovery factor ( 99.9%) and a good concentration factor ( 33)

	Stage number	ORG / AQ	Aq solution kg/m <sup>3</sup>	Org solution kg/m <sup>3</sup>
EXTRACTION	8	0.2	Au 5 × 10 <sup>-5</sup>	Au 0.255 Cu 0.021
SCRUBBING	2	5	Au 0.025 Cu 0.052	Au 0.25 Cu 1.3 × 10 <sup>-5</sup>
STRIPPING	4	6.7	Au 1.65 Cu 9 × 10 <sup>-5</sup>	Au 1.8 × 10 <sup>-3</sup>

### SURFACTANT LIQUID MEMBRANE EXTRACTION

This process involved the formation of a water in oil emulsion ( stripping phase in the organic solution), stabilized by a surfactant, ECA 4360. This emulsion was then dispersed in the

aqueous solution containing Au and Cu. Au was selectively transferred, purified and concentrated.

Two different stripping reagents ( thiourea and sodium sulfite) were tested. Several chemical and operating parameters were investigated.

### THIOUREA

Preliminary experiments showed that a minimum of 2% ECA was necessary to stabilize the emulsion. The breaking rate was less than 10% which is satisfactory for such a process.

The general conditions were the following:

- external aqueous solution: HCl ( 2 kmol/ m<sup>3</sup>); Au ( 0.05 to 0.15 kg/m<sup>3</sup>); Cu ( 0 or 5 kg/m<sup>3</sup>)
- organic phase: TLA ( 0.9 to 7 mol/m<sup>3</sup>); ECA ( 2 to 3%); dodecane
- internal phase: Thiourea ( TU) ( 0.1 to 0.5 kmol/m<sup>3</sup>)
- volume ratio External phase / Emulsion: 5:1
- volume ratio of the emulsion ORG/AQ: 1:3

The first part of this study was devoted to the extraction and concentration of Au in the absence of Cu. Several experiments were performed to study the transfer of copper.

### Kinetics of gold extraction

The residual concentration of Au in the external phase was measured for different contacting times ( figure 2) and different TU concentrations. The conditions were the following: initial Au concentration = 0.15 kg/m<sup>3</sup>; [TLA] = 3.4 mol/m<sup>3</sup>; [ECA] = 2%; ORG/AQ = 1.

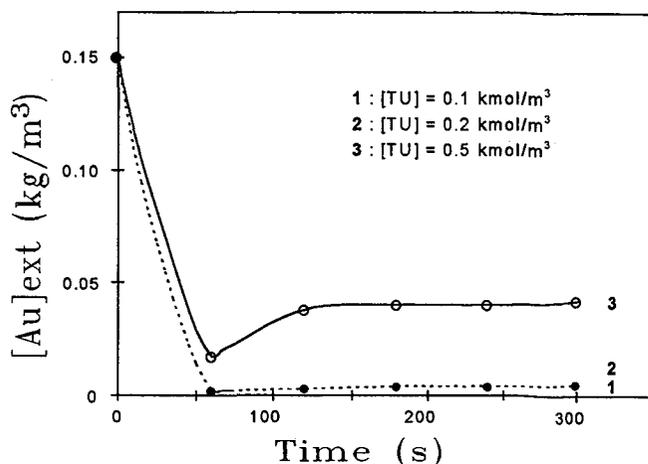


Figure 2: Kinetics of gold extraction by TLA

A minimum in the curve of  $[Au]_{ext}$  against time suggests a slight breaking of the emulsion. The extraction was much more efficient for lower TU concentrations ( 0.1 and 0.2 kmol/m<sup>3</sup>). It can be explained by the emulsion instability resulting in ejection of TU into the external phase. Au remaining in this phase was complexed and further extraction of the metal is prevented. It is therefore necessary to minimize the emulsion breaking and the TU concentration. One minute of contact time was sufficient and this value will be used in the study.

By measuring the Au concentration in the internal phase after the emulsion coalescence, it can be seen that the stripping efficiency was poor for 0.1 and 0.2 kmol/m<sup>3</sup> TU concentrations ( less

than 3%). For 0.5 kmol/m<sup>3</sup> the stripping efficiency was good (92%). The TU concentration was therefore an important parameter which influences both the extraction and the stripping.

#### **Influence of thiourea concentration**

For the following conditions: [HCl] = 2 kmol/m<sup>3</sup>, [Au] = 0.05 kg/m<sup>3</sup>; [TLA] = 3.4 mol/m<sup>3</sup>; [ECA] = 3%; ORG/AQ = 1, the stripping efficiency was studied for different TU concentrations. For [TU] > 0.3 kmol/m<sup>3</sup> the stripping efficiency was greater than 90%. The value of 0.3 kmol/m<sup>3</sup> seems to be the optimal TU concentration for stripping.

#### **Influence of TLA concentration**

Using the same conditions as above, the extraction of gold was studied at various TLA concentrations ([TU] = 0.3 kmol/m<sup>3</sup>; 1 minute contact).

The results are reported in the following table:

[TLA] mol/m <sup>3</sup>	1.7	3.4	5.2	6.9
% Extraction	86	96	60	50

The stripping efficiency obtained was greater than 90%.

The extraction efficiency first increased with the TLA concentration up to 3.4 mol/m<sup>3</sup>; this is a standard behaviour in solvent extraction where the kinetics of the extraction generally increases with increasing extractant concentrations. The extraction efficiency then decreased with increasing TLA concentrations which is characteristic of liquid membranes and attributed to an increase in viscosity of the organic phase. This phenomenon was already observed for other systems (Samar et al).

A concentration of TLA between 1 and 3 mol/m<sup>3</sup> was then used.

#### **Influence of the ratio ORG / AQ**

Two series of experiments were performed under the following conditions: HCl (2 kmol/m<sup>3</sup>), Au (0.050 kg/m<sup>3</sup>), ECA (3%); TU (0.3 kmol/m<sup>3</sup>).

The results slightly depended on the TLA concentrations (1.7 and 3.4 mol/m<sup>3</sup>) and the ORG/AQ ratio (1 to 3). In almost all cases, the extraction and stripping were efficient (> 90%). These conditions seemed to be close to the optimum.

#### **Influence of ECA concentration**

The influence of ECA was studied under the following conditions: HCl (2 kmol/m<sup>3</sup>), Au (0.06 kg/m<sup>3</sup>), TLA (1.7 mol/m<sup>3</sup>), TU (0.3 kmol/m<sup>3</sup>), ORG/AQ = 1.

For 2 and 3% ECA the extraction efficiencies were 88 and 94% respectively. The stripping efficiency was greater than 90% in both cases. As explained above, the emulsion breaking, more important with 2% ECA, had a negative influence on the gold extraction.

#### **Extraction of copper**

The transfer of both metals was studied from a solution containing 0.05 kg/m<sup>3</sup> Au and 5 kg/m<sup>3</sup> Cu, under the optimum conditions: TLA (1.7 and 3.4 mol/m<sup>3</sup>), ECA (3%), ORG/AQ = 1.

The results were the following:

TLA (mol/m <sup>3</sup> )	[Au] <sub>ext</sub> (kg/m <sup>3</sup> )	[Au] <sub>int</sub> (kg/m <sup>3</sup> )	[Cu] <sub>int</sub> (kg/m <sup>3</sup> )
3.4	2.2×10 <sup>-3</sup>	0.47	0.75
1.7	2.6×10 <sup>-3</sup>	0.46	0.46

Au remaining in the external phase was complexed with thiourea, it was therefore not extractible. In addition the separation of Au from Cu is not sufficiently good, even with lower

concentrations of TLA where the Cu extraction was minimal. The settling of the external phase and the emulsion was slow. The contamination of the internal phase by traces of Cu from the external phase was possible and explains the high Cu contents obtained. The amount of Cu in the internal phase was found to correspond to the inclusion of less than 1.5% of the external solution.

As a result of this, thiourea was not selected and the sodium sulfite stripping behaviour was then investigated.

### SODIUM SULFITE

Since sodium sulfite is a powerful stripping agent, the experiments were performed with ratios ORG/AQ greater than 1, in order to obtain a high concentration factor of gold. The settling of the external phase and the emulsion was rapid.

The general conditions were the following: HCl ( 2 kmol/m<sup>3</sup>), Au ( 0.06 kg/m<sup>3</sup>), Cu ( 5 kg/m<sup>3</sup>), TLA ( 1.7 mol/m<sup>3</sup>), ECA ( 2%), Na<sub>2</sub>SO<sub>3</sub> ( 0.1 to 0.5 kmol/m<sup>3</sup>), contacting time ( 1 minute).

#### Influence of sodium sulfite concentration

With ORG/AQ = 3 the results were the following:

Na <sub>2</sub> SO <sub>3</sub> ( kmol/m <sup>3</sup> )	0.2	0.3	0.4	0.5
[Au] <sub>ext</sub> ( kg/m <sup>3</sup> )	10 <sup>-4</sup>	10 <sup>-3</sup>	9×10 <sup>-4</sup>	2×10 <sup>-4</sup>
[Au] <sub>int</sub> ( kg/m <sup>3</sup> )	0.84	0.87	0.93	0.97
[Cu] <sub>int</sub> ( kg/m <sup>3</sup> )	0.13	< 10 <sup>-3</sup>	< 10 <sup>-3</sup>	0.05

The swelling of the emulsion was measured ( ~ 20%). The concentration factor was about 16 compared with the theoretical factor of 20. The extraction and the stripping of gold were quantitative for [Na<sub>2</sub>SO<sub>3</sub>] > 0.3 kmol/m<sup>3</sup>. The selectivity was better than in the previous experiments with thiourea. The relatively high value of [Cu]<sub>int</sub> obtained for sulfite 0.2 and 0.5 kmol/m<sup>3</sup> were probably due to an incomplete settling. If the settling was good, the concentration of copper in the internal phase would have been smaller than 1 mg/L which is acceptable.

Attempts to obtain higher concentration factors were not successful. With ORG/AQ = 7, the gold stripping ( with 0.5 kmol/m<sup>3</sup> of sodium sulfite) is not quantitative ( about 40%).

### CONCLUSION

The feasibility of the separation of Au from Cu by solvent extraction and liquid membranes was demonstrated. By liquid membranes a solution of 1 kg/m<sup>3</sup> Au was obtained with one stage of mixer-settler, compared to the conventional solvent extraction which would require about ten stages. This confirms the superiority of liquid membranes when high concentration factors are needed.

In future, the continuous operation in SLM must be studied in a column or in a stage of mixer-settler with emphasis being given to the settling section which was shown to be the most important factor which affects the selectivity of the process.

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## THE EXTRACTION OF SOME METALS SULPHATES BY METHYLCYCLOHEXYLDIOCTYLAMMONIUM SULPHATE

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### ABSTRACT

The extraction of Cu(II), Zn(II), Co(II) and Ni(II) sulphates by methylcyclohexyldioctylammonium sulphate was investigated, using methods: distribution, mathematical modelling of extraction isotherms, IR- and PMR- spectroscopy. The formation of monosolvates  $(R_4N)_2SO_4 \cdot MeSO_4$  which partially dissociate in organic phase, was established. The mechanism of extraction of metals sulphates is discussed. Thermodynamic constants of extraction equilibrium are calculated.

### INTRODUCTION

It was established during synthesis of methylcyclohexyldioctylammonium sulphate (MChDOAS), that the molecules of alkaline metal sulphates:  $Na_2SO_4$ ,  $K_2SO_4$ ,  $Li_2SO_4$ , were extracted into the organic phase. The quantitative analysis of organic phase after extraction of  $Na_2SO_4$  showed that molar ratio  $Na_2SO_4 : (R_4N)_2SO_4$  was near 1 ( $R_4N$  indicates quaternary ammonium cation of MChDOAS). Preliminary experiments have estimated, that MChDOAS extracted sulphates of Fe(II), Al(III), Cu(II), Zn(II), Co(II) and Ni(II).

It is known (Seeley and Crouse, 1971), that quaternary ammonium sulphates (Q.A.S.) extract such metals sulphates in quantities of 2-3 order less than the initial extractant concentration. This is due to the physical mechanism of its distribution. One of the required conditions for the extraction of metal salts by Q.A.S. via mechanisms of anion-exchange or solvation is the ability of metal to form anionic complexes in water or organic phases. The bivalent metals in sulphate media investigated in this work, are not capable of doing so.

The fact of substantial extraction of alkaline and some non-ferrous metals by Q.A.S. was not published and discussed in the literature and is essential new.

This work involves the investigation of the distribution of divalent Cu, Zn, Ni and Co sulphates from neutral water solutions, using MChDOA.

### EXPERIMENTAL

The sulphate form of MChDOA was prepared from methylsulphate by contacting with some water solutions: 50%  $H_2SO_4$ , 10% NaOH and 10%  $Na_2SO_4$ . Sodium sulphate formed was separated from the extractant by precipitation of the  $Na_2SO_4$  in pure acetone. MChDOAS was isolate from

the solution by evaporating acetone under vacuum.  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{CoSO}_4$  and  $\text{NiSO}_4$  of analytical grade were used without purification. The extraction was carried out in thermostatic separate funnels at temperature  $25 \pm 0.1^\circ\text{C}$  with initial ratio of organic and water phase  $\text{O:W}=1:1$  and contacting time of 15 min. Organic and water phases were separated and its equilibrium volumes were measured in thermostatic test tubes at  $25 \pm 0.1^\circ\text{C}$ . Then, metal contents in water and organic solutions were determined by complexometric methods (Schwarzenbach and Flaschka, 1970) and water in organic phase was determined by electrometric titration using the Karl Fisher reagent. The solvent mixture contains 70% vol. toluene + 30% vol. tri-n-butylphosphate (TBP). It was established, that extraction of  $\text{MeSO}_4$  into solutions of MChDOAS in aromatic solvents is accompanied by stratification of organic phase. The analysis showed, that "heavy" organic phase consisted of the extractant, metals salt and water, and "light" organic phase contains only the solvent ( concentrations of MChDOAS and  $\text{MeSO}_4$  in it were less than  $0.001 \text{ M}$  ). The solvents with high solvating ability suppress the extraction of  $\text{MeSO}_4$ . The selected mixture enabled the extract metal sulphates without stratification of organic phase at high metal concentrations but stratification occurs when the concentrations  $< 0.25 - 0.75 \text{ M}$ .

IR-spectra were obtained using spectrometer M-40, Carl Zeiss Jena, and PMR-spectra -pulse NMR spectrometer CXP 200 "Bruker".

For determination of quantitative extraction of  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{CoSO}_4$ ,  $\text{NiSO}_4$  and coextracted water, the isotherms of their partitions into  $0.17 \text{ M}$  solutions of MChDOAS were obtained.

## RESULTS AND DISCUSSION

Fig.1 and Fig.2 show the extraction isotherms for the metal sulphates using MChDOAS.

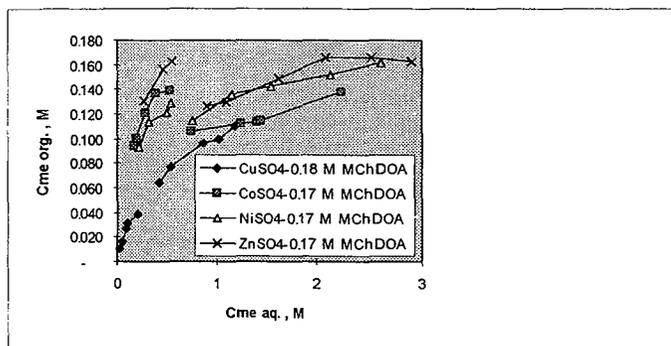


Fig.1 The isotherms of  $\text{MeSO}_4$  extraction by MChDOAS under  $25^\circ\text{C}$ .

As one can see the isotherms are separated into two groups of curves, which correspond to three-phase ( $C < 0.75 \text{ M}$ ) and two-phase systems (Fig.1). The extraction of metals is accompanied by a high water coextraction into organic phase. A direct consequence of this is a change of volume of the organic and the aqueous phases, the stratification of organic phase and the concentration of equilibrium water solution by about 1.05-1.20 times. The distribution of metal sulphates decreases

in the order:  $ZnSO_4 > CoSO_4 > NiSO_4 > CuSO_4$ . Molar ratio of  $MeSO_4 : (R_4N)_2SO_4$  in loaded organic phase is near 1.

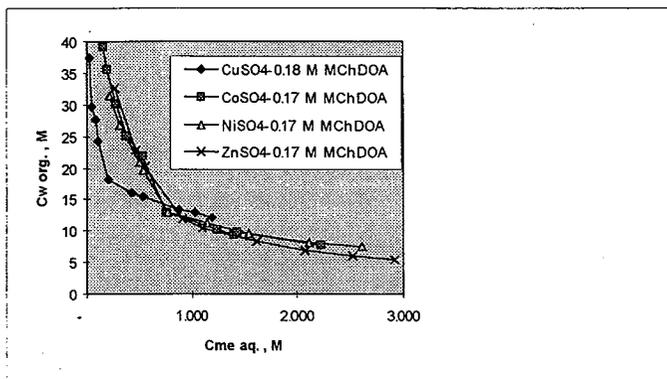
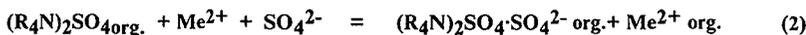
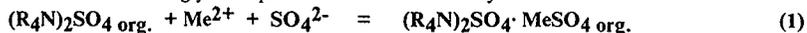


Fig.2 The isotherms of  $H_2O$  coextraction with  $MeSO_4$  by MChDOAS under  $25^\circ C$

Two suggestions can be made to explain the extraction of  $MeSO_4$  by MChDOAS. The first is the physical partition of  $MeSO_4$  in the organic phase; the second is the formation of the monosolvate with the extractant. The mathematical modelling of the extraction isotherm by method, suggested by V.V.Sergievsky (Sergievsky, 1976), using software "EXTREQ" for PC IBM, worked out by I.A.Fradkin, was carried out for a variety of models. Relative error of the isotherms and standard deviation of experimental results were used as a criteria of the accuracy.

Analysis of the calculations shows, that extraction isotherms are close to each other which suggest the formation of monosolvate and its partial dissociation in organic phase under water activities is close to 1. Accordingly the equations of extraction may be written as:



The extraction constants, which take into account the hydration of the organic components according to Sergievsky, (1976), may be written as:

$$K_{111} = C_{Me} \cdot Y_{Me}^* \cdot e^{H_{111}(1-a_w)} / a_{MeSO_4} \cdot C_s \cdot Y_s^* \quad (3)$$

$$K_{112} = C_{Me}^2 \cdot Y_{Me}^* \cdot e^{2H_{112}(1-a_w)} / a_{MeSO_4} \cdot C_s \cdot Y_s^* \quad (4)$$

or in logarithmic form:

$$\ln K_{111} = \ln (C_{Me} / a_{MeSO_4} \cdot C_s) + \ln (Y_{Me}^* / Y_s^*) + H_{111}(1-a_w) =$$

$$\text{Ln}K_{111}^C + \text{Ln}(Y_{\text{Me}}^* / Y_s^*) + H_{111}(1-a_w) \quad (5)$$

and

$$\text{Ln}K_{112} = \text{Ln}(C_{\text{Me}}^2 / a_{\text{MeSO}_4} \cdot C_s) + \text{Ln}(Y_{\text{Me}}^* / Y_s^*) + 2H_{112}(1-a_w) =$$

$$\text{Ln}K_{112}^C + \text{Ln}(Y_{\text{Me}}^* / Y_s^*) + 2H_{112}(1-a_w) \quad (6)$$

where:  $K_{111}$ ,  $K_{112}$ ,  $K_{111}^C$ ,  $K_{112}^C$  are thermodynamic and extraction constants of solvated species respectively,  $C_{\text{Me}}$  and  $C_s$  are the concentrations of the extracted complex and the free extractant respectively,  $Y_{\text{Me}}^*$  and  $Y_s^*$  are the activity coefficients of extractable complex and free extractant in dry solvent (equal 1 or constant),  $H_{111}$  and  $H_{112}$  - hydration parameters, which were determined by the equation  $H_{111} = q \cdot h_s - h_{111}$ , where:  $h_s$  and  $h_{111}$  are hydration numbers of extractant and extractable complex respectively under  $a_w=1$ ,  $a_w$  is water activity,  $q$  is the solvation number.

In Table 1 the results of the mathematical calculations of the organic solvated extracted complex concentrations in the frame of selected model for  $\text{CuSO}_4$  extraction by MChDOAS are presented. In Table 2 calculated parameters and relative errors of calculations for all systems are presented. Indexes 112 and 111 indicate dissociated and non-dissociated solvates respectively.

Table 1. Extraction of  $\text{CuSO}_4$  by 0.18 M MChDOAS in 70% vol. toluene+ 30% vol. TBP. 25°C. Experimental and calculated data.

N	$C_{\text{Me}}^{\text{exp.}}$ , M	$C_{\text{Me}}^{\text{calc.}}$ , M	% error	$C_s$ , M	$C_{112}$ , M	$C_{111}$ , M
1	0.0129	0.0129	0.0	0.167	0.00450	0.00841
2	0.0312	0.0312	0.0	0.149	0.00700	0.0242
3	0.0365	0.0364	-0.4	0.144	0.00740	0.0290
4	0.0507	0.0541	6.7	0.126	0.00812	0.0460
5	0.0794	0.0824	3.7	0.098	0.00753	0.0748
6	0.0955	0.0926	-3.1	0.087	0.00684	0.0857
7	0.119	0.115	-3.6	0.065	0.00482	0.110
8	0.124	0.124	0.0	0.056	0.00392	0.120
9	0.128	0.132	3.2	0.048	0.00314	0.129

Table 2. Thermodynamic parameters of  $\text{MeSO}_4$  extraction by MChDOAS and their relative errors.

$\text{MeSO}_4$	$\text{Ln}K_{112}$	$\text{Ln}K_{111}$	$H_{112}$	$H_{111}$	% error
ZnSO <sub>4</sub>	4.592	7.887	17.2	-43.6	1.47
CoSO <sub>4</sub>	3.372	8.172	113.3	24.5	2.15
CuSO <sub>4</sub>	0.676	6.636	74.2	-24.2	2.08
NiSO <sub>4</sub>	2.084	7.173	39.7	-77.6	1.48

An additional verification of the validity of the chosen model is by using equation proposed by Sergievsky, (1976):

$$C_w^{exp.} > \sum_i C_i h_i a_w + C_s h_s a_w \quad (6)$$

where:  $C_w^{exp.}$  - experimental water concentration in organic phase,  $C_i$  - concentration of  $i$  extractable solvate,  $h_i$  - its hydration number under  $a_w=1$ . In the present work, investigations of the hydration of pure MChDOAS and its solutions in selected organic solvents were not carried out, which would have allowed the calculation of  $h_s$  values under  $a_w=1$ . But the data of the water coextraction isotherms allow the possibility of their estimation. Under this assumption an extrapolation of water distributions curves was carried out as a function of water activity of  $a_w=1$ . The water solubility in pure extractant or in its solution without the metal was estimated and  $h_s$  was calculated using the well known formula (Sergievsky, 1976). The water solubility in pure solvent have been determined experimentally. The values of  $h_i$  for extractable solvates, which were calculated using  $h_s$  and parameters  $H$ , together with literature data of Gibbs hydration energy ( $\Delta G^{hyd.}$ ) and enthalpy ( $\Delta H^{hyd.}$ ) of two valence cations (Izmaylov, 1976) are presented in Table 3. It is easily seen, that in general there is good relationship between values of  $h_s$ ,  $\Delta G^{hyd.}$  and  $\Delta H^{hyd.}$ , which confirms indirectly the validity of the chosen model.

Table 3. Hydration numbers of MChDOAS and extractable solvates.

MeSO <sub>4</sub>	$\Delta G^{hyd.}$ , kcal/M	$\Delta H^{hyd.}$ , kcal/M	$h'_s$ *	$h''_s$ **	$h_{112}$	$h_{111}$
ZnSO <sub>4</sub>	479	496	194.9	69.5	177.7	109.3
CoSO <sub>4</sub>	480	499	228.6	77.5	117.3	53
CuSO <sub>4</sub>	491	509	205.9	100.3	131.7	79.1
NiSO <sub>4</sub>	491	511	240.6	77.7	200.9	155.3

\* hydration number in three-phase system; \*\* hydration number in two-phase system.

In Table 4 experimental and calculated (according to the equation (6)) isotherms of water coextraction are presented. The calculated values are somewhat higher, than the experimental one. This gives an approximate value of  $h_s$  which neglect the contribution of  $Y^*_{Me}$  and  $Y^*_s$  in the calculation using equation (3). However, general, the data of water partition support the validity of the chosen model, which was used for the description of extraction equilibrium.

Table 4. Experimental and calculated (equation (6)) isotherms of water coextraction with CuSO<sub>4</sub> into 0.18 M MChDOAS in 70% vol. toluene+30% vol. TBP. 25°C.

$a_w$	0.9996	0.9991	0.9986	0.9982	0.9966	0.9929	0.9910	0.9855	0.9826	0.9796
$C_w^{exp.}, M$	37.4	29.7	27.7	24.2	18.1	16.1	15.6	13.5	13.0	12.2
$C_w^{calc.}, M$	35.6	34.9	33.5	32.8	30.5	16.6	16.2	15.6	15.4	15.1

The results confirm the partition of non-ferrous metal sulphates by a solvation mechanism involving monosolvate complex  $(R_4N)_2SO_4 \cdot MeSO_4$ , which partially dissociates by the first step under high water activity.

Other, quaternary ammonium sulphates, which contain other substituents, for example, trioctylmethylammonium or tetraoctylammonium sulphates, do not extract  $MeSO_4$  in substantial quantities and, therefore will not form monosolvate in the organic phase. The difference in extraction properties of Q.A.S. was explained in the term of the solvate structure formed. In MChDOA sulphate cyclohexyl substituent is connected with the positively charged nitrogen atom. Partial delocalization of the positive charge to the carbon atoms of cyclohexyl substituent results in interaction with the negatively charged anion, at the cavity of the cyclohexyl substituent. The metals ions are then transferred into the organic phase by electrostatic interaction. This mechanism is analogous to the mechanism of the metal extractions by crown ethers (Hiraoka, 1986). However, in the case of crown ethers, the positive charged metal ions go into the cavity via the electron donor oxygen atoms; but in case of MChDOAS the negatively charged anion is introduced into the positively charged cavity, via the carbon atoms. The first mechanism may be termed as "cation intercalation", the second one as "anion intercalation".

Some of the supporting evidence for interaction between anion and cyclohexyl substituent comes from IR and PMR spectra of extractant and its solvates. There are four bands (Nakamoto, 1966), which belong to  $SO_4^{2-}$  ion:  $\nu_1=1060-1080\text{ cm}^{-1}$ ,  $\nu_2=465\text{ cm}^{-1}$ ,  $\nu_3=1230-1260\text{ cm}^{-1}$ ,  $\nu_4=602\text{ cm}^{-1}$  in IR-spectrum of MChDOAS. In spectrum of the monosolvate with  $ZnSO_4$  displacement of  $\nu_3=1230-1260\text{ cm}^{-1}$  to  $1160-1230\text{ cm}^{-1}$  and splitting of  $\nu_4=602\text{ cm}^{-1}$  into two bands:  $598\text{ cm}^{-1}$  and  $620\text{ cm}^{-1}$  are observed, suggesting that the interaction of  $ZnSO_4$  occurs through the S=O groups. There are four signals: 1.55, 1.69, 2.04, 2.10 ppm., which belong to protons of cyclohexyl radical in PMR-spectrum of MChDOAS. In the spectrum of the monosolvate of  $ZnSO_4$  shift of signal under 1.55 ppm. to 2.65 ppm., and broadening of another lines are observed suggesting that the interaction MChDOAS occurs through the cyclohexyl substituent.

## CONCLUSION

MChDOAS is an extractant for bivalence copper, zinc, cobalt and nickel sulphates by solvation mechanism involving the transfer of the sulphate anion into cavity of the cyclohexyl substituent. In organic phase, monosolvates are partially dissociated under high water activities.

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# THE EXTRACTION OF DIVALENT COBALT, NICKEL AND COPPER FROM HYDROCHLORIC ACID SOLUTIONS BY AN $\alpha$ -HYDROXYOXIME

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## ABSTRACT

The extraction of divalent cobalt, nickel and copper from aqueous hydrochloric acid solutions has been investigated using LIX 63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime,  $H_2Ox$ ) in kerosene under different conditions. The organic extracts were examined by infrared, visible and electron-spin resonance spectroscopies. It is found that the extraction efficiency of LIX 63 is in the order  $Cu > Ni > Co$  and  $Ni > Cu > Co$  at below and above pH 5, respectively;  $Cu > Ni > Co$  at the aqueous acidity concentration range of 1 to 9 mol  $dm^{-3}$  hydrochloric acid. Consequently, the following equilibrium equations are proposed: in a weakly acid region,  $M^{2+}(aq) + 2H_2Ox(org) \rightleftharpoons M(HOx)_2(org) + 2H^+(aq)$  and  $Ni^{2+}(aq) + 3H_2Ox(org) \rightleftharpoons Ni(HOx)_2 \cdot H_2Ox(org) + 2H^+(aq)$  where  $M = Co$  and  $Cu$ ; at  $[HCl] > 1$  mol  $dm^{-3}$ ,  $MCl_2(aq) + 2H_2Ox(org) \rightleftharpoons MCl_2 \cdot 2H_2Ox(org)$  and  $NiCl_2(aq) + 3H_2Ox(org) \rightleftharpoons NiCl_2 \cdot 3H_2Ox(org)$ , and in addition  $CoCl_2(aq) + 2HCl(aq) + 2H_2Ox(org) \rightleftharpoons H_2CoCl_4 \cdot 2H_2Ox(org)$  at  $[HCl] > 6$  mol  $dm^{-3}$ ;  $aq =$  aqueous and  $org =$  organic.

## INTRODUCTION

The extraction of metal ions from aqueous solutions by  $\alpha$ -hydroxyoximes, such as 5,8-diethyl-7-hydroxy-6-dodecanone oxime ( $H_2Ox$ , the active component of LIX 63) and its analogous, has been reported previously (Ritcey et al., 1984). Studies have also been conducted on the complexes formed in the extraction of copper from hydrochloric acid solutions by an  $\alpha$ -hydroxyoxime, and in addition the extraction of trivalent metals in IIIB group elements (Sato et al., 1987, 1989). In the present paper, the work is extended to the extraction of divalent cobalt, nickel and copper from hydrochloric acid solutions by  $\alpha$ -hydroxyoxime.

## EXPERIMENTAL

### Reagents

LIX 63 (Henkel Corp.) used as an  $\alpha$ -hydroxyoxime was purified by the method according to earlier papers (Al-Diwan et al., 1977), and diluted with purified kerosene. Stock solutions of cobalt, nickel and copper were prepared by dissolving their chlorides ( $CoCl_2 \cdot 6H_2O$ ,  $NiCl_2 \cdot 6H_2O$  and  $CuCl_2 \cdot 2H_2O$ ) in deionized water. In general, the concentrations of their metal salts were 1 g  $l^{-1}$  except for the loading test at the concentrations of 2–200 g  $l^{-1}$ . Chemicals were of analytical reagent grade.

### Extraction and analytical procedures

Equal volumes (15  $cm^3$  each) of the aqueous and organic phases were shaken for 20 min – 2 h in 50  $cm^3$  stoppered conical flask at 20°C (except for the experiments on investigating the temperature effect). The extraction was carried out in air, except for the extraction of cobalt which was carried out under the atmosphere of nitrogen. The equilibrations were achieved in 20 min for all metals, except for nickel in 2 h at 1–9 mol  $dm^{-3}$  HCl. The mixture was centrifuged and separated, and then the aliquots of both phases were pipetted out to determine the distribution coefficient ( $E_a^0$ ; the ratio of the equi-

librated (denoted as eq) concentration of divalent metal in organic phase to that in aqueous phase). Divalent metal in the organic phase was stripped with 1 mol dm<sup>-3</sup> hydrochloric acid, and with the cobalt system using 10 mol dm<sup>-3</sup> hydrochloric acid. The concentrations of divalent metals in aqueous solutions were determined by EDTA titration using xylenol orange (XO) as indicator. The chloride concentration and the water content of the organic phase were determined by the use of Volhard's method in the presence of nitrobenzene and Karl Fisher titration, respectively.

#### IR, VS and ESR spectral measurements

The infrared (IR) spectra of the organic extracts were determined on JASCO models IRA-1 (4000-650 cm<sup>-1</sup>) and IR-F (700-200 cm<sup>-1</sup>) using a capillary film between thallium halide plates or polyethylene films. The visible (VS) absorption spectra were recorded on a Hitachi model 340 spectrophotometer using 1.0 x 1.0 cm fused silica cells. The electron spin resonance (ESR) spectra of the organic extracts were measured on a JEOL JES-FE1XG X-band spectrometer.

## RESULTS AND DISCUSSION

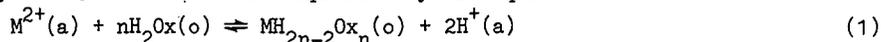
### Extraction isotherms

The distribution of divalent cobalt, nickel and copper between aqueous solutions containing hydrochloric acid and/or sodium acetate and kerosene solution of LIX 63 at 20°C gives the results as shown in Figs. 1-2.

The extraction of metals from aqueous solutions shows a decrease in the distribution coefficient at lower pH values, and the extraction efficiency of LIX 63 is in the order Cu > Ni > Co at below pH 5, whereas probably Ni > Cu > Co above this pH value. At higher acidities over the concentration range of 1-9 mol dm<sup>-3</sup> hydrochloric acid, the distribution coefficients of divalent cobalt, nickel and copper rise with increasing aqueous acidity to the maxima which occur at initial hydrochloric acid concentrations in 4, 4 and 4-5 mol dm<sup>-3</sup>, respectively, and then fall. For the extraction of cobalt, however, the increase in the distribution coefficient again appears at above 6 mol dm<sup>-3</sup> acid concentration.

In the extraction of cobalt(II), nickel(II) and copper(II) using lithium chloride aqueous solutions, the distribution coefficients rise with the total chloride ion concentration, suggesting that the total chloride concentration is the controlling factor. From these results it is deduced that there are two different regions in which the extraction occurs involving different mechanism.

In the weak acid region, the variation of the distribution coefficient is attributed to the chelation mechanism similar to the cation-exchange mechanism. It is thus assumed that the extraction of divalent metal from aqueous solutions above pH 1 by LIX 63 in kerosene is expressed by the equation



where (a) and (o) denote aqueous and organic phases, respectively, and M = Co, Ni or Cu. The log-log plots of  $E_a^0$  vs.  $[H_2Ox]_{eq}$  at constant equilibrated aqueous pH yield straight lines with slopes of ~2 at pH 4.6-4.9 for cobalt, ~3 at pH 5.0-5.25 for nickel and ~2 at pH 2.0-3.0 for copper, indicating that their distribution coefficients have the second-, third- and second-power dependency on LIX 63 concentrations, respectively. This is also supported by the continuous variation in  $[M]_{org}$  plotted as a function of  $[M]_{init\ aq} / ([M]_{init\ aq} + [H_2Ox]_{init})$  at a fixed total concentration of  $[M]_{init\ aq} + [H_2Ox]_{init}$  at a constant pH, which exhibits a maximum at the mole fraction: A maximum at 0.33 at  $[Co]_{init\ aq} + [H_2Ox]_{init} = 0.1$  mol dm<sup>-3</sup> at pH 5.5; 0.25 at  $[Ni]_{init\ aq} + [H_2Ox]_{init} = 0.1$  mol dm<sup>-3</sup> at pH 5.4; 0.33 at  $[Cu]_{init\ aq} + [H_2Ox]_{init} = 0.05$  mol dm<sup>-3</sup> at pH 3.5. In addition, for the extraction of cobalt(II), nickel(II) and copper(II) from aqueous solutions with 0.023, 0.016 and 0.01 mol dm<sup>-3</sup> LIX 63, respectively, when the con-

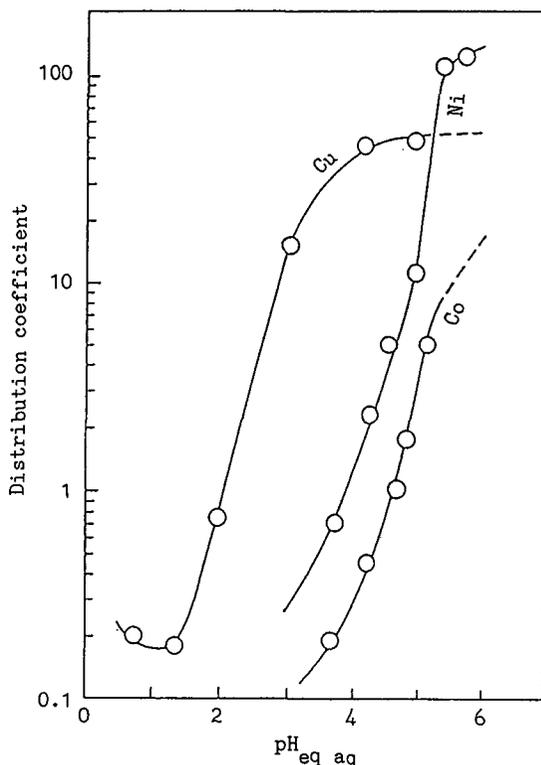
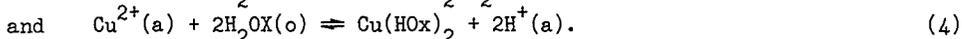
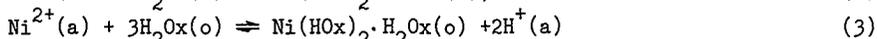
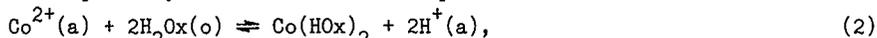


Figure 1. Extraction of divalent cobalt, nickel and copper from aqueous solutions in the region of pH with  $0.16 \text{ mol dm}^{-3}$  in kerosene at  $20^\circ\text{C}$  ( $\text{pH}_{\text{eq aq}}$  denotes equilibrated aqueous pH).

centration of metals in aqueous solutions are increased at the constant pH 5.5, it was found that the metal-loaded organic phases do not contain water molecule and chloride ion. Therefore the species formed in the organic phases have the stoichiometry of  $\text{Co}(\text{HOx})_2$ ,  $\text{Ni}(\text{HOx})_2 \cdot \text{H}_2\text{Ox}$  and  $\text{Cu}(\text{HOx})_2$ .

If the extraction of divalent metals follows Eq. (1), the distribution coefficient should be inversely proportional to  $[\text{H}^+]^2$ . The log-log plots of  $E_a^0$  vs.  $\text{pH}_{\text{eq aq}}$  at  $[\text{H}_2\text{Ox}]_{\text{init}} = 0.064\text{--}0.64 \text{ mol dm}^{-3}$  show that the distribution coefficients are proportional to the second-power hydrogen ion concentration in the regions of  $4.2 \leq \text{pH} \leq 5.0$ ,  $4.5 \leq \text{pH} \leq 5.2$  and  $2.0 \leq \text{pH} \leq 3.0$  for cobalt, nickel and copper, respectively. Hence it is assumed that the extraction of divalent metals from aqueous solutions at  $\text{pH} > 1$  by LIX 63 follows the equations:



At hydrochloric acid concentrations above  $1 \text{ mol dm}^{-3}$ , the distribution behaviour is similar to that for the extraction using the neutral organophosphorus compounds such as TBP (tributyl phosphite) and TOPO (trioctyl phosphine oxide). The log-log plots of  $E_a^0$  vs.  $[\text{H}_2\text{Ox}]_{\text{eq}}$  give straight lines with slopes of  $\sim 2$ ,  $\sim 3$  and  $\sim 2$ , showing the second-, third- and second-power dependencies on LIX 63 concentrations for cobalt, nickel and copper, respectively. This is in accordance with the results

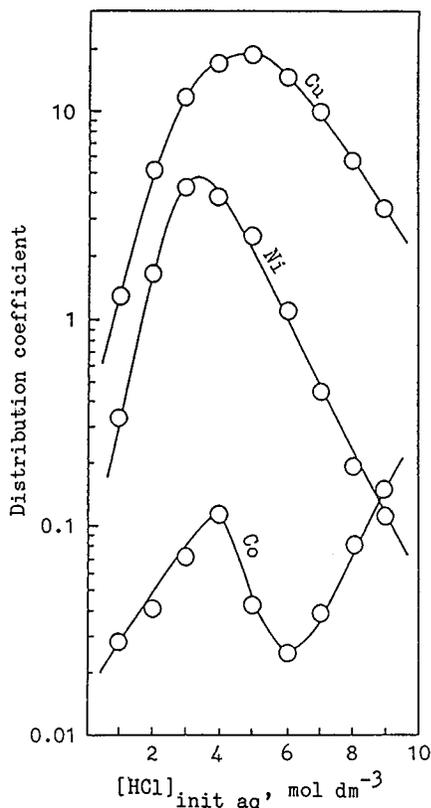
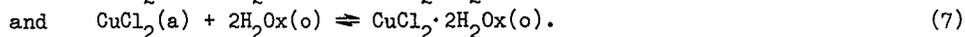
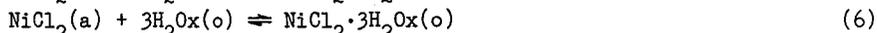
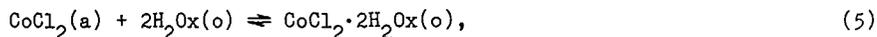


Figure 2. Extraction of divalent cobalt, nickel and copper from hydrochloric acid solutions with  $0.16 \text{ mol dm}^{-3}$  in kerosene at  $20^\circ\text{C}$ .

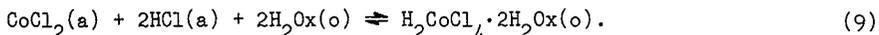
for the continuous variation method.  $[M]_{\text{org}}$ , plotted as a function of  $[M]_{\text{init aq}} / ([M]_{\text{init aq}} + [\text{H}_2\text{Ox}]_{\text{init}})$  at a fixed total concentration of  $[M]_{\text{init aq}} + [\text{H}_2\text{Ox}]_{\text{init}}$  at a constant hydrochloric acid concentration, reveals a maximum at the mole fraction: A maximum at 0.33 at  $[\text{Co}]_{\text{init aq}} + [\text{H}_2\text{Ox}]_{\text{init}} = 0.1 \text{ mol dm}^{-3}$  at 4 and 9 mol  $\text{dm}^{-3}$  HCl; 0.25 at  $[\text{Ni}]_{\text{init aq}} + [\text{H}_2\text{Ox}]_{\text{init}} = 0.1 \text{ mol dm}^{-3}$  at 4 mol  $\text{dm}^{-3}$  HCl; 0.33 at  $[\text{Cu}]_{\text{init aq}} + [\text{H}_2\text{Ox}]_{\text{init}} = 0.03 \text{ mol dm}^{-3}$  at 3 mol  $\text{dm}^{-3}$  HCl. In the extraction of cobalt(II), nickel(II) and copper(II) from aqueous solutions with  $0.02 \text{ mol dm}^{-3}$  LIX 63 in kerosene, when the concentration of metals in aqueous phase is increased, the molar ratio  $[M]/[\text{Cl}^-]$  in the organic phases approaches to a limiting value of 1:2 for all metals at  $4 \text{ mol dm}^{-3}$  HCl, and in addition 1:4 for cobalt at  $9 \text{ mol dm}^{-3}$  HCl. Accordingly the loading test suggests the formation of the species  $\text{CoCl}_2 \cdot 2\text{H}_2\text{Ox}$ ,  $\text{NiCl}_2 \cdot 3\text{H}_2\text{Ox}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{Ox}$ . It is thus considered that the extraction of divalent metal from aqueous solutions at  $[\text{HCl}] > 1 \text{ mol dm}^{-3}$  proceeds as follows:



In contrast, when the change in the molar ratio of LIX 63 to the chloride ion concentration in the organic phase was examined as a function of the initial concentration of hydrochloric acid, the molar ratio of  $[H_2Ox]/[Cl^-]$  in the organic phase decreased with increasing the aqueous acidity and then approached a limiting value of 1:1 at the concentrations of hydrochloric acid above  $6 \text{ mol dm}^{-3}$ , indicating that the compound  $HCl \cdot H_2Ox$  is formed in the extraction of hydrochloric acid by LIX 63



Thus the extraction of cobalt(II) from hydrochloric acid solutions at above  $6 \text{ mol dm}^{-3}$  can be expressed by the following equilibrium equation:



#### IR, VS and ESR spectral studies

The organic extracts from  $0.02 \text{ mol dm}^{-3}$  LIX 63 in n-hexane, using aqueous solutions containing chlorides of divalent cobalt, nickel and copper at pH region of 4.50-5.50 or using 4 and  $9 \text{ mol dm}^{-3}$  hydrochloric acid, were examined by IR spectroscopy. For all the organic extracts, the C-O stretching vibration which should appear at  $1030 \text{ cm}^{-1}$  shifts to higher frequencies of  $1030-1090 \text{ cm}^{-1}$  for free extractant, whereas the C=N stretching vibration at  $1650 \text{ cm}^{-1}$  shifts to lower frequencies of  $1640-1600 \text{ cm}^{-1}$ . From this result, it is deduced that the species formed in the organic phases possess the structure in which oxime group coordinates to metal through the oxygen and nitrogen atoms. On the other hand, the OH stretching band at  $3260 \text{ cm}^{-1}$  for free extractant shifts to lower frequencies, and the intensity of its band decreases in the extraction from aqueous solutions at pH region, and also in the extraction from hydrochloric acid solutions at higher acidities. Simultaneously the intensity of the band due to the C-H-O out-of-plane vibration decreases in the extraction at low acidity, and negligible change in the extraction at higher acidities. Therefore the IR results confirm the relevance of Eqs. (2)-(7) and (9).

The spectrum of the organic extract of cobalt(II) from aqueous solution at pH 3.91 using  $0.64 \text{ mol dm}^{-3}$  LIX 63 in kerosene shows the very broad band of the charge-transfer transition. The organic extract of nickel(II) from aqueous solution at pH 3.9 with  $0.32 \text{ mol dm}^{-3}$  LIX 63 in kerosene exhibits the absorption bands assigned to the transitions from the ground state  ${}^3A_{2g}(F)$  to the states  ${}^3T_{2g}(F)$ ,  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$  at  $9520$ ,  $16555$  and  $26040 \text{ cm}^{-1}$ , which are the characteristic features of octahedral species. In contrast, the absorption spectra of the organic extracts of copper(II) from aqueous solutions at different pH values reveal the shift of the maximum bands to lower frequencies as the pH values are decreased (Sato et al., 1987):  $16665$ ,  $16230$ ,  $14390$  and  $13735 \text{ cm}^{-1}$  at pH 4.30, 3.50, 2.32 and 1.39, respectively. However, the ESR spectra of those organic extracts show the typical features of the square-planar structure (Sato et al., 1987). The organic extracts of cobalt(II) from hydrochloric acid solutions in 4 and  $8 \text{ mol dm}^{-3}$  using  $0.64 \text{ mol dm}^{-3}$  LIX 63 in kerosene exhibit the following absorptions: for  $4 \text{ mol dm}^{-3}$  HCl, the transitions from  ${}^4T_{1g}(F)$  to  ${}^4A_{2g}(F)$  and  ${}^4T_{1g}(P)$  at  $20000$  and  $21275 \text{ cm}^{-1}$ , respectively, which are characteristic of an octahedral species: for  $8 \text{ mol dm}^{-3}$  HCl, the transition from  ${}^4A_2(F)$  to  ${}^4T_1(P)$  at  $14450 \text{ cm}^{-1}$  which is characteristic of a tetrahedral species. For the organic extract of nickel(II) from hydrochloric acid solution in  $2 \text{ mol dm}^{-3}$  with  $0.32 \text{ mol dm}^{-3}$  LIX 63 in kerosene, the absorptions are due to the transitions from  ${}^3A_{2g}(F)$  to  ${}^3T_{2g}(F)$ ,  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$  which appear at  $27625$ ,  $16610$  and  $9615 \text{ cm}^{-1}$ , respectively, which are characteristic of an octahedral species. In the extraction of copper(II) from hydrochloric acid solutions in  $4-8 \text{ mol dm}^{-3}$  using  $0.64 \text{ mol dm}^{-3}$  LIX 63 in kerosene, the absorption maximum appears at about  $12500 \text{ cm}^{-1}$  which is a feature of octahedrally-coordinated species. This is also supported by ESR spectral of (Sato et al., 1987).

### CONCLUSION

When the distribution coefficients in the extraction of cobalt(II), nickel(II) and copper(II) from hydrochloric acid solutions using LIX 63 in kerosene are compared in Figs. 1-2, it is found that the extraction efficiency of LIX 63 is in the order of  $\text{Cu} > \text{Ni} > \text{Co}$  for the extraction from aqueous solutions at  $\text{pH} < 5$ , while it is in the order of  $\text{Cu} > \text{Ni} > \text{Co}$  for the extraction from hydrochloric acid solutions of  $< 9 \text{ mol dm}^{-3}$ . It is seen that the extraction mechanism of divalent cobalt, nickel and copper from aqueous solutions in this pH region involves the chelating reactions expressed in Eqs. (2)-(4), and from hydrochloric acid solutions at higher acidities involves the solvating reactions according to Eqs. (5)-(7) and (9).

### ACKNOWLEDGEMENT

We wish to thank Mr. T. Nonaka for assistance with experimental work.

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# THE EXTRACTION OF TRIVALENT GALLIUM AND INDIUM FROM HYDROCHLORIC ACID SOLUTIONS BY HIGH MOLECULAR WEIGHT AMINES

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## ABSTRACT

The distributions of trivalent gallium and indium between hydrochloric acid solutions and solutions of trioctylamine (TOA,  $R_3NH$ ) or trioctylmethylammonium chloride (TOMAC,  $R_3R'NCl$ ) in benzene have been examined under different conditions. The organic extracts were also studied by infrared and nuclear magnetic resonance spectroscopies. The results found that the extraction efficiency of metals using TOA and TOMAC is in the order  $Ga > In$ , and for gallium(III) and indium(III) of amines is in the order  $TOMAC > TOA$ , although the extraction of gallium(III) is limited to the range of acid concentrations below  $5 \text{ mol dm}^{-3}$ . The following equilibrium expressions are proposed based on the distribution data:  $GaCl_3(a) + R_3NHCl(o) \rightleftharpoons R_3NHGaCl(o)$ ,  $GaCl_4(a) + R_3R'NCl(o) \rightleftharpoons R_3R'NGaCl_4(o) + Cl^-(a)$ ,  $InCl_3(a) + 2R_3NHCl(o) \rightleftharpoons (R_3NH)_2InCl_5(o)$  and  $InCl_4(a) + R_3R'NCl(o) \rightleftharpoons R_3R'NInCl_4(o) + Cl^-(a)$  where (a) and (o) denote aqueous and organic phases, respectively. From the measurement of apparent molecular weights of organic extracts, it is deduced that the extracted species of gallium(III) and indium(III) with TOA and TOMAC consist of the complexes  $R_3NHGaCl_4$ ,  $R_3R'NGaCl_4$ ,  $(R_3NH)_2InCl_5$  and  $(R_3R'N)_2InCl_8$ , respectively. The composition of these complexes is also supported by the results obtained from the thermal analysis of organic extracts.

## INTRODUCTION

Recently the development of high-technology electronics has caused an increase in the demand of gallium and indium metals for industrial needs. Besides we have investigated the extractions of some metals from aqueous acid solutions by trioctylamine (TOA) and trioctylmethylammonium chloride (TOMAC). The present paper extends the work to the extraction of trivalent gallium and indium from hydrochloric acid solutions by TOA and TOMAC.

## EXPERIMENTAL

### Reagents

TOA and TOMAC ( $R_3N$  and  $R_3R'NCl$ , Koei Chemical Co., Ltd.) of high purity were used without further purification and diluted with benzene. Aqueous gallium chloride solution was prepared by dissolving gallium metal (99.9999 %, Swiss Aluminium, Switzerland) in concentrated hydrochloric acid and diluted with deionized water to produce a selected concentration. The stock solution of indium(III) was prepared by dissolving indium chloride in hydrochloric acid solution. In general the metal concentration was  $1 \text{ g dm}^{-3}$  gallium or indium chloride except for the loading test. Other chemicals were of analytical reagent grade.

### Extraction and analytical procedures

Equal volumes ( $10 \text{ cm}^3$  each) of organic and aqueous phases placed in  $50 \text{ cm}^3$  stoppered conical flasks were shaken for 10 min in a thermostated water bath at  $20^\circ\text{C}$  except for the investigation of the temperature effect. Preliminary experiments

showed that equilibration was complete in 10 min. The mixture was centrifuged and separated, and then both phases were assayed to determine the distribution coefficient ( $E_a^0$ , the equilibrium concentration of metal in the organic phase to that in the aqueous phase). Gallium and indium were stripped from the organic phase with  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid solution. The concentrations of gallium and indium in aqueous solutions were determined by titration with EDTA using xylenol orange (XO) as indicator. The concentration of chloride and the water content in the organic phase were examined by Volhard's method with nitrobenzene and Karl Fischer titration, respectively.

#### IR and NMR spectroscopies

Infrared (IR) spectra of the samples prepared by evaporation of the organic diluent were measured on JASCO models IRA-1 ( $4000\text{--}650 \text{ cm}^{-1}$ ) and IR-F ( $700\text{--}200 \text{ cm}^{-1}$ ) using capillary film between thallium halide plates or polyethylene films. Nuclear magnetic resonance (NMR) spectra of the organic solutions from the extraction with carbon tetrachloride as diluent were obtained on a JEOL model JNM-PMX60SI NMR spectrometer by using tetramethylsilane as an internal reference.

#### Measurement of apparent molecular weight

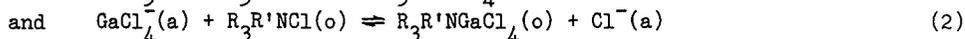
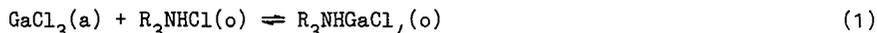
The apparent molecular weight was determined in benzene on a Hitachi model 115 isothermal molecular weight apparatus.

### RESULTS AND DISCUSSION

#### Extraction isotherms for gallium(III)

The distribution isotherms for the extraction of gallium(III) from hydrochloric acid solutions by TOA and TOMAC in benzene showed the results given in Fig.1. Although the extraction efficiency for gallium using TOMAC is higher than that of TOA, the steep rise in distribution coefficient with increasing aqueous acidity is observed in these extraction systems. The log-log plots of  $E_a$  vs.  $[\text{TOA}]_{\text{eq}}$  or  $[\text{TOMAC}]_{\text{eq}}$  at constant hydrochloric acid concentration reveal straight lines with the slopes of 1-2 for TOA and  $\sim 1$  for TOMAC: that is, 1.0, 1.4, 1.8 and 1.8 for TOA and 0.73, 0.80, 0.81 and 0.81 for TOMAC at hydrochloric acid concentrations of 1, 2, 3 and 5  $\text{mol dm}^{-3}$ . It appears that the extractant dependency of TOA does not always give a definitive result with regard to the stoichiometry of the extraction equilibrium.

The solvent-dependency is examined by a loading test of gallium to the organic phase. The molar ratios of  $[\text{Ga}]/[\text{Cl}]/[\text{R}_3\text{N}]$  and  $[\text{Ga}]/[\text{Cl}]/[\text{R}_3\text{R}'\text{N}]$  in metal-saturated organic phase were found to be both 1:4:1 in the extraction from 5  $\text{mol dm}^{-3}$  hydrochloric acid solutions with TOA and TOMAC of  $0.02 \text{ mol dm}^{-3}$  each. On the other hand, the continuous variation of  $[\text{Ga}]_{\text{org}}$  as a function of the mole fraction  $[\text{Ga}]_{\text{init aq}}/([\text{TOA}]_{\text{init}} \text{ or } [\text{TOMAC}]_{\text{init}} + [\text{Ga}]_{\text{init aq}})$  at a fixed total concentration of  $[\text{Ga}]_{\text{init aq}} + [\text{TOA}]_{\text{init}} \text{ or } [\text{TOMAC}]_{\text{init}} = 0.02 \text{ mol dm}^{-3}$  gave the results that a maximum in  $[\text{Ga}]_{\text{org}}$  appears at the mole fraction of one and a half for TOA or one for TOMAC at initial aqueous hydrochloric acid of  $5 \text{ mol dm}^{-3}$ . Hence it is presumed that the extraction of gallium(III) by TOA and TOMAC is written as follows:



where (a) and (o) denote aqueous and organic phases, respectively.

#### Extraction isotherms for indium(III)

The extraction of aqueous solutions containing indium chloride in hydrochloric acid by TOA in benzene gives the results shown in Fig.2. This indicates that the distribution coefficient rises with increasing aqueous acidity to the maximum which occurs at initial hydrochloric acid concentration of  $6 \text{ mol dm}^{-3}$  and

then falls. When hydrochloric acid in the aqueous phase is partly replaced by lithium chloride, it is observed that the distribution coefficient from mixed aqueous solutions of  $0.2 \text{ mol dm}^{-3}$  hydrochloric acid and lithium chloride by TOA increases with the chloride ion concentration. In the extraction of indium(III) by TOMAC (Fig.3), the shape of the extraction curve is similar to that by TOA, although the extraction efficiency for indium(III) is in the order TOMAC > TOA. The distribution coefficient from hydrochloric acid solutions passes through the maximum at  $6 \text{ mol dm}^{-3}$  hydrochloric acid concentration; while the distribution coefficient from mixed aqueous solutions of  $0.2 \text{ mol dm}^{-3}$  hydrochloric acid and lithium chloride increases with aqueous chloride concentration. The log-log plots of  $E_a^0$  vs.  $[\text{TOA}]_{\text{init}}$  or  $[\text{TOMAC}]_{\text{init}} - n[\text{In}]_{\text{org}}$ , where  $n$  is the solvation number, at constant hydrochloric acid concentration give a straight line with the slope of  $\sim 2$  for TOA and  $\sim 1$  for TOMAC which gives  $n=2$  and  $1$  for TOA and TOMAC, respectively. These results reveal the second- and first- power dependences on TOA and TOMAC concentrations, respectively. In addition, the stoichiometry of the extracted species was examined by a loading test of indium to the organic phase with increasing indium concentra-

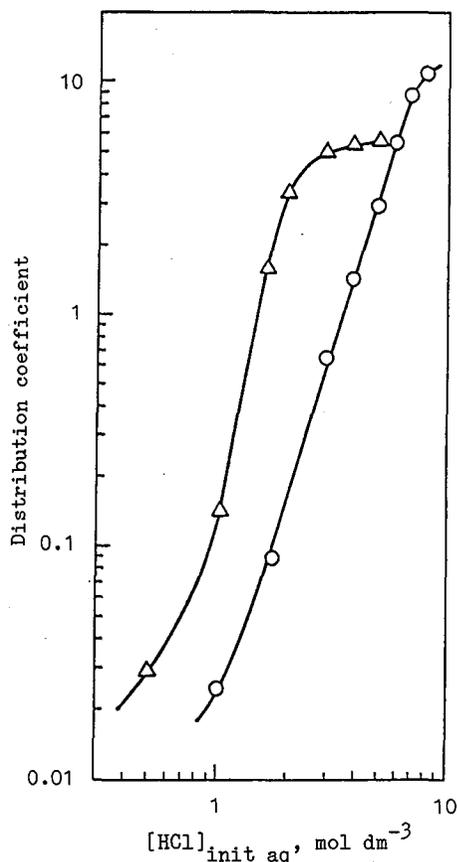
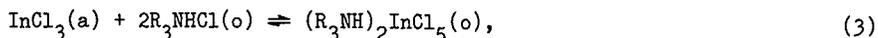
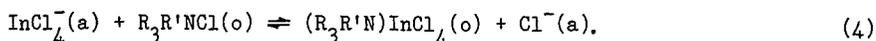


Figure 1. Extraction of gallium(III) from HCl solutions with  $0.02 \text{ mol dm}^{-3}$  TOA (○) and  $0.006 \text{ mol dm}^{-3}$  TOMAC (△) in benzene at  $20^\circ\text{C}$ .

tion in aqueous phase. The molar ratios  $[\text{In}]/[\text{Cl}]/[\text{R}_3\text{N}]/[\text{H}_2\text{O}]$  and  $[\text{In}]/[\text{Cl}]/[\text{R}_3\text{R}'\text{N}]/[\text{H}_2\text{O}]$  approach 1:5:2:0 and 1:4:1:0. Hence it is considered that the extraction of indium(III) from hydrochloric acid solutions by TOA and TOMAC are expressed as the following equilibrium equations: For the extraction by TOA



and for the extraction by TOMAC



#### IR and NMR spectra

The organic extracts of indium(III) from hydrochloric acid solutions by TOA and TOMAC in benzene at 20°C were examined by IR spectrophotometry. With increasing the indium concentration in the organic phase, the OH stretching band at 3000  $\text{cm}^{-1}$  and the OH bending band at 1640  $\text{cm}^{-1}$  decrease in the intensities, and their bands disappear in the metal-saturated organic extracts. This suggested that the extracted species have no water molecule. This result is also supported by the

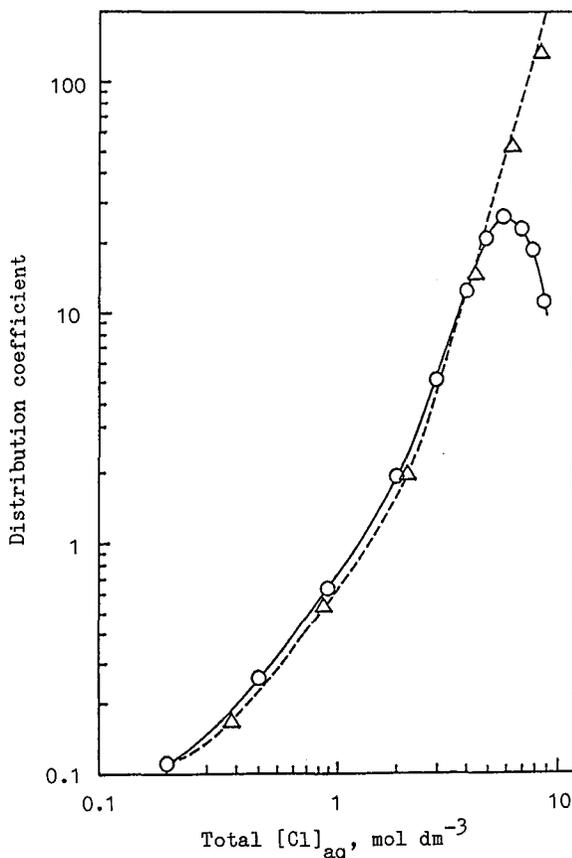


Figure 2. Extraction of indium(III) from HCl solutions with 0.1  $\text{mol dm}^{-3}$  TOA in benzene at 20°C (continuous and broken lines represent the extraction from HCl solns. and mixed 0.2  $\text{mol dm}^{-3}$  HCl/LiCl solns., respectively).

measurement of water content in the organic phase. The organic extracts exhibit the following absorptions in addition to the absorption bands of alkyl groups due to TOA and TOMAC (Sato et al., 1965, 1975): for the extracts by TOA, the band at  $2510\text{ cm}^{-1}$  is due to the NH stretching frequency and shifts to the absorption at  $2430\text{ cm}^{-1}$  for the TOA HCl salt, and the In-Cl stretching band is centered at  $332\text{ cm}^{-1}$ . For the extracts by TOMAC, the absorption around  $332\text{ cm}^{-1}$  is due to the In-Cl stretching frequency. Thus the IR spectra indicate the formation of the species in which the chloride is coordinated to indium, supported by the result obtained from the determination of chloride concentration in the organic phase. Similar IR spectral results are also observed for the organic extracts of gallium(III) by TOA and TOMAC: the Ga-Cl stretching band suggests the formation of the species  $\text{R}_3\text{NHGaCl}_4$  and  $\text{R}_3\text{R}'\text{NGaCl}_4$ . The organic phases from the extraction of aqueous solutions containing indium chloride in hydrochloric acid by TOA and TOMAC in carbon tetrachloride at  $20^\circ\text{C}$  were examined by NMR spectroscopy. The organic extracts show the shifts of the methylene protons (and/or methyl proton for TOMAC), which are attached immediately adjacent to the nitrogen, to a lower field and the disappearance of the water

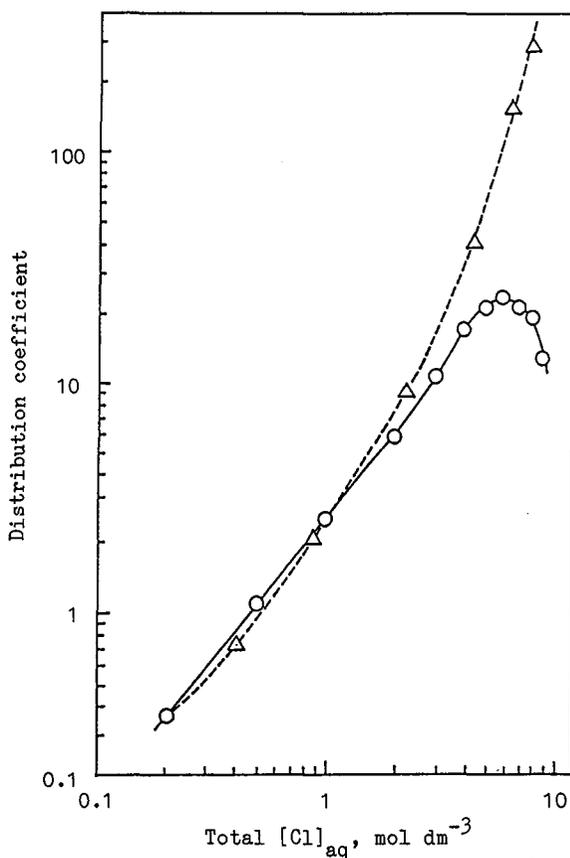


Figure 3. Extraction of indium(III) from HCl solutions with  $0.1\text{ mol dm}^{-3}$  TOMAC in benzene at  $20^\circ\text{C}$  (continuous and broken lines represent the extraction from HCl solns. and mixed  $0.2\text{ mol dm}^{-3}$  HCl/LiCl soln., respectively).

proton signal, with increasing the concentration of indium in the organic phase (Sato et al., 1970, 1971). These results are similar to the IR results. The data for the apparent molecular weights suggest that the complexes extracted by TOA and TOMAC exist as monomer for gallium(III), and monomer and dimer for indium(III). It is thus proposed that the extracted species of indium(III) according to Eqs. (3) and (4) consist of the complexes  $(R_2NHCl)_2InCl_5$  and  $(R_2R'N)_2In_2Cl_8$ , respectively, displaying a coordination number of five (Sato et al., 1992). The extracted species of gallium(III),  $R_3NHGaCl_4$  and  $R_3R'NGaCl_4$ , display a coordination number of four. The composition of the chloro complexes of gallium(III) and indium(III) with TOA and TOMAC is also supported by the results from the thermal decomposition of the organic extracts, saturated with metals and freed from benzene (Sato et al., 1986).

#### ACKNOWLEDGEMENTS

The authors wish to thank Messrs.T.Higashi and T.Nishimura for assistance with experimental work, and also thank the Koei Chemical Co., Ltd. for the samples of TOA and TOMAC.

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## ADSORPTION OF EXTRACTANTS AND MODIFIERS IN EXTRACTION SYSTEMS

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### ABSTRACT

Interfacial tension was measured for two-component systems containing various types of hydroxyoximes (2-hydroxy-5-*t*-butylbenzophenone (E)-oxime, 9-hydroxy-8-hexadecanone oxime and 13-hydroxy-12-tetrazonone oxime) or an extractant (Hostarex A 327 and decyl picoliniate) and a modifier (decanol and isodecanol). The interfacial concentrations of adsorbed species were determined. The relative content of the adsorbed species depends upon the ratio of their bulk concentrations and interfacial activity and hydrophobicity of individual components.

### INTRODUCTION

Almost all types of hydrophobic extractants show an amphiphilic character as a result of the presence of a long hydrophobic group(s), usually an alkyl chain, and some characteristic hydrophilic fragments that are usually chemically active and react with the considered metal ions. As a result, extractant molecules adsorb at the liquid/liquid interface and decrease the interfacial tension. The adsorption at the liquid interface may induce an advantageous orientation of extractant molecule and enhance the rate of the process. It can, however, block the interface and retard the process. Various aspects of extractant adsorption and the effect of adsorption upon extraction kinetics were discussed recently (Szymanowski, 1993; Szymanowski and Tondre, 1994).

Individual extractants are very seldom used in industrial applications. Usually they are complex mixtures of active and non-active components present in the post-reaction mixture (unreacted reagents, by-products) or specially added to modify the solubility and/or extraction ability (hydrophobic alcohols, alkylphenols, esters, etc.) and to enhance the rate of extraction (extractants of another type and even typical surfactants; usually they are less hydrophobic than basic extractants). These substances can promote the extraction by phase transfer catalysis, formation of reverse micelles in the organic phase, formation of micelles in the aqueous phase, microemulsion formation and interface modification. In each case considered, the amphiphilic molecules adsorb at the interface. The adsorption of individual extractants and industrial extractants treated as individual species was studied by several authors (Osseo-Asare, 1984; Szymanowski, 1993; Szymanowski and Tondre, 1994). Very seldom the co-adsorption of two different components of extractant mixtures was considered (Szymanowski, Blonde et al, 1992 and in press; Szymanowski, Cote et al, 1994; Szymanowski, Miesiąc et al, 1992). The aim of this work is to present the interfacial tension and adsorption data, and the method of their interpretation for two component mixtures containing: i) an extractant and a less surface active modifier, ii) an extractant and a more surface active modifier and iii) two different extractants.

## EXPERIMENTAL

### Materials

The following model extraction two-component systems were considered: i) 13-hydroxy-12-tetrakozanone oxime (HTO) - 2-hydroxy-5-*t*-butylbenzophenone (E)-oxime (HBBO) dissolved in toluene and redistilled water ii) 9-hydroxy-8-hexadecanone oxime (HHO) - 2-hydroxy-5-*t*-butylbenzophenone oxime dissolved in toluene and redistilled water iii) Hostarex A327 (tri-*n*-octyl/decylamine) - isodecanol (ID) dissolved in kerosene (aliphatic fraction, below 1% aromatics) and aqueous solutions containing 6 and 12% of lactic acid and iv) dodecyl picolinate (DP) - decanol (D) dissolved in toluene and 0.1 M HCl (Szymanowski, Cote et al, 1994). These systems are considered as models for commercial hydroxyoxime extractants containing LIX 63 as accelerator (systems i and ii) and ACORGA CLX 50 proposed for copper extraction from chloride media (system iv). Only system iii contains commercial extractant modified with isodecanol and commercial diluent. The system is used for the extraction of lactic acid.

### Interfacial Tension Determination

The volume drop method (a Lauda volume drop tensiometer, Germany) was used for systems i and ii; a Du Noüy Tensiometer (Lauda, Germany) with a ring for system iii and with a stirrup for system iv. The presaturated phases were used and the measurements were carried out at 20 or 25°C for systems containing individual extractants/modifiers and their mixtures of the constant ratios.

### Interpretation of Interfacial Tension Measurements

The method of interpretation is the same as that used by Rosen (Rosen, M.J., 1986; Hua, X.Y. and Rosen, M.J., 1982; Rosen, M.J. and Murphy, D.S., 1986 and 1989) in his studies of two component surfactant systems which was initially derived for the air/aqueous interfaces and then broadened to liquid/liquid systems. The non-ideal solution theory is used to estimate the relative effectiveness of adsorption defined by the mole fractions of co-adsorbed substances. The molar concentrations of two amphiphilic substances (extractant and modifier) in the solution ( $c_1$  and  $c_2$ ) are given by the equations:

$$c_1 = \alpha_1 c_{12} = c_1^0 f_1 x_1 \quad (1)$$

$$c_2 = \alpha_2 c_{12} = c_2^0 f_2 x_2 \quad (2)$$

where:  $\alpha_1$  and  $\alpha_2$  are mole fractions of extractant 1 and modifier 2 in the total concentration  $c_{1,2}$  in the solution phase, respectively  $\alpha_1 = 1 - \alpha_2$ ;  $c_1^0$ ,  $c_2^0$  and  $c_{12}$  are solution phase molar concentrations of extractant, modifier and their mixture, respectively, required to produce a given interfacial tension value;  $f_1$  and  $f_2$  are activity coefficients of extractant and modifier, respectively, in the mixed adsorption monolayer;  $x_1$  and  $x_2$  are their mole fractions in the adsorption monolayer,  $x_1 = 1 - x_2$ . It is assumed that the solubility of the extractant and modifier are negligible in the aqueous phase and the total concentrations can be considered.

From non-ideal solution theory, the activity coefficients at the interface can be approximated by relationships:

$$\ln f_1 = \beta^\sigma (1 - x_1)^2 \quad (3)$$

$$\ln f_2 = \beta^\sigma (1 - x_2)^2 \quad (4)$$

where  $\beta^\sigma$  is the molecular interaction parameter for mixed monolayer formation.

Equations 1-4 give relationships which are valid for nonionic amphiphilic substances:

$$\frac{x_1^2 \ln(c_1 / c^0_1 x_1)}{(1-x_1)^2 \ln[c_2 / c^0_2 (1-x_1)]} = 1 \quad (5)$$

$$\beta^\sigma = \frac{\ln(\alpha_1 c_{12} / c^0_1 x_1)}{(1-x_1)^2} \quad (6)$$

from which the relative effectiveness of adsorption at the interface and the molecular interaction parameter can be determined. The value of  $\beta^\sigma$  is a measure of the synergism in surface/interfacial tension reduction. The synergism in this respect is present in binary mixture of amphiphilic substances when a given surface tension (reduction) can be attained at a total mixed surfactant concentration lower than that required of either component by itself.

Equations 4 and 5 are also valid for mixtures containing nonionic and ionic amphiphilic substances when a swamping constant concentration of electrolyte is present. In another case, the activity coefficients of both solutes at the interface ( $f_1$  and  $f_2$ ) and in solutions containing only one amphiphilic substance ( $f^0_1$  and  $f^0_2$ ) must be known and equation 7 be used.

$$\frac{x_1^2 \ln(c_1 f_1 / c^0_1 f^0_1 x_1)}{(1-x_1)^2 \ln[c_2 f_2 / c^0_2 f^0_2 (1-x_1)]} = 1 \quad (7)$$

For a given ratio of two species and imposed interfacial concentration, their bulk concentrations  $c_1$  and  $c_2$  can be easily determined if they do not associate together. In the opposite case the association constant must be known. Furthermore, the bulk concentrations  $c^0_1$  and  $c^0_2$  can be easily derived from the plots  $\gamma$  vs  $c_1$  and  $\gamma$  vs  $c_2$  obtained from solutions containing only one type of species (extractant or modifier). By introducing the values  $c^0_1$ ,  $c^0_2$ ,  $c_1$  and  $c_2$  into equation 5 or 7, one can derive iteratively the values of  $x_1$  and  $x_2=(1-x_1)$ . Thus, the relations  $\gamma$  vs  $c$  for individual reagents and their fixed mixture must be known.

## RESULTS AND DISCUSSION

Exemplary interfacial tension isotherms for systems i and ii are presented in Figures 1 and 2. The data for systems iii and iv were reported previously (Szymanowski, Miesiac, 1992; Szymanowski, Cote et al, 1994). They indicate that i) HBBO is more surface active in interfacial tension reduction than HTO, ii) HHO is more surface active than HBBO, iii) Hostarex A 327 is more surface active than isodecanol. In all these three systems the isotherms obtained for two component mixtures lie between those obtained for individual components, and iv) decanol is somewhat more surface active than decyl picoliniate and the isotherms obtained for the two-component mixtures lie below those obtained for decanol and decyl picoliniate used alone.

The co-adsorption of extractant and modifier molecules is observed only in a narrow range of interfacial tension (Table 1-4). The interfacial concentrations of adsorbed species depend significantly upon their relative bulk content. When the excess of 2-hydroxy-5-t-butylbenzophenone (E)-oxime in the organic phase is used (HBBO:HTO and HBBO:HHO equal to 3:1 mol/mol) than its interfacial concentration amounts to 0.76 - 0.95 and 0.56 - 0.67 for systems i and ii, respectively, which is in

agreement with the considered extractants' interfacial activities. The lower interfacial concentration of HBBO is observed in the presence of the less hydrophobic and more surface active  $\alpha$ -acyloin oxime (HHO).

However, in each case HBBO species are dominant in the adsorption layer. Similar results are obtained for the system iii (Table 3). Hostarex A 327 is significantly more surface active than isodecanol and its interfacial concentration amounts to 0.6 - 0.75 already at the mole ratio of Hostarex A 327 to isodecanol equal to 0.72. In the system iv (Table 4) the mole fraction of less surface active decyl picolinate at the interface is about 0.4. Thus, this value is significantly lower in comparison to that obtained for Hostarex A 327 and isodecanol. This explains well the retardation of copper extraction with decyl picolinate observed in the presence of alcohol. It is also of interest to note that the mole fraction of decyl picolinate at the interface is independent of the molar ratio of decyl picolinate and decanol in the considered range of concentrations.

The  $\beta^\sigma$  coefficients values obtained are positive and negative but close to zero which suggest rather weak interactions in the adsorbed layer and the lack of synergism. The results obtained for system iv should be reexamined.

TABLE 1

Co-adsorption (mole fraction) of 13-hydroxy-12-tetrakozanone oxime (HTO) and- 2-hydroxy-5-t-butylbenzophenone oxime (HBBO) toluene/ redistilled water

Interfacial tension mN m <sup>-1</sup>	HBBO:HTO 1:3mol/mol		HBBO:HTO 1:1 mol/mol		HBBO:HTO 3:1 mol/mol	
	x <sub>HBBO</sub>	$\beta^\sigma$	x <sub>HBBO</sub>	$\beta^\sigma$	x <sub>HBBO</sub>	$\beta^\sigma$
33	0.10	1.18	0.43	1.01	0.76	0.40
32	0.14	1.05	0.51	0.92	0.82	0.60
31	0.17	0.57	0.57	0.88	0.88	0.93
30	0.21	0.96	0.64	0.87	0.95	1.71

TABLE 2

Co-adsorption (mole fraction) of 9-hydroxy-8-hexadecanone oxime (HHO) and- 2-hydroxy-5-t-butylbenzophenone oxime (HBBO) toluene/ redistilled water

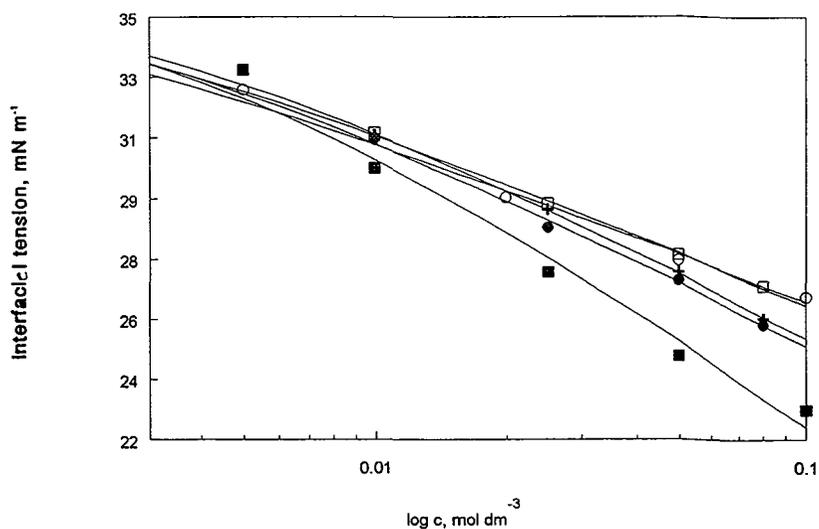
Interfacial tension mN m <sup>-1</sup>	HBBO:HHO 1:3mol/mol		HBBO:HHO 1:1 mol/mol		HBBO:HHO 3:1 mol/mol	
	x <sub>HBBO</sub>	$\beta^\sigma$	x <sub>HBBO</sub>	$\beta^\sigma$	x <sub>HBBO</sub>	$\beta^\sigma$
33	0.30	-0.30	0.37	-1.21	0.56	-2.82
32	0.28	0.30	0.36	-0.96	0.57	-2.28
31	0.25	0.66	0.35	-0.69	0.60	-1.69
30	0.21	1.06	0.34	-0.41	0.64	-1.00

**TABLE 3**  
Co-adsorption (mole fraction) of Hostarex A 327 and isodecanol (ID) kerosene/ aqueous solution of lactic acid (Hostarex A 327:ID=0.72:1 mol/mol)

Interfacial tension $\text{mN m}^{-1}$	Lactic acid concentration=6%		Lactic acid concentration=12%	
	$x_{\text{Ho}}$	$\beta\sigma$	$x_{\text{DP}}$	$\beta\sigma$
19			0.65	-3.70
20			0.69	-2.92
21	0.71	-1.42	0.74	-3.04
22	0.68	-0.94		
23	0.58	-0.04		

**TABLE 4**  
Co-adsorption (mole fraction) of decyl picoliniate (DP) and decanol at toluene/0.1 M HCl interface

Interfacial tension $\text{mN m}^{-1}$	Decyl picoliniate: decanol=1:1 mol/mol		Decyl picoliniate: decanol=1:2 mol/mol	
	$x_{\text{DP}}$	$\beta\sigma$	$x_{\text{DP}}$	$\beta\sigma$
26			0.42	-7.97
27	0.41	-2.93	0.40	-5.19
28	0.41	-3.29	-	-
29	0.42	-4.26	-	-



**FIGURE 1.** Interfacial tension isotherms (■- HBBO, □-HTO, ●-HBBO:HTO=1:3 mol/mol, ○-HBBO:HTO=3:1 mol/mol, ■-HBBO:HTO=1:1 mol/mol)

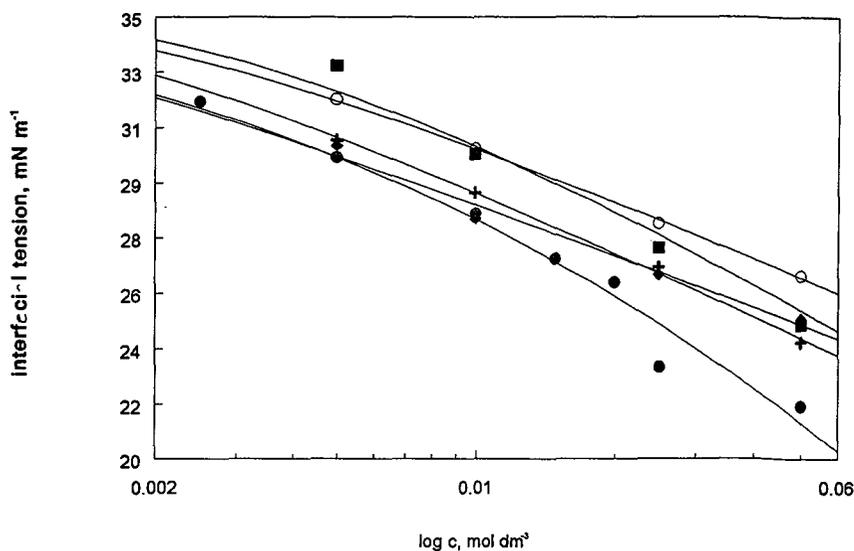


FIGURE 2. Interfacial tension isotherms (○- HBBO, ●-HHO, ◆-HBBO:HHO=1:3 mol/mol, ■-HBBO:HHO=1:3 mol/mol, □-HBBO:HHO=1:1 mol/mol)

#### ACKNOWLEDGEMENT

The work was supported by the University grant BW PP No 32/233

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## SOME DIFFICULTIES IN TREATING ZIRCONIUM ORES CONTAINING HIGH CONCENTRATIONS OF SILICON BY SOLVENT EXTRACTION

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### ABSTRACT

This paper reviews research largely carried out at the Mendeleev University over many years on the extraction of zirconium and the behaviour of solutions containing high concentrations of silicic acid. The problems associated with the formation of stable interfacial films, 'structural mechanical barriers', and polymerised oxo-species in the aqueous phase, 'stable polymeric compounds', on extraction are discussed and techniques are presented which largely overcome such difficulties. Such techniques are applicable to the extraction of other elements from solutions high in silicic acid.

### INTRODUCTION

Currently the main world industrial source of zirconium is still  $ZrSiO_4$  ( $ZrO_2$  67%,  $SiO_2$  32%) which is one of the most resistant minerals to decomposition. Industrial methods of decomposition are based on sodium hydroxide fusion, fusion with sodium carbonate, complex fluorosilicates and chlorination. This resistance of Zircon is determined by the unique strength of the crystal lattice. A potential alternative industrial source of zirconium is eudialyte, a complex zirconosilicate ( $ZrO_2$  10-15%,  $SiO_2$  50%) whose structure can be represented in the general form,  $Na_{12}Ca_6Fe_3Zr_3[Si_3O_9]_2[Si_9O_{24}(OH)_3]_2$  which, unlike zircon, easily lends itself to dissolution in mineral acids. Along with zirconium, eudialyte also contains rare earths, niobium, tantalum and titanium and considerable resources of this mineral are available in Russia, USA, Canada, Greenland, Sweden and the Republic of South Africa. The use of this mineral resource is limited by the absence of an economically suitable technology. However, investigations carried out in Russia, particular at the Mendeleev University, (Chekmarev (1989), Chizhevskaya(1994a)), and the developments made by Molycorp, (Anon (1989a,1989b)), allow eudialyte to be considered as a potential raw material for rare metals.

The main difficulties in the hydrometallurgy of both zircon and eudialyte are associated with the presence of large amounts of silica in the ores; the silica passes into solution on leaching with mineral acids and readily undergoes polymerisation and condensation in solution forming polynuclear silicic acid species with various composition and structure up to stable gels. These gels impede filtration, reduce the extraction of desired components and inhibit subsequent solvent extraction, (Chekmarev (1989), Chizhevskaya (1994a), Ritcey (1986), Solovkin (1970), Nikolski (1983)). Therefore to minimise the formation of these gels the mineral acid leaching of the sodium cake must be preceded by water washing. This is to eliminate as far as possible the sodium silicate and other water soluble impurities as well as the excess decomposing reagent. However in practice, it is impossible to eliminate silica totally by this technique because of the presence of water insoluble silicates, e.g. zirconosilicates, along with the soluble species. The elimination of silica from eudialyte concentrate is even more complicated, chemical treatment by sodium hydroxide by a fortunate chance allows removal of up to 32% of  $SiO_2$  due to the presence of other minerals in the eudialyte concentrate, (Chizhevskaya (1994)). However during acid decomposition greater than 50% of the silica content passes into the resulting solution. A large proportion of this silica leads to formation of unfilterable pulps, so

that subsequent processing of the resulting jelly-like systems by solvent extraction becomes impossible. Investigation of the kinetics of the eudialyte concentrate decomposition (phase ratio solid:liquid = 1:250) by 11 mole/dm<sup>3</sup> HNO<sub>3</sub> at 90°C showed that complete decomposition was reached in 10-15 minutes, while the process of coagulation of the silicic acid gel was not complete even after 3 hours. In practice it is impossible to carry out the decomposition of eudialyte concentrate with the formation of subsequent solutions suitable for solvent extraction without special techniques.

It is well known that even small quantities of silicic acid present in the system can cause the formation of gels and interfacial films during the course of extraction, (Nikolski (1983), Ritcey (1986), Solovkin (1970)). This phenomenon inhibits and in a number of cases, totally prevents the extraction process. A review of the techniques aimed at either reducing the silica content or the elimination of its influence in hydrometallurgy of various elements has been presented by Chizhevskaya (1994a).

In this communication the results of several years of systematic studies of the nature of stable emulsions in extraction systems with neutral organophosphorus compounds and solutions containing zirconium and silicic acid, as well as the techniques for preventing such emulsions will be presented.

## DISCUSSION

The dispersion of contacting phases is an inevitable consequence of liquid-liquid extraction. The finer the dispersion, the greater is the interfacial area and the more efficient the mass-transfer. On the other hand, the finer the dispersion the greater is the difficulty in phase separation. In multicomponent systems the rate of coalescence depends on a number of factors, e.g. the presence of surfactants influencing the interfacial tension, the formation of double electric layers, etc. Due to such phenomena the interfacial processes are of great importance. The emulsions generated in the course of extraction of rare metals, in particular zirconium, are saturated, that is with a relatively high concentration of the disperse phase. Aggregation and coalescence of drops in these emulsions proceed by breaking the films of the dispersed medium. Therefore these emulsions may be stable only in the presence of strong stabilising forces, with the outer surface of the drops forming a colloidal adsorption layer of the emulsifier with a gel-like structure or a so-called *structural mechanical barrier* (SMB) is formed. Chizhevskaya et al (1977), showed that polynuclear species of silicic acid formed stable interfacial films at the interface between the diluent (decane) and air which can lead to the formation of a SMB which decreases the settling time for the emulsion. The formation of very stable emulsions with half-lives ( $\tau_{0.5}$ ) ranging from hours to days and even weeks occurs in the presence of  $\beta$  - form of silicic acid, which possesses  $\alpha$  - bridges, which is adsorbed at the interface and forms stable structured films which behave as a SMB, (Chizhevskaya (1977), Sinegribova (1986)). In the course of polycondensation at the interface and in the treatment of solution, by long conditioning or temperature treatment, it was observed that the silicic acid polymers were transformed into the  $\gamma$ -form, which consists of oligomers with oxo-bridges. The strong mechanical structures at the interface disappeared and the rate of separation increased steeply, (Chizhevskaya (1977)). It was also observed that the addition of tri-n-butylphosphate (TBP) ( $\geq 0.01\%$  v/v) to decane accelerated the film formation at the interface, (Sinegribova (1988)).

It is likely that the formation of SMB would be determined mainly by the type of emulsion ('oil-in-water' or 'water-in-oil') because silicic acid is virtually unextracted by TBP but concentrates and intensively polymerises at the interface, (Chizhevskaya (1977), Sinegribova (1986)). Sinegribova (1992) found that even small additions of silicic acid (0.07 mol/dm<sup>3</sup> SiO<sub>2</sub>) to the 2 and 5 mol/dm<sup>3</sup> nitric acid solutions did not alter either the density or viscosity of the solutions but increased to some extent the interfacial tension of the system. However, such additions did lead to a steep decrease of the rate of separation on contact with 30 - 100% TBP. This was

more distinctly shown by systems with well-developed formation of emulsions of the first type. To prevent the formation of stable emulsions caused by the presence of polymeric forms of silicic acid, it is possible to carry out the extraction under special conditions, e.g. by 'lazy stirring' which generates a small interfacial area, (Sinegribova (1988)); inversion of the type of emulsion, (Sinegribova (1989a)); or by initial decrease of the silica content by means of coagulants or flocculants, (Chekmarev (1991)).

In the extraction of zirconium there are two important problems which are not related to silica. These are the incomplete transfer of zirconium to the organic phase, and the formation of stable emulsions by polynuclear zirconium compounds. Both these problems arise because of the lack of control of the hydrolysis which accompanies the water leaching of the sodium cake. In the course of this process which is usually performed with hot water, hydrolysis of sodium zirconate and the formation of hydroxides of various composition occurs. In solutions at concentrations above the polymerisation threshold the zirconium may exist in three different forms distinguished by the nature of the bonds in the tetramer structure. The  $\alpha$ -form contains hydroxyl groups, the  $\gamma$ -form oxo-bridges, and the  $\beta$ -form has a sequence of -OH and O- bonds (Zaitsev (1984)). According to Kudryavtzev (1981) and Sarsenov (1974) these structural units are retained during acid dissolution especially in nitric acid. Thus the nitrate compounds in the solution 'remember' the structure of the original species and of these three forms the  $\gamma$ -form was found to be most stable.

The nature of this initial zirconium nitrate solution significantly affects the subsequent behaviour during TBP extraction from aqueous solutions containing 4 - 6 mol/dm<sup>3</sup> of nitric acid (Kudryavtzev (1981), Sarsenov (1974)). The highest distribution coefficient was observed with extraction from solutions of  $\alpha$ -zirconium nitrate, the compound with -OH groups in the tetramer structure. With aging these M-OH bonds transform to M-O-M with a subsequent decrease in the extractability (Kudryavtzev (1981)). Zirconium hydroxide without -OH groups in the tetramer structure dissolves in nitric acid to form the  $\gamma$ -nitrate. These  $\gamma$ -nitrates, or '*stable polynuclear compounds*' (SPC), are the species which are not extracted by neutral organophosphorus extractants (Yagodin(1970)). It is interesting to note that the extraction of zirconium from solid nitrates of various compositions by TBP saturated with nitric acid (Lavrenteva (1990)) follows the same behaviour as observed by Sarsenov (1974) in that the highest extraction was observed for compounds without the oxo-bonds.

Sinegribova et al (1981) have also observed that for solutions of zirconium in nitric acid the interfacial concentration at the air interface considerably exceeds its concentration in the bulk volume. Moreover the greater the hydrolysis of the zirconium the higher is the 'surface activity' observed. Also the concentration of zirconium at the interface increases in the presence of a monomolecular TBP layer (Sinegribova (1980a, 1981)), similar to the behaviour of silicic acid. The presence of this surface excess concentration leads to the polymerisation and the formation of stable interphase structures which inhibit the separation rate of the zirconium  $\gamma$ -nitrate in systems with diluent, even in the absence of mass-transfer (Sinegribova (1980b)). The separation rate decreases with increasing zirconium concentration and decreasing acid content. The most stable emulsions were observed at the interface between decane and zirconium solutions of up to 3 mol/dm<sup>3</sup> nitric acid. Uncharged or weakly charged complex zirconium compounds of the type  $[\text{Zr}(\text{OH})_3\text{NO}_3]^0$ ,  $[\text{Zr}(\text{OH})_2\text{NO}_3]^+$  (Solovkin (1970)) dominate and are adsorbed in the surface layer and easily form associates. In systems containing  $\beta$ - and especially  $\gamma$ -nitrates stable emulsions are also formed in 5 - 6 mol/dm<sup>3</sup> nitric acid solutions (Sinegribova (1989b)). As a consequence the formation of stable interfacial structures occur, which behave as SMB's and impede coalescence. The purification of zirconium nitrate from SPC leads to an increase in zirconium extraction and the enhancement of the emulsion separation rate. When investigating the formation of interfacial structures in the system: silicic acid-zirconium  $\alpha$ -nitrate-nitric acid; using two ranges of acid concentration different rates of formation were observed (Sinegribova (1980c)). The first was between 1 - 3 mol/dm<sup>3</sup> nitric acid where the mixture behaviour was similar to that of zirconium  $\alpha$ -nitrate, and the second between 4 - 6

mol/dm<sup>3</sup> where the behaviour was similar to silicic acid but the maximum structural strength after 24 hours phase contact was much higher than the system without zirconium. Even small additions of zirconium nitrate to silicic acid solutions accelerates the interfacial film formation (Sinegribova (1988)). Where the extraction emulsion separation rate is high and the emulsion separates completely then the separation time correlates with the interfacial tension for the system.

It should be noted that the behaviour of ideal solutions can be quite different from that of real process solutions. Thus mixtures of zirconium nitrate and silicic acid solutions were characterised by lower separation rates when contacted with decane than solutions of the individual components. However, a solution obtained by leaching of a sodium zirconate cake containing zirconosilicates on contact with TBP leads to the formation of an emulsion which is stable for over 70 hours. This implies that the nature of the species in solution have a large influence on its behaviour in the extraction process. As an example, the influence of inorganic salts on the formation of stable emulsions in extraction systems with an ideal solution of  $\beta$ -zirconium species was studied. Sinegribova et al (1988) found that only zirconium nitrate with oxo-bridges in the structure (SPC) promoted stable extraction emulsions. Analysis of the interfacial precipitates isolated by centrifugation from the stable emulsion, and measurement of interfacial tension in mixed solutions of zirconium nitrate and silicic acid, (Sinegribova (1992)), indicated that hydrolysed zirconium nitrates with oxo-bridges were the catalysts for polymerisation of  $\beta$ -silicic acid species at the interface with TBP. If the polycondensation of silicic acid at the interface occurs by the formation of hydrogen bonds followed by condensation into oxo-bonds, then the addition of substances capable of forming hydrogen bonds should prevent the formation of a stable extraction emulsion. It was found that the addition of 5 - 10% methyl or ethyl alcohol to the aqueous phase before contact with TBP does prevent stable emulsion formation but makes zirconium extraction worse. Another way to prevent the formation of a stable emulsion in systems with zirconium and silicic acid is to conduct the extraction in the absence of an aqueous phase, by treating the solid phase with the extractant (TBP) saturated with nitric acid (Chizhevskaya (1994a)). Thus in extraction from eudialyte and other zirconium containing compounds ( $\alpha$ - and  $\beta$ -nitrates) only the ionic associate  $[(TBP)_2H^+][Zr(NO_3)_5^-]$  was formed, similar to that found in zirconium extracts from 12 - 15 mol/dm<sup>3</sup> nitric acid (Stoyanov (1983)). The combination of the two processes, mechanoactivation of the mineral and leaching in a special apparatus, allows the rapid and easy extraction of zirconium and rare earth elements from eudialyte concentrate. Other processes for preventing stable emulsion formation in the extraction of eudialyte have also been devised.

The results of mechanoactivation of zircon (Chizhevskaya (1994b)) confirm the possibility of obtaining acid soluble zircon without preliminary caking and provide an opportunity for alternative processes for the extractive purification of zirconium to those currently in use.

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## REFINING OF THORIUM FROM MONAZITE BY SOLVENT EXTRACTION

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### ABSTRACT

The distribution of Th (IV) between aqueous  $H_2SO_4$  solutions and organic phases of LA-2 has been described. The dependence of extraction on the aqueous acidity and the metal and extractant concentrations was investigated. The possible extraction mechanism is discussed on the basis of the results obtained. A flowsheet for production of high-grade thorium from monazite is suggested.

### INTRODUCTION

The development of amine extraction systems and their potential applications in nuclear fuel reprocessing has been reported (Marcus, Kertes, 1969; Coleman, 1970). Both primary and secondary amines were used for the extraction of thorium sulphate and the secondary amines have proved effective (Awwal, Carswell, 1968). In a previous work (El-Yamani, Abd El-Messieh, 1993), refining of cerium from monazite by solvent extraction was described. The present investigation pertains to the production of high-grade thorium from monazite through extraction with LA-2, a long-chain secondary amine; extraction is achieved from sulphuric acid medium.

### EXPERIMENTAL

#### Reagents

Amberlite LA-2, N-lauryl (trialkyl methyl) amine, Rohm and Haas Co., was used as received.  $^{234}Th$  was milked from uranium (Carswell, Lawrence, 1959). Other tracers were obtained through ( $n, \gamma$ ) reactions or by separation of the initial nuclide from the daughter product ( $^{95}Zr$ ) (El-Yamani et al., 1978). The radiochemical purity of the isotopes was checked by  $\gamma$ -ray spectrometry. Odourless kerosene (aliphatic) obtained from the Misr Petroleum Co. was used as a diluent. Other chemicals were of reagent grade.

## Procedure

The aqueous stock thorium solution (0.01 M) was prepared by dissolving  $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$  in the appropriate concentration of  $\text{H}_2\text{SO}_4$  and the exact metal content was determined complexometrically by EDTA and xylenol orange as indicator (Körbl, Pribil, 1956). Equal volumes (5 ml) of the aqueous phase containing the tracer [or the tracer-labelled or even the unlabelled species, the latter being uranium (VI)] in  $\text{H}_2\text{SO}_4$  of appropriate concentration and of the organic phase, pre-equilibrated with  $\text{H}_2\text{SO}_4$ , were shaken mechanically in glass-stoppered tubes at room temperature ( $20 \pm 3^\circ$ ) for 20min. to ensure complete equilibration. After centrifugation, aliquots of both phases were taken and the  $\beta$ -activity of  $^{234}\text{Th}$  was counted with an end-window Geiger-Müller counter. The  $\gamma$ -activities were measured with a scintillation counter and NaI (TI) crystal. U(VI) and Ti(IV) were determined spectrophotometrically by the hydrogen peroxide method. Experiments were conducted in duplicate and the distribution ratio,  $D$ , was calculated as the ratio of the activities of the tracer (or the metal concentrations) in the organic and aqueous phases. The separation factor (selectivity,  $S$ ) was computed from  $S = D_{\text{Th}}/D_{\text{M}}$ , where  $M$  is the metal ion concerned.

## RESULTS AND DISCUSSION

### Effect of Initial $\text{H}_2\text{SO}_4$ Concentration

The extraction of Th (IV) from  $\text{H}_2\text{SO}_4$  solutions using 0.07 and 0.14 M LA-2 sulphate in kerosene was examined for various acidities. Results are shown in Figure 1 in which the distribution ratios of  $\text{H}_2\text{SO}_4$  are also compared with those for mixtures of 0.1 M  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  at various concentrations. Higher  $D$  values achieved at lower acidities (0.02 - 0.1M) are ascribed to formation of a thorium amine sulphate complex while the lower values obtained at higher acid concentrations are due to competition between thorium and  $\text{H}_2\text{SO}_4$  for association with the amine and/or to formation of less-readily extractable complexes. From Figure 1, it may be inferred that extraction is dominated by solvation and ion-exchange reaction mechanisms at lower ( $\leq 0.1$  M) and higher

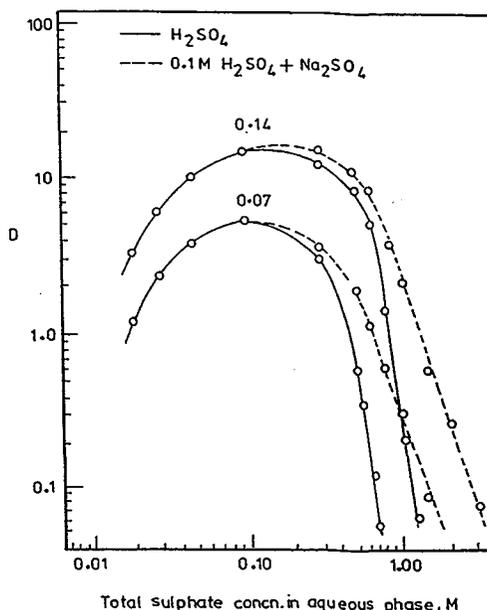
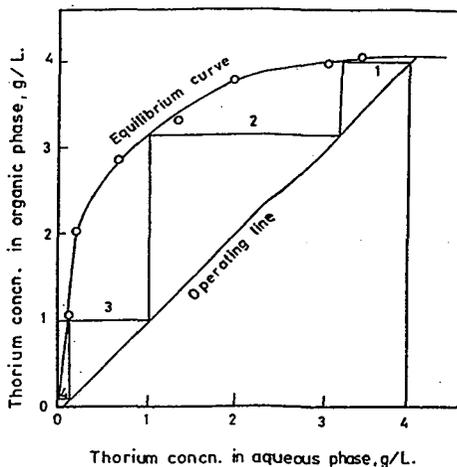


Figure 1. Effect of initial aqueous total sulphate concentration on the extraction of Th(IV) by LA-2 in kerosene (Numerals on curves are LA-2 concentrations, M).

acidities respectively. The figure also implies that, although the D value of the H<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub> mixture is markedly higher than that of H<sub>2</sub>SO<sub>4</sub> solutions, the D of the mixture decreases gradually with the total concentration of sulphate ion, analogous to that in the presence of H<sub>2</sub>SO<sub>4</sub> alone. The results in Figure 1, suggest that the in-extractable anionic species is formed with increasing aqueous acidity since the species Th(SO<sub>4</sub>)<sub>2</sub>, Th(SO<sub>4</sub>)<sub>3</sub><sup>2-</sup> and Th(SO<sub>4</sub>)<sub>4</sub><sup>4-</sup> exist in aqueous sulphate solution containing sulphate ion (Allen, McDowell, 1963).

The optimum acidity recommended is 0.1 M.



**Effect of Metal and Extractant Concentrations**

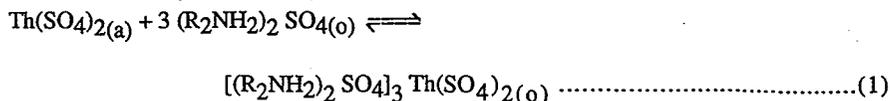
An extraction isotherm was plotted for Th(IV) using 30.1M LA-2 in kerosene; the results are shown in Figure 2.

Figure 2. McCabe - Thiele diagram for the extraction of Th(IV) from 0.1M H<sub>2</sub>SO<sub>4</sub> using 0.1 M LA2 in kerosene

A maximum loading charge of 4.1 g/L Th(IV) in the organic phase was obtained at 0.1 M H<sub>2</sub>SO<sub>4</sub>, implying that six amine molecules are associated with each metal ion. The association is identified by the dependence of D on the concentration of LA-2. The equilibrium concentration of LA-2 was calculated on the assumption that :

$C_{LA-2} = C_{Tot} - nC_{Th(IV)}$ , where  $C_{Tot}$  is the total LA-2 concentration and  $C_{Th(IV)}$  is the thorium concentration in the organic phase and  $n(=6)$  as calculated above. Log D increases linearly with rise of log LA-2 concentration up to ca.0.1 M beyond which a remarkable bending of the curve is observed, presumably owing to non-ideality of the organic phase. At low LA-2 concentration (<0.1M), the plots give straight lines with slopes of approximately three, indicating a third power dependence of D on the LA-2 concentration. If Th(SO<sub>4</sub>)<sub>2</sub> is considered to be the neutral species, and Th(SO<sub>4</sub>)<sub>3</sub><sup>2-</sup> and Th(SO<sub>4</sub>)<sub>4</sub><sup>4-</sup> the anionic species, Th(SO<sub>4</sub>)<sub>3</sub><sup>2-</sup> existing predominantly (Allen, Mc Dowell, 1963), and, if the reagent species is (R<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>SO<sub>4</sub> at lower acidities and (R<sub>2</sub>NH<sub>2</sub>)HSO<sub>4</sub> at higher acid concentrations analogous to di-n-octylamine, a secondary amine extractant (Sato, 1970), the extraction mechanism may be expressed as follows :

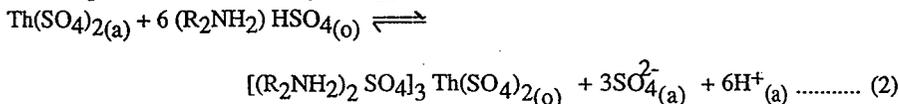
i) At lower acidities (0.03 - 0.05 M):

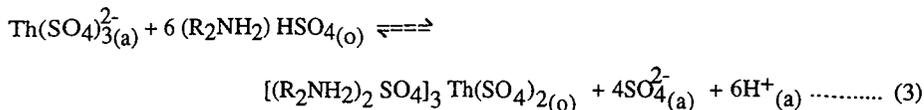


where (o) and (a) denote the organic and aqueous phases, respectively

ii) At higher acidities :

Two equilibrium reactions may be suggested :





Similar stoichiometries have been suggested for other amines (Sato, 1970). From the extraction isotherm (Figure 2), the number of theoretical stages concluded was four and countercurrently five; five stages are proposed for security.

**Stripping of Thorium**

Thorium extracted into the organic phase from 0.1M H<sub>2</sub>SO<sub>4</sub> by 0.1 M LA-2 in kerosene may be readily stripped with sodium or ammonium carbonate. Quantitative stripping of thorium is achieved in 10 min. with 0.5 M sodium carbonate .

**Effect of Diverse Ions**

Table 1 shows the separation factors for various metal ions from Th (IV). The higher extractability of Th(IV), compared to those of the rare earths, Co (II), Ni (II), Zn (II) .... etc, affords a useful approach to separating Th(IV) from rare earths, prevailing in monazite and fission products. U (VI) , Zr (IV), Hf (IV) and Fe (III) should be separated or masked before thorium determination or production. The separation of Th (IV) from trivalent Ce, La, Eu, and Y is shown by γ-spectrometry to be practically complete.

**TABLE 1**  
Separation factors for various metal ions (0.01 M) with respect to Th (IV) extracted into 0.1 M LA-2 in kerosene from 0.1 M H<sub>2</sub>SO<sub>4</sub>.

Ion	S	Ion	S
U (VI)	0.02	Ce (III)	3.9 x 10 <sup>2</sup>
Zr (IV)	1.07	Eu (III)	5.8 x 10 <sup>2</sup>
Hf (IV)*	1.87	Y (III)	1.5 x 10 <sup>2</sup>
Ti (IV)	82.9	Be (II)	1.2 x 10 <sup>4</sup>
Fe (III)	14.5	Zn (II)	5.8 x 10 <sup>4</sup>
Cr (III)	1.2 x 10 <sup>2</sup>	Ni (II)	1.5 x 10 <sup>5</sup>
La (III)	2.9 x 10 <sup>2</sup>	Co (II)	1.2 x 10 <sup>6</sup>

\* Carrier - free

**Production of High Grade Thorium**

Crude thorium sulphate feed was processed by soda leaching of monazite and removal of U (VI) through extraction with tri-iso-octylamine (TIOA) in kerosene (Crouse, Brown, 1959). Extraction of Th (IV) from the feed was carried out using 0.1 M LA-2 in kerosene. The loaded extractant was scrubbed with 0.1 M H<sub>2</sub>SO<sub>4</sub> while Th (IV) from the back-washed extract was stripped with 0.5 M sodium carboante. High-grade thoria (99.8%) with more than 90% recovery was obtained after precipitation of thorium with oxalic acid and calcination to the oxide. A diagrammatic flowsheet for the suggested process of thorium refining is presented in Figure 3

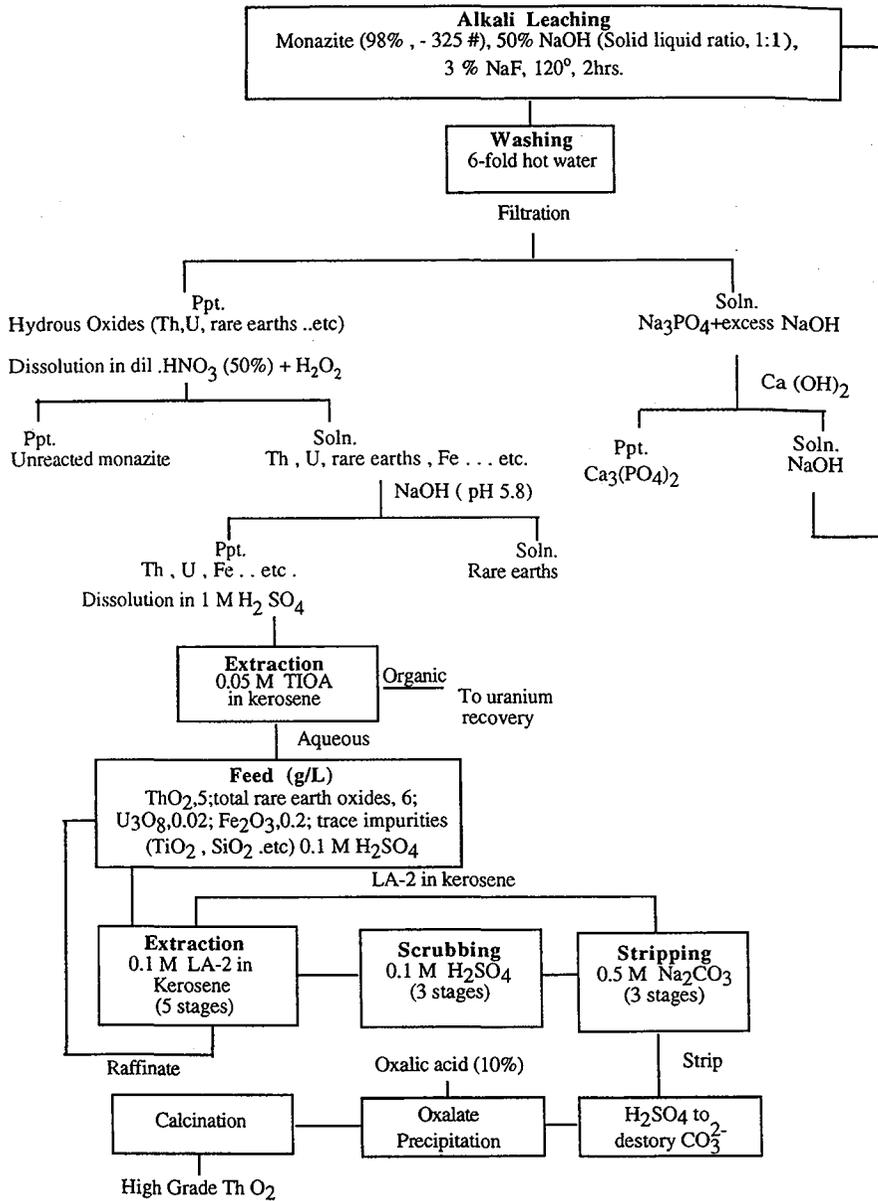


Figure 3. Diagrammatic flowsheet for refining of thorium from Egyptian monazite

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## Adding VALUE TO ZINC RESOURCES by MEANS OF NEW SELECTIVE SOLVENT EXTRACTION REAGENTS

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### ABSTRACT

A programme of research work by ZENECA Specialties has led to the development of a novel class of selective zinc extractants. The reagents operate on a proton exchange principle loading zinc efficiently from weakly acidic leach solutions, without the need for neutralisation, yet can be readily stripped by contact with acidic spent zinc sulfate electrolyte. Another unique and important feature of these reagents is their exceptionally high selectivity for zinc over iron. One of the main challenges in development of a solvent extraction process for zinc has been to meet the more stringent requirements of electrolyte purity required for efficient operation of a zinc tankhouse. This paper considers the properties of a member of this novel class of extractant and how it may be integrated into a circuit to meet the requirements for the efficient electrowinning of zinc.

### INTRODUCTION

Though in widespread use in the copper industry, solvent extraction has so far found little application in the recovery and processing of zinc. This is despite the ready availability of numerous primary and secondary sources of zinc that could readily be leached and the zinc recovered by a process based on solvent extraction. There are also potentially great economic and environmental advantages to be gained by producing zinc metal directly at the mine site rather than the current practice of having the production facility remote from the deposit with all the consequent problems of disposal of the waste products. Conceptually this could be accomplished, as in the case of copper, by the leaching of currently under utilised oxidic deposits and by the bio leaching of low grade sulfidic ores, the zinc being recovered by means of an integrated leach - solvent extraction - electrowinning process. It is suggested that the low uptake of solvent extraction technology in the zinc industry so far, however, is due in part to the difficulties inherent in the electrowinning of zinc, that requires an extremely pure electrolyte, and also to the past absence of suitable selective reagents compatible with such an integrated process.

A programme of research work at ZENECA Specialties has now led to the development of a novel class of solvent extraction reagents for zinc based on bisdithiophosphoramides (Figure 1).

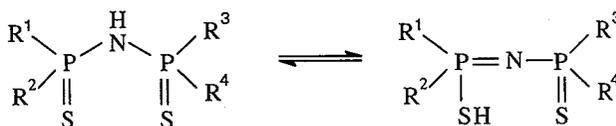
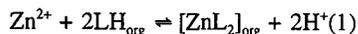


Figure 1. Tautomeric structures of a substituted bisdithiophosphoramide

These reagents act as chelating bidentate ligands towards zinc and operate on a proton exchange principle (1) loading zinc efficiently from weakly acidic leach solutions, without the need for neutralisation, yet can be readily stripped by contact with typical acidic spent zinc sulfate electrolytes. (Campbell, J., Dalton, R., F. and Quan, P.M., 1993).



In earlier publications we referred to a development reagent of this type designated DS5846 (R.F.Dalton and P.M.Quan, 1993,1994). We are now able to report on an improved reagent of this class designated as DS5869. Further improvements to performance have also been brought about by developments in manufacturing technology resulting in an extractant which, compared with its predecessors, has improved strength, exceptionally high selectivity for zinc over iron, faster rates of extraction and stripping, and more facile stripping of cadmium.

#### PROPERTIES OF REAGENT DS5869

##### Selectivity

Table 1 shows a comparison of both the relative strength and selectivity for zinc over ferric iron of DS5869 compared with the well known reagents D2EHPA and CYANEX 302, both of which have been considered as potential reagents for the solvent extraction of zinc (Dreisinger, D., West-Sells, P., King, J.A., and Patel C., 1993). These results were obtained by equilibration at 25°C of 0.2 molar solutions of each reagent at an A/O ratio of 2 with an aqueous feed solution containing 2.95g/l zinc and 4.3g/l iron(III) at pH 2.0.

**TABLE 1**  
Extraction of zinc and iron by different reagents.

Reagent	Metals extracted into organic phase (g/l)	
	Zn	Fe
Reagent DS5869	4.74	0.001
Dialkylthiophosphinic acid (Cyanex 302)	0.72	0.69
Di-2-ethylhexylphosphoric acid (D2EHPA)	0.03	4.04

The strength of the complex formed by D2EHPA with iron (III) prevents extraction of all but a few mg/l of zinc when iron (III) is present. In the case of Cyanex 302 both zinc and iron are extracted in approximately equal amounts making it impractical unless ferric iron is removed first. With DS5869, however, zinc is extracted strongly with exceedingly high selectivity over ferric iron, in this test only 1ppm iron being detected in the organic phase.

Although DS5869 has high selectivity for zinc over numerous other metals that are of importance in zinc processing, such as calcium, magnesium, and cobalt, it is not specific for zinc and will also extract strongly copper and some other metals, particularly those that form strong complexes with ligands containing "soft" donor atoms such as sulfur. Table 2 classifies a number of the metals of importance in zinc circuits into two distinct groups - those that are rejected by DS5869 and those, such as copper and cadmium, that are extracted strongly and require special consideration if present in a zinc feed. These data were obtained by contacting a 0.3 molar solution of DS5869 for one hour

with an aqueous solution containing 10.7 g/l of zinc, 4.1 g/l of iron(III) and various other metal ions, each at a level of approximately 100 mg/l (or saturation amount), added as a soluble salt, at an initial pH of 2.0, and analysing for the amounts of each metal in the aqueous and organic phases.

**TABLE 2**  
Metals extracted and rejected by ACORGA Reagent DS5869  
(concentrations in organic phase after equilibration)

Metals extracted (mg/l)		Metals rejected (mg/l)	
Zinc	6400	Iron	1
Cadmium	110	Germanium	4
Copper	105	Tin	4
Mercury	100	Arsenic	<5
Silver	99	Indium	<5
Bismuth	65	Calcium	<1
Lead	12	Magnesium	<1
		Nickel	<1
		Manganese	<1
		Cobalt	<1

The co-extraction, and hence recovery from the feed solution, of some heavy metals such as cadmium can be viewed as a positive feature as long as it is possible to effect a subsequent separation within the process.

#### Extraction behaviour of DS5869

Figure 2. shows a series of extraction isotherms at 40 °C for a 0.3 molar solution of extractant contacted with feeds containing 5, 10, and 22 g/l zinc, and various amounts of ferric iron at an initial pH of 2.0. These isotherms were generated without any neutralisation and are indicative of the high distribution obtained of zinc into the organic phase from feeds of different compositions.

An indication of typical extraction and stripping behaviour of DS5869 is given in Figure 3 which shows isotherms at 40°C with McCabe-Thiele constructions for the recovery of zinc from a possible heap leach solution containing 5 g/l zinc, and 3 g/l ferric iron at pH 2. Stripping was by a simulated spent zinc tankhouse electrolyte containing 70 g/l zinc and 180 g/l sulphuric acid.

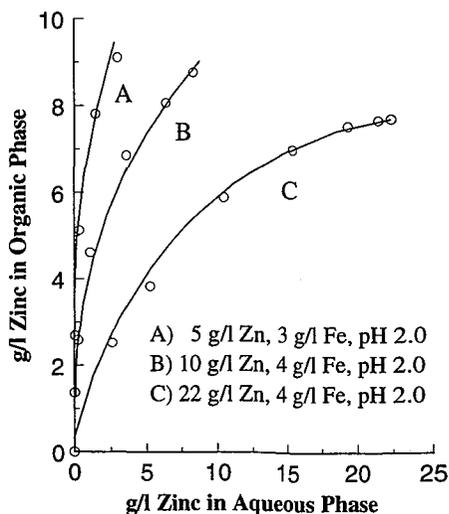


Figure 2. Extraction isotherms at 40°C for DS5869 (0.3 molar extractant) contacted with various zinc feeds.

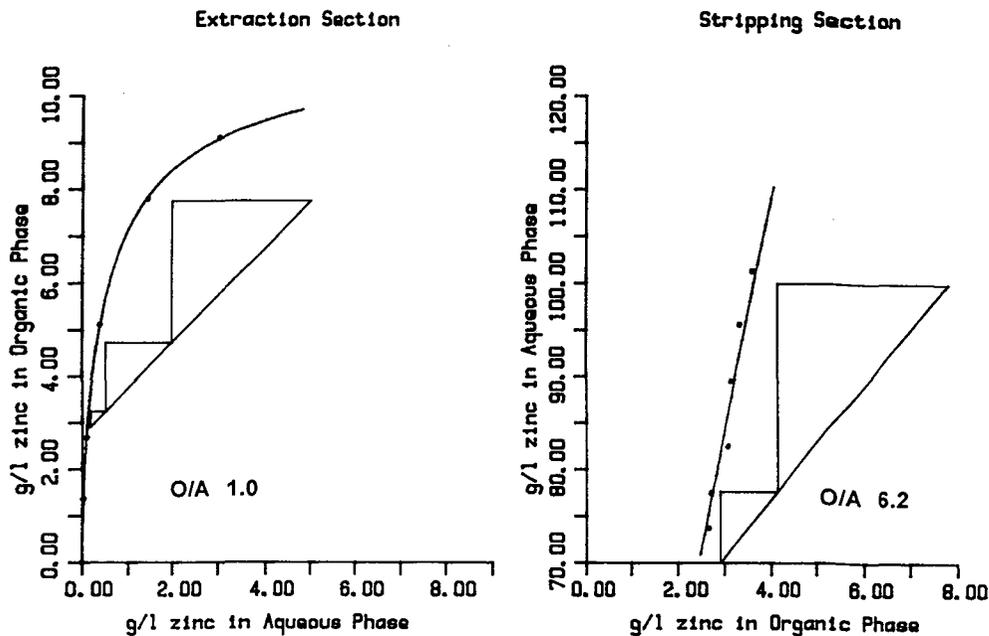


Figure 3. McCabe-Thiele constructions for the recovery of zinc using reagent DS5869 (5 g/l zinc feed, 0.3 molar extractant in Escaid 100)

McCabe-Thiele data was computed using the Zeneca MINCHEM program (Morrison, J., and Townson, B., 1989) for a process based on 3 stages of extraction and 2 stages of stripping with 90% stage efficiency at every stage. This indicates that a zinc in raffinate concentration of 0.16 g/l may be expected, representing a recovery exceeding 97%, while producing a regenerated electrolyte concentration of 100g/l zinc. Isotherms have been generated and McCabe-Thiele data computed for a wide range of possible feeds and conditions and the results are summarised in Table 3.

**TABLE 3**  
Recovery of zinc by Reagent DS5869

Zinc in feed (g/l)	Extractant concentration (M)	Number of extraction stages	Predicted zinc recovery (%)
22	0.3	3	86.4
10	0.3	3	92.2
5	0.3	3	96.7
5	0.3	2	91.8
3	0.2	3	94.1

## Zinc circuit development

The operation of a solvent extraction-electrowinning process for zinc, analogous to the very successful copper operations, will involve recycling of the electrolyte between electrowinning and stripping. Consequently, careful attention must be paid to the potential build up of impurities in the electrolyte which would have an adverse effect on tankhouse efficiency or cathode quality. As indicated earlier (Table 2), DS5869 complexes strongly with both copper and cadmium which are extracted almost quantitatively. Copper is not readily stripped and if present in the feed solution is best reduced to low levels first, by solvent extraction and/or cementation. Cadmium is also extracted strongly by DS5869 which ensures its removal from zinc process streams. It is barely stripped by sulfate electrolyte solutions and therefore tends to accumulate in the organic phase. When a 0.3 molar solution of DS5869 containing cadmium is contacted with strip electrolyte at an O/A ratio of 8, levels of up to 400 mg/l of cadmium can be tolerated in the organic phase before transfer of cadmium to the electrolyte reaches 0.5 mg/l. However, without some means of removing cadmium from the organic phase it would eventually build up to higher concentrations, lowering the zinc loading capacity of the extractant. One method that has been shown to be very effective at removing the cadmium from loaded organic is by taking a bleed from the organic stream and stripping it with 5 molar hydrochloric acid. Alternative options for the control of cadmium and other minor metals at the low levels demanded for zinc electrowinning are also being explored.

## Proposed zinc recovery process

Figure 4 shows a flowsheet for a possible process for the recovery of zinc by solvent extraction - electrowinning, based on the properties of DS5869.

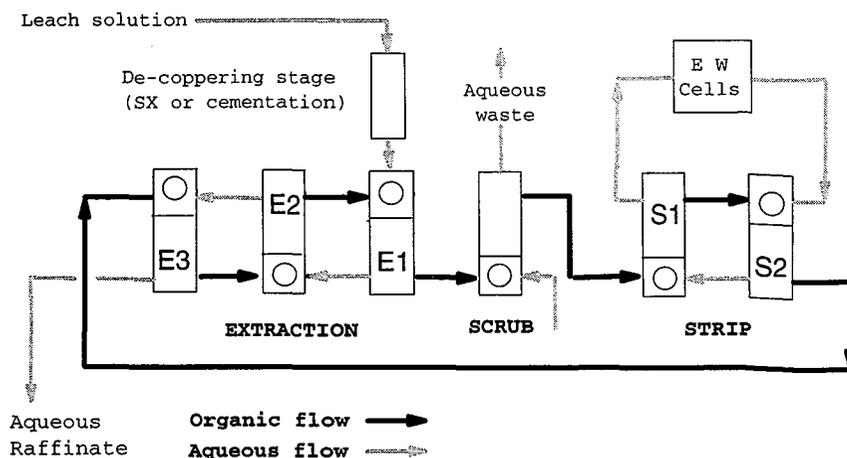


Figure 4. Proposed Zinc Recovery Process using DS5869

The solvent extraction circuit has been tested in mini-rig trials for a number of feeds and conditions and Table 4 summarises data obtained during a laboratory trial for the recovery of zinc from a relatively concentrated leach solution containing 10 g/l zinc. The trial utilised a 0.3 Molar solution of extractant and was operated at 40°C with mixer residence times of 5 minutes.

**TABLE 4**

Summary of Mini-rig Data for recovery of zinc by solvent extraction

Stream analysed	Zinc (g/l)
Feed	10.00
E3 raffinate	1.40
E1 organic	8.73
S1 advanced electrolyte	98.50
S2 stripped organic	4.22

The raffinate of 1.4 g/l in this laboratory mini-rig trial represents a recovery of 86%, close to the predicted recovery of 92% indicated by the computed McCabe-Thiele data (Table 3).

Smooth zinc cathode was successfully electrowon from the accumulated electrolyte with high current efficiency (>90%) and at a current density of 420 A/m<sup>2</sup>.

#### CONCLUSIONS

The new development reagent DS5869 is a strong extractant of zinc from aqueous sulfate solutions showing exceptionally high selectivity for zinc over iron. The hydrometallurgical properties of the reagent have been confirmed by continuous laboratory scale trials and ancillary processes are being developed to enable its satisfactory integration into a proposed zinc recovery process.

The extraction and stripping properties of DS5869, and its ability to effect a major separation of zinc and iron, represents a significant step forward in hydrometallurgy and greatly facilitates the development of new cost effective options for zinc recovery based on solvent extraction.

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## OPERATION OF A COBALT PURIFICATION PILOT PLANT

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### ABSTRACT

Laboratory bench scale studies initiated in 1990 progressed to the design and operation of a Pilot Plant in 1993 and 1994 to recover high purity cobalt from an impure cobalt sulphide slurry.

The cationic impurities iron, zinc, manganese, copper, nickel, calcium and magnesium together with anionic impurities, especially sulphate, were eliminated by a combination of solvent extraction and ion exchange resin treatment.

The resulting cobalt product low in impurities has found ready acceptance with cobalt users and the data obtained from the Pilot Plant operation has been applied to the design of a 2000 tpa cobalt plant.

### INTRODUCTION

Queensland Nickel refines nickel and cobalt from laterite ores found in New Caledonia and Indonesia. Details of the refining process have been described previously by Reid (1982, 1994) and Price (1993). Some modifications to the process have been made in recent years, including a new Ammoniacal Solvent Extraction (ASX) step to separate nickel from cobalt. This has allowed the production of nickel metal and a cobalt sulphide precipitate containing a high proportion of cobalt.

The cobalt sulphide intermediate is refined overseas. The Queensland Nickel cobalt purification process was developed to refine the cobalt at Yabulu hence retaining the benefits of further processing within the company.

### PROCESS OUTLINE

The aim of the cobalt purification process is to produce a pure cobalt intermediate which can either be sold or further processed to a range of cobalt products that are widely available on the international market, for example, cobalt metal and cobalt oxide.

The purification process consists of six steps

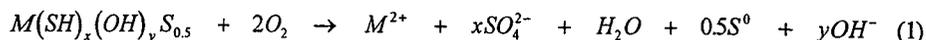
- leaching - to oxidise insoluble cobalt sulphide to soluble cobalt sulphate.
- zinc & iron removal - removes two of the major cationic impurities using solvent extraction.

- cobalt transfer to ammine form - removes anions such as sulphate by transfer to an ammoniacal matrix using solvent extraction.
- nickel removal - removes nickel by an analogue of the ASX process.
- calcium and magnesium removal - using standard ion exchange resins.
- cobalt precipitation - steam strips the complexing ammonia to precipitate the cobalt as cobalt oxide hydroxide (CoOOH).

### COBALT LEACHING

The first step in the cobalt purification process uses an oxidative leach of cobalt sulphide slurry at atmospheric pressure to liberate soluble cobalt sulphate.

The general reaction may be considered as



where M = Co, Ni, Fe, Zn, Mn, Cu, Ca, Mg etc. and  $x + y = 2$

The kinetics of the leaching reaction have been well modelled on the basis of reaction rate proportional to the concentration of cobalt in the solid phase. Using a mixture of low pressure compressed air and pure oxygen it has been possible to achieve greater than 97% dissolution of cobalt.

The resulting solution of cobalt has a typical composition shown below

**TABLE 1**  
Typical Composition of Aqueous Phase Resulting From Oxidative Leach

Element	Concentration, g dm <sup>-3</sup>
Co	60 - 61
Ni	2 - 2.5
Zn	1.5 - 2.0
Fe	0.1 - 0.5
Mg	0.05 - 0.06
Ca	0.01 - 0.02

Reaction (2) producing acid is not favoured at atmospheric pressure and the resulting filtrate has a pH of 1.8 - 2.0.

### IRON & ZINC REMOVAL

The crude cobalt sulphate solution from the leaching step contains significant quantities of iron and zinc (see Table 1). The next step in the cobalt purification process is the selective removal of iron and zinc using solvent extraction under pH control. The aim of this step is to produce a cobalt rich raffinate containing <1 ppm each of iron & zinc.

The organic solution used for this process is prepared by diluting Cyanex-272™ [bis(2,4,4-trimethylpentyl) phosphinic acid] in Escald 110™ (an aliphatic hydrocarbon) to a concentration of 10% (v/v) extractant. No modifier is required. Cyanex-272 has been found to be superior to a number of other extractants studied, including D<sub>2</sub>EHPA™ and Ionquest 801™, both with and without modifiers.

The correct pH profile through the extract cells must be maintained to achieve the final product purity. Extraction curves have been derived for several of the important metal cations (Figure 1). These curves clearly show that both the iron and zinc can be completely extracted, with the iron loading first. Provided the pH profile is adjusted carefully, it is possible to remove the iron without precipitating ferric hydroxide (which is extremely undesirable since it forms crud).

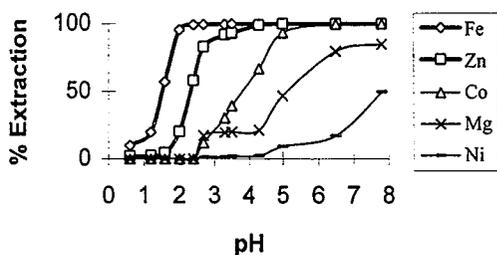


Figure 1. Extraction Curves vs pH for Fe, Zn, Co, Mg & Ni

An undesirable effect of raising the pH to extract all the iron and zinc is that some of the cobalt will load on to the organic. This is clearly shown in Figure 1 where the extraction curves overlap from pH 2.7 onwards. Thus it is necessary to have two scrub cells under pH control to strip the cobalt from the loaded organic. A recycling load of zinc is then established between the scrub cells and the first extract cell. Provided the loading of zinc on to the organic is significantly greater than the stripping of zinc in the scrub cells, few operating problems are experienced.

The scrubbed, loaded organic is stripped using sulphuric acid, a minimum concentration of 2N H<sub>2</sub>SO<sub>4</sub> has been found necessary to completely strip the iron and zinc from the organic. A practical operating limit of 35-40 g dm<sup>-3</sup> of zinc in the final strip liquor has been used to control the flow of fresh strip acid.

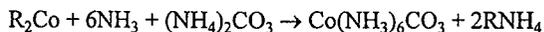
#### COBALT TRANSFER TO AMMINE FORM

The objective of the next step in the cobalt purification process is to transfer the cobalt to an organic phase in order that the cobalt can be converted to an ammoniacal complex during stripping. This transfer eliminates sulphate, and other anions such as chloride, from the final product and allows the removal of nickel by the ASX process.

To effect this step, the iron & zinc - free cobalt sulphate solution from the previous stage is contacted with an organic extractant, Di-2-Ethyl Hexyl Phosphoric Acid (D<sub>2</sub>EHPA™, 10% v/v) in Escaid 110 diluent. Isotridecanol is also added to the organic as a stripping modifier (5% v/v). After passing through the extraction cells the raffinate contains less than 100ppm cobalt, an overall extraction of at least 99.8%. Residual cobalt is recovered from the raffinate by precipitation with ammonium hydrosulphide.

The loaded organic is scrubbed with hot water to remove any entrained sulphate anions. In order to achieve the desired final product purity with respect to sulphur, the concentration of sulphate in the final strip aqueous must be less than 50ppm. This parameter defines a requirement for a minimum of two scrub cells.

Finally, the scrubbed loaded organic is stripped with high strength ammoniacal ammonium carbonate strip liquor (>280g dm<sup>-3</sup> NH<sub>3</sub>) to form the cobalt ammine complex. This proceeds according to the reaction



where R = D<sub>2</sub>EHPA.

The solution leaving the stripping cells has an optimum concentration of ~60g dm<sup>-3</sup> cobalt. This is controlled by the flow of fresh strip liquor into the strip cells. Nickel extraction follows cobalt closely and results in ~2.3g dm<sup>-3</sup> nickel in the aqueous phase. Calcium and magnesium likewise follow cobalt and hence require later removal.

### NICKEL REMOVAL

A nickel removal stage follows ammine transfer using an analogous process to the main nickel & cobalt ASX process. Stripped organic from the main nickel refinery (LIX87QN™ - 2-hydroxyl-5t-nonyl acetophenoneoxime) is contacted in three counter current stages with strip liquor, which lowers the residual nickel from an initial concentration ~2g dm<sup>-3</sup> to approximately 60ppm.

To effect the separation of nickel and cobalt using the oxime extractant it is first necessary to oxidise the cobaltous complex to the cobaltic state and reduce the free ammonia concentration. Oxidation is achieved by first aerating, and then injecting hydrogen peroxide solution. The aim is to achieve less than 20ppm Co<sup>2+</sup> after oxidation. Ammonia removal is achieved by partial steam stripping of the cobalt ammonia solution using a distillation column.

The treated cobalt (III) ammoniacal solution is then contacted with the stripped organic and the nickel loaded on to the organic, any unoxidised Co<sup>2+</sup> is likewise loaded on the organic. The cobaltic ammine raffinate thus contains the majority of the cobalt and < 5ppm nickel.

Calcium and magnesium pass through to the raffinate and must be treated in the final purification step.

## CALCIUM AND MAGNESIUM REMOVAL

The final step in the overall cobalt purification process involves passing the ammoniacal cobalt solution through an ion exchange bed arrangement to remove calcium and magnesium cations. Several different resins were trialed in the pilot plant including Purolite S930™, Amberlite IRC-718™ and Chelex-20™. All these resins are crosslinked macroreticular cation resins bonded to a styrene/divinylbenzene support. They are designed for selectivity of heavy metal cations over the common alkali or alkaline earth cations (including sodium, potassium, calcium and magnesium). Rather than use the sodium form of the resin and risk contamination of the final product, the resin is first changed to the ammonium form using 2.5% ammonia solution prior to loading.

Laboratory tests indicated that stripping would be possible with acetic acid, however in practice incomplete stripping occurred and a suitable substitute had to be found. Nitric acid was then successfully tested and a test program to find the lowest possible concentration necessary was initiated. The results from these trials indicated 0.15N HNO<sub>3</sub> would be suitable. The cycles are (1) load, (2) rinse (2.5% ammonia), (3) strip (0.15N HNO<sub>3</sub>), (4) regenerate (2.5% ammonia).

To achieve low contaminant levels in the final product a minimum of three columns is required. While one column is being regenerated, the other two are being loaded with calcium and magnesium. To prevent breakthrough, a lead/trail configuration is used. When the lead column shows signs of breakthrough, the trail column becomes the lead, the standby column is brought on line and the loaded column stripped and regenerated.

## COBALT PRECIPITATION

To recover the valuable cobalt from the ammine complex, steam is injected to strip the ammonia and carbon dioxide. A series of small scale batch distillation studies in the laboratory showed that this was possible in either a column or autoclave arrangement. Figure 2 below shows the progress of the distillation. Initially steam strips the free ammonia from the solution. When this nears completion, precipitation commences with the complexed ammonia and carbon dioxide being driven off. At the point of incipient precipitation, rapid evolution of gas was observed which caused violent boiling.

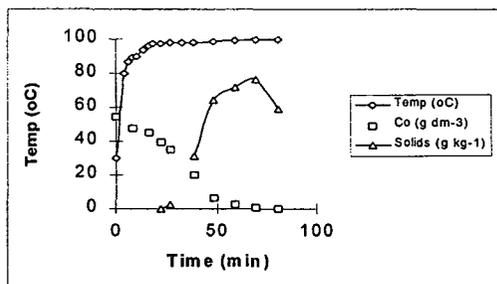


Figure 2. Progress of Cobalt Precipitation in a Laboratory Batch Distillation

Continuous steam stripping was trialled in the pilot plant in a sieve tray column used for preboil duty, this was unsuccessful due to rapid boiling causing the column to flood. Cobalt precipitation was then successfully achieved in a larger splash tray column.

### SUMMARY

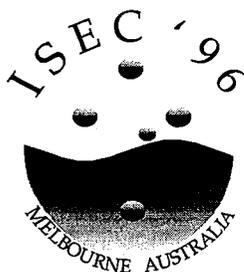
The cobalt purification process developed by Queensland Nickel successfully treats the impure cobalt sulphide intermediate to produce a cobalt oxide hydroxide solid containing very low impurity levels. The process involves three solvent extraction stages and one ion exchange stage which together remove iron, zinc, manganese, copper, nickel, calcium and magnesium, as well as undesirable anions such as sulphate, reducing the total impurities to less than 0.01%. The refined cobalt oxide hydroxide can be sold in this form or further processed into oxide, metal or other products.

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### ACKNOWLEDGEMENTS

D<sub>2</sub>EHPA & Ionquest 801, Cyanex-272, Escaid 110, & LIX87QN are trademarks of Albright & Wilson Inc., Cytec Canada Inc., Exxon Chemical Company and Henkel Corporation respectively. Purolite, Amberlite & Chelex are trademarks of CSR, Rohm & Haas and Bio-Rad respectively. The authors thank QNI management for permission to publish this paper.



## SOLVENT EXTRACTION AND PRECIPITATION STRIPPING: EFFECT OF METAL SPECIATION ON THE RATE OF STRIPPING AND YTTRIA PRECURSOR MORPHOLOGY

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### ABSTRACT

Yttria precursor powders have been obtained in a combined stripping precipitation process. When D2EHPA organic solutions are loaded with yttrium several species are formed depending on the aqueous solution content. Thus, in the extraction from chloride media,  $YA_3 \cdot 2HA$  (HA representing D2EHPA) and  $YA_3 \cdot HA$  were found in the organic phase, while from nitrate media only the species  $YA_3 \cdot 2HA$  appears to form. The differences observed in the precipitation stripping process which follows the extraction of the metal were related to the chemical composition of the organic phase. In this sense, the influence of oxalate concentration (the precipitating agent) and of the acid concentration in the aqueous oxalic solution follows a different trend in the systems studied, chloride and nitrate. From these results, a kinetic control of the precipitation and, thus, of the size and morphology of the yttrium oxalate powders, can be predicted, which has a great influence in the industrial applications of yttria powders.

### INTRODUCTION

Solvent extraction has been widely used to recover and purify yttrium and rare earth elements (Ritcey, 1979). A variety of advanced technological applications require rare earth as powders with specific particle sizes, morphologies and composition (Matijevic, 1987). This objective is generally accomplished by solvent extraction and stripping, followed by precipitation of the desired rare earth compound (Lee, 1991).

Rare earths may be extracted using liquid cation exchangers, anion exchangers or solvating extractants. Cation exchangers are used most widely commercially, in which case stripping is achieved by contacting the loaded solvent with a strong mineral acid solution. The precipitation step then follows, via the addition of a neutralizing agent or an appropriate salt.

The need to obtain particles with controlled size dictates homogeneous precipitation processes. Metal oxides or their precursors can be precipitated homogeneously from aqueous solutions by controlled decomposition of other species that release the precipitant.

A combined stripping precipitation process, in which metal ions are stripped from a metal loaded organic solution by hydrogen ions and simultaneously precipitated as a chemical compound, was described as an alternative to conventional homogeneous precipitation (Yoon, 1988). In this way, mass transfer between immiscible solvents controls the solution composition, and hence the nucleation and growth behaviour.

Yttrium oxalate has been precipitated from rare earth-loaded solutions of either carboxylate extractants (Yoon, 1991), or di-2-ethylhexylphosphoric acid, D2EHPA (Lee, 1991).

Lee and Doyle (1991) described the preparation of yttrium oxalate powders from yttrium-loaded D2EHPA solutions. In addition to examining the influence of the chemical composition of the organic phase and aqueous stripping phase, special emphasis was given to the type of emulsion in the system, and how it affected the rate of mass transfer across the aqueous-organic interface, and

hence the particle characteristics.

Hung et al. (1992) described the precipitation of yttrium oxalate in solvent extraction processes as an alternative stripping operation after accomplishing separation and purification. The precipitation stripping of rare earth from loaded D2EHPA solutions may also be accomplished by precipitating double sulphates (Zielinski, 1991).

Little information on the solvent extraction process appears in these previous studies dealing with the precipitation stripping technique. In particular, no thermodynamic characterization of these systems has been attempted to date.

The present work focuses on a systematic study of the chemical reactions responsible for the extraction of Y(III) by organic D2EHPA solutions. Extraction of yttrium from both chloride and nitrate solutions was studied, along with the influence of different chemical parameters on the precipitation-stripping process. Some information about powder morphology is also included.

## EXPERIMENTAL PROCEDURE

### Reagents and solutions

Di-2-ethylhexylphosphoric acid, D2EHPA, 97% Aldrich-Chemie D-7924 Steinheim, Germany, was used as received. The purity of the product, evaluated by titration against a 0.1 M NaOH standardized solution, was between 92.3% and 94.6%. Kerosene "purum", Fluka Chemie AG., CH-9470 Buchs, Switzerland, was employed as the organic diluent after washing with H<sub>2</sub>SO<sub>4</sub> and then several times with distilled water. The D2EHPA concentration in the kerosene solutions varied between 0.04 M and 0.10 M. Aqueous YCl<sub>3</sub> stock solution at pH 1.0 was prepared by dissolving YCl<sub>3</sub>·6H<sub>2</sub>O (99.9%, Aldrich-Chemie D-7924 Steinheim, Germany) in double distilled water. The pH was adjusted using standardized HCl solution. The metal concentration of the stock solution was determined by EDTA titration, using Arsenazo III as the indicator (Fritz, 1958). Aqueous YNO<sub>3</sub> stock solution was prepared from YNO<sub>3</sub>·5H<sub>2</sub>O (99.9%, Aldrich Chemical Company, Inc., Milwaukee, WI 53233, USA) and standardized in the same way. Working solutions with metal concentrations in the range 13 to 72 ppm were prepared by dilution. Their ionic strengths were adjusted to 2.0 M and their H<sup>+</sup> concentrations to 1.0 M with appropriate volumes of NaCl, NaNO<sub>3</sub>, HCl or HNO<sub>3</sub> standardized solutions. The Y(III) concentration in working solutions was determined spectrophotometrically at 658 nm (Marczenko, 1986).

Oxalic acid, Panreac (Spain) analytical grade, was employed to prepare 0.5 M and 0.75 M solutions having HCl or HNO<sub>3</sub> concentrations of 2.0 M and 3.0 M.

Other reagents used were Panreac (Spain) analytical grade.

The experimental procedure included the following steps:

### Solvent extraction

Experiments were carried out as described elsewhere (Hidalgo, 1991). In this case, 1 hour was sufficient to attain chemical equilibrium between the phases.

From the data on metal concentration, the distribution coefficient, *D*, was determined as the ratio

$$D = \frac{[Y(III)]_{org}}{[Y(III)]_{aq}} \quad (1)$$

The excess of acid in the aqueous phase was determined by titration with sodium hydroxide solution using methyl red as indicator.

For experiments using chloride media, the presence of chloride in the metal-loaded organic solution was determined directly by analyzing the organic phase using ion chromatography, and indirectly by stripping with 6.0 M HNO<sub>3</sub>, then using potentiometry with a chloride-selective electrode, Orion model 94-17B.

### Precipitation stripping

10 ml of aqueous oxalic acid/HCl or HNO<sub>3</sub> solution was added to 50 ml of yttrium-loaded D2EHPA solution (yttrium concentration 0.05 M) in a beaker and then agitated by both ultrasonic and mechanical stirring to produce an emulsion. 2 ml samples were periodically withdrawn at 5 min, 15 min, 30 min and 60 min during treatment. These samples were immediately cooled with ice and centrifuged. The precipitation yield was determined from the metal remaining in the organic solution. The yttrium oxalate powders in the bulk were then separated, washed with acetone several times and stored in an oven at 50 C before characterization.

### Powder characterization

The precipitate particle size distribution was measured with a Malvern Mastersizer/E.

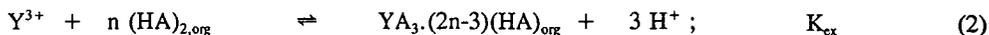
The particle size and morphology were observed by scanning electron microscopy, using a Zeiss model DSM 960 A microscope. Infrared spectra of the powders were obtained with a Nicolet 205 FT-IR. The absence of phosphorus in the yttrium oxalate powder (< 50 ppm P) was determined by ICP-AES analysis.

## RESULTS AND DISCUSSION

### Solvent extraction

The behavior of yttrium(III) during extraction from hydrochloric and nitric acid solutions by D2EHPA in kerosene is presented in Figure 1. At constant acidity, the distribution coefficient increases with increasing D2EHPA concentration.

The extraction of Y(III) by D2EHPA can be expressed by the equation



where (HA)<sub>2,org</sub> refers to dimeric species of D2EHPA.

Equation (2) leads to the relationship

$$\log D = \log K_{ex} - 3 \log [H^+] + n \log [(HA)_2] \quad (3)$$

The plots of log D vs. log [D2EHPA]<sub>tot</sub> in Figure 1 at constant aqueous acidity and different initial metal concentration yield straight lines with slopes n of 2.3 (chloride media) and 2.4 (nitrate media). Values of [H<sup>+</sup>] and [(HA)<sub>2</sub>] at equilibrium are considered to be equal to the initial values, since the metal concentration was very low.

Different values of n appear in the literature. A complex YA<sub>3</sub>·3HA (n = 3) has been reported most commonly (Sato, 1973) when kerosene was used as the diluent, but the complex YA<sub>3</sub>·2HA (n = 2.5) (Mason, 1976) has appeared with n-heptane as diluent. Some authors have concluded that the value of n depends mainly on the nature of the diluent (Lunqvist, 1983).

The experimental data in Figure 1 and the corresponding value of n suggest that YA<sub>3</sub>·2HA is formed in the organic phase during extraction from dilute yttrium solutions with high ionic strength. Figure 2 shows the ratio of extractability of yttrium from nitrate system to that from chloride system as a function of total D2EHPA at different yttrium concentrations. The ratio is almost constant at a value around 1.3, which is consistent with the tendency of nitrate to form less stable complexes with yttrium than does chloride (Sillen, 1964). The same behaviour was observed by Harada et al. (1971).

Equations (2) and (3) should be corrected to take into account the fact that yttrium forms complexes with either chloride ions or nitrate ions in the aqueous phase.

To evaluate the compositions of the extracted species and their formation constants, the experimental data were analyzed numerically by least-square analysis (Liem, 1971).

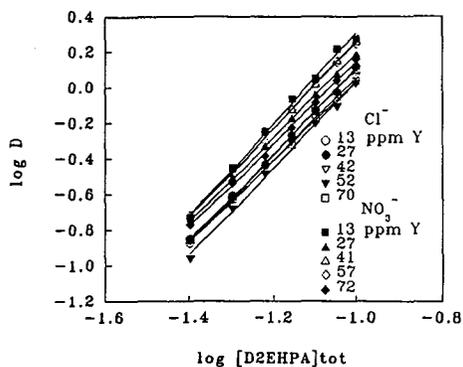


Figure 1. Log D as a function of log total D2EHPA concentration for different yttrium concentrations.

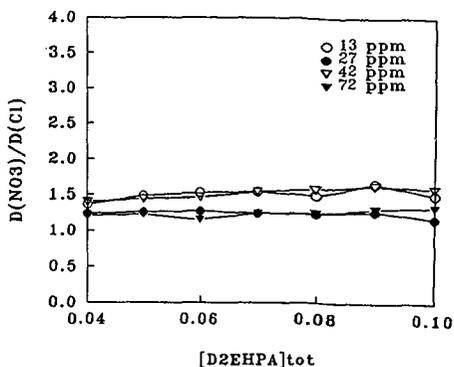


Figure 2. The ratio of extractability of yttrium from nitrate solutions to that from chloride solutions vs. total D2EHPA concentration.

To model the chemical system, all possible interactions of Y(III) have been considered, including aqueous and organic complexes. D2EHPA equilibria were also taken into account from the work of Liem (1972) in the toluene / 0.01 M (Na,H) ClO<sub>4</sub> system. Different YA<sub>3</sub>.nHA species were considered, as well as mixed species YX<sub>a</sub>(HA<sub>2</sub>)<sub>3-a</sub> where X is the anion present in the aqueous solution.

Table I presents results for some selected chemical models.

Table I. Least Square Analysis of Extraction Data

	model	media	log $\beta$	$\sigma$	U
I.	YA <sub>3</sub> .3HA	Cl <sup>-</sup>	20.9	0.063	0.094
II.	YA <sub>3</sub> .2HA	Cl <sup>-</sup>	17.6	0.034	0.028
III.	YA <sub>3</sub> .2HA YA <sub>3</sub> .HA	Cl <sup>-</sup>	17.3-17.7 14.0-14.3	0.031	0.021
IV.	YA <sub>3</sub> .3HA	NO <sub>3</sub> <sup>-</sup>	19.6	0.100	0.241
V.	YA <sub>3</sub> .2HA	NO <sub>3</sub> <sup>-</sup>	16.4	0.090	0.194

From the results of the numerical analysis we observe that extraction of yttrium from chloride media is better explained when the formation of the species YA<sub>3</sub>.2HA<sub>org</sub> and YA<sub>3</sub>.HA<sub>org</sub> is considered. In contrast, only YA<sub>3</sub>.2HA seems to be formed during extraction from nitrate media. YA<sub>3</sub>.2HA would also be the predominant species in the chloride media in the whole range of D2EHPA concentration, but the formation of YA<sub>3</sub>.HA is also important. In both cases mixed species were rejected. This is consistent with the fact that no chloride was detected for the corresponding system.

### Precipitation stripping

The precipitation stripping process can be described by the reaction



Figures 3 to 6 show kinetic data for the precipitation of yttrium oxalate.

The influence of acidity is shown in Figures 3 and 4. It was observed that increasing  $\text{H}^+$  concentration mostly affected precipitation in the nitrate system. The same effect was observed when the oxalic acid concentration increased from 0.5 to 0.75 M (Figure 5). Both results may be due to the species  $\text{YA}_3 \cdot \text{HA}_{\text{org}}$ , only present in the chloride system, having a lower reactivity.

Increasing D2EHPA in the organic solution (Figure 6) led to a decrease of the total yttrium oxalate precipitated according to a left shift in equation (4).

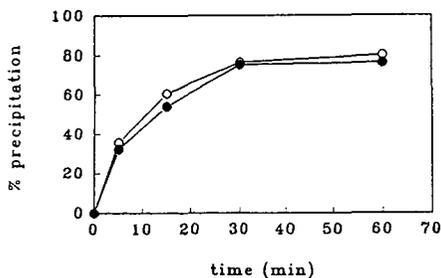


Figure 3. Kinetics of precipitation from 0.05M Y, 0.5M D2EHPA solutions. Loading and stripping in chloride media o and nitrate media ●. Precipitation with 0.5 M oxalic acid solutions, 2 M  $\text{H}^+$ .

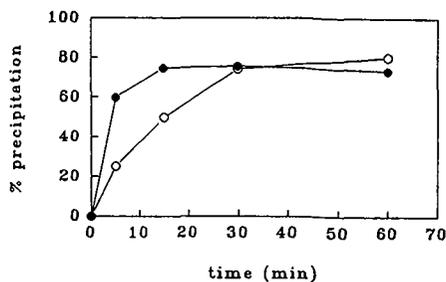


Figure 4. Kinetics of precipitation from 0.05M Y, 0.5M D2EHPA solutions. Loading and stripping in chloride media o and nitrate media ●. Precipitation with 0.5 M oxalic acid solutions, 3 M  $\text{H}^+$ .

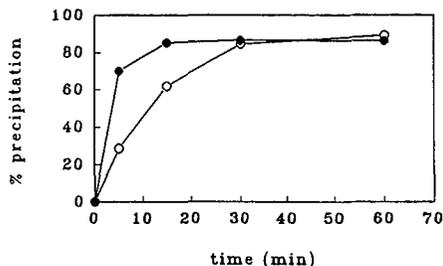


Figure 5. Kinetics of precipitation from 0.05M Y, 0.5M D2EHPA solutions. Loading and stripping in chloride media o and nitrate media ●. Precipitation with 0.75 M oxalic acid solutions, 2 M  $\text{H}^+$ .

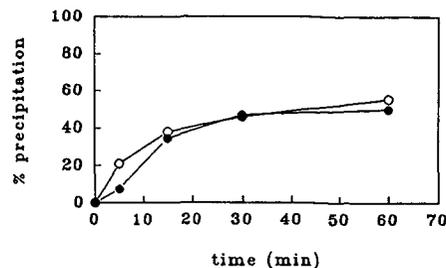


Figure 6. Kinetics of precipitation from 0.05M Y, 1.0M D2EHPA solutions. Loading and stripping in chloride media o and nitrate media ●. Precipitation with 0.5 M oxalic acid solutions, 2 M  $\text{H}^+$ .

### Precipitate characteristics

When yttrium oxalate was precipitated directly from 50 ml of 0.05 M aqueous  $\text{Y}(\text{NO}_3)_3$  using 10 ml of 0.5 M oxalic acid, 2.0 M  $\text{HNO}_3$ , the rate of precipitation was so rapid that in 5 minutes 100% of the yttrium precipitated as oxalate. Under these conditions a heterogeneous precipitate was obtained with 14% of the particles less than 1  $\mu\text{m}$  in size.

Conversely, when yttrium oxalate was precipitated from loaded D2EHPA solutions, precipitation occurred slowly, allowing for more control over nucleation and growth. Larger particles were obtained, with a particle size distribution with a maximum around 6.0-7.6  $\mu\text{m}$  for both the nitrate and the chloride systems (precipitation from 0.5 M D2EHPA loaded solutions with 0.05 M oxalic

acid solution, 2.0 M H<sup>+</sup>).

The morphologies of the particles were observed by SEM. For 0.5 M oxalic acid, 2.0 M H<sup>+</sup> solutions, tubular particles appeared, along with a number of agglomerates. On increasing H<sup>+</sup> to 3.0 M, agglomeration was enhanced in the chloride system, but not in the nitrate system. The powder precipitated by 0.75 M oxalic acid solution was different from those precipitated with more dilute oxalic acid solutions; thin, rectangular platelets formed in the chloride system, whereas the nitrate system gave more regular equiaxed particles, somewhat smaller than those precipitated from the chloride system. This is consistent with the faster stripping rate observed for nitrate solutions. When 1.0 M D2EHPA solutions were stripped, slightly larger particles were obtained, which reflects the slower rate. The particle size distribution was somewhat narrower, with a maximum at 15.1 μm for both chloride and nitrate systems.

As expected, the IR spectra of the yttrium oxalate powders confirmed the absence of D2EHPA in the precipitate. This has important ramifications for commercial adoption of this process.

#### Credit

E. Anticó thanks the Spanish Ministry of Education to support her stay at the University of California at Berkeley.

This work has been carried out under CICYT (Spanish Commission for Research and Development) project No. MAT93-0621.

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# SOLVENT EXTRACTION WITH CYANEX 301 AND 302 FOR THE UPGRADING OF CHLORIDE LEACH LIQUORS FROM LATERITIC NICKEL ORES

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## ABSTRACT

A hydrochloric acid leaching route for the recovery of Ni from lateritic ores (both high Fe and high Mg) has been investigated at Leeds University. An essential requirement for success of the process is concentration of the nickel content from dilute (1-5 g/L) leach liquors, containing high  $MgCl_2$  concentrations to a level suitable for recovery by electrowinning or pressure reduction, with regeneration of HCl by spray roasting. Solvent extraction with alkylthiophosphinic acids, Cyanex 301 and 302 in Escaid 110 diluent have been studied. Results for the kinetics and extraction and HCl stripping isotherms are reported. The co-extraction of Mg and the effect of adding long-chain alcohol modifiers, e.g. octan-1-ol or TOPO are also summarised. Ammoniacal stripping agents for Cyanex 301 were also investigated with less success. Results for Cyanex 302 were very encouraging. Ni can be extracted at about pH 5-6 using recycled MgO to adjust the pH and then stripped by dilute HCl or  $H_2SO_4$  to give a final pH suitable for electrolytic recovery.

## INTRODUCTION

A possible hydrochloric acid based leaching route for the recovery of nickel from lateritic ores of both high iron and high magnesia types has been investigated (Barber 1971; Carter 1980; Noone 1980; Rice 1989). A flow sheet of the proposed route is shown in figure 1.

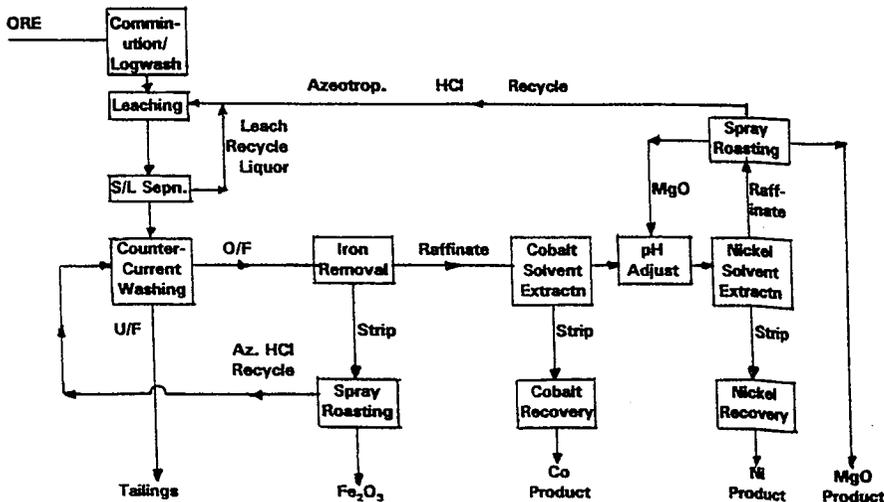


Figure 1. Conceptual flowsheet for HCl leaching of lateritic nickel ores.

Azeotropic HCl (5.5 M or 18 % w/v), is a powerful but non-selective lixiviant for Ni from all types of lateritic ore at atmospheric pressure and temperatures below 100°C (Rice 1974, 1975; Strong 1978; Jimenez-Novoa 1980; Hayman 1984). Furthermore the MgCl<sub>2</sub> and FeCl<sub>3</sub> produced can in principle be spray roasted (Conners 1972) to regenerate HCl and provide MgO for process pH control. The process should be energy efficient compared to other routes particularly those involving pyrometallurgy (O'Kane 1979). The resulting leach liquor contains typically 180g/L Cl<sup>-</sup>, 1-5 g/L Ni, 30-40 g/L Fe, 5-40 g/L Mg, 0.1-0.3 g/L Co, 0.5-1 g/L Mn and small amounts of Cr, Ca and Al but negligible dissolved Si. Residues were white granular aluminosilicates. Separation of Fe and Mg and concentration and recovery of Ni and Co are therefore essential process steps. Attempts to increase the Ni concentration by recycling the leach liquor caused decreased recovery (Lupton 1972; Perry 1972) owing to crystallisation of a layer of NiCl<sub>2</sub> in the pores of residue particles. (Jimenez-Novoa 1980). This could be overcome by counter-current washing allowing an increase in Ni concentration to 7-15 g/L, still too low for easy recovery, but required many expensive washing stages. Ni and Co can be precipitated as sulphides with H<sub>2</sub>S (Price 1993), requiring complex further treatment processes (Nishimura 1981). Solvent extraction (or ion exchange) concentration of Ni would be advantageous. Recently ammoniacal leach liquors from the Caron process (Boldt 1967; Canterford 1975) have been processed by solvent extraction using hydroxyoxime extractants (Price 1993). A key step in the successful application of chloride hydrometallurgy to Ni laterites is concentration of Ni to a level (around 40-100 g/L) suitable for electrowinning or pressure reduction with H<sub>2</sub> in a Sherritt-Gordon (Boldt 1967) or similar type of process (Derry 1970).

Synergistic extraction with di-nonyl-naphthalene sulphonic acid aromatic amine mixtures (Grinstead 1980,1983) or ion exchange with the related chelating resins, Dow XFS4195 or 43084, (Grinstead 1984) can selectively recover Ni from chloride media, but the reagents were not commercially available. Di-2-ethylhexyl phosphoric acid and other alkylphosphorus extractants PC-88A (Flett 1983) and Cyanex 272 (Rickelton 1982,1984) have been used commercially for the extraction of Ni and Co from sulphate media (e.g. Clarke 1993). The selectivity for Co over Ni increases in the order given above (Preston 1982). Co-extraction with Mg (Rickelton 1984; Tait 1992; Clarke 1993) would cause difficulties in the present system. Synergistic combinations of alkylphosphoric acid reagents with non-chelating oximes such as octanaldoxime are powerful extractants for Ni from chloride media at pH < 1 and give excellent separation from Mg. Unfortunately the high acidity - > 5 M - needed for stripping led to degradation of the oxime (Rice 1986a,b). Other reported synergistic combinations of acidic extractants with various oximes (Flett 1971,1974,1975; Nyman 1974; Osseo-Asare 1984; Preston 1983) also have drawbacks including slow loading or stripping kinetics. Recently alkylthiophosphinic reagents from the Cyanex series (American Cyanamid 1992) have been applied to Co/Ni separation (Avila Rodriguez 1992; Belfer 1992; Facon 1991,1993; Rickelton 1988,1990; Sole 1992; Tait 1993a,b). They show improved stability in acidic media compared to alkylthiophosphoric acids (Nedjate 1978; Cote 1984,1989) and do not co-extract Mg and Ca to the same extent as oxyhydril based reagents (Rickelton 1992; Tait 1993a,b). Sole and Hiskey (1992) have compared in detail the characterisation and chemistry of Cyanex 301, 302 and 272 and their application to extraction of common base metals. Tait (1992, 1993a,b) has investigated them in comparison to Cyanex 272 for Co/Ni separation and concluded that Cyanex 302 was the best reagent. The addition of long-chain alcohol modifiers (Facon 1993; Tait 1993b) led to improved rates of extraction. Facon (1993) reported in detail the extraction and stripping of several metals with Cyanex 301 including Ni and Co. Cyanex 301 has been used to extract other metals from strongly acidic media such as flue dust leach liquor (Avila Rodriguez 1992). Such a strong reagent needs very acidic stripping media but possesses long term stability in HCl (Facon 1993). To date very little has been reported on the use of these reagents for Ni extraction as such. Their application to chloride laterite leach liquors is reported here including the use of ammoniacal

stripping agents and effect of modifiers on kinetics for Cyanex 301, loading and stripping isotherms and the co-extraction of Mg. The data appear to be encouraging as a method for concentrating Ni and hence of adding value to HCl leach liquors.

## EXPERIMENTAL METHODS

Aqueous phases were prepared from A.R. grade reagents and pH adjusted using a Jenway 3020 meter. Organic phases were prepared using appropriate quantities of Cyanex 301 (Bis(2,4,4-trimethylpentyl)dithiophosphinic acid) or Cyanex 302 (Bis(2,4,4-trimethylpentyl)monothiophosphinic acid) (Cytec) in Escaid 110 (Esso) after standardisation by pH titration in alcohol/water media. A modifier was added as required. The phases were shaken for 1 hour (Cyanex 302) or 24 hours (Cyanex 301) using a wrist-action shaker. Kinetics were measured at 298 K (except where stated) in a 1 L thermostatted cylindrical baffled vessel stirred at  $850 \pm 10$  rpm with a propeller stirrer. Analysis of aqueous phases for metals was by AAS on a Varian AA-10 and matrix matched standards. Organic phase concentrations were obtained by mass balance and occasionally checked by stripping with 8 M HCl.

## RESULTS AND DISCUSSION

### Cyanex 301

**Loading kinetics:** The rate of loading of nickel increased with increasing pH up to 0.88 and then remained unaffected by pH up to 4.02. Equilibrium was achieved within 2-3 hours. Increasing chloride concentration from 0.17 M to 5.37 M NaCl (saturated) at pH 4.0 resulted in an increase in equilibrium time from less than 30 minutes to over 3 hours. Increasing extractant concentration from 10% to 20% v/v increased the rate at pH 4.0 but 30% had no further effect. Raising temperature from 298 to 328 K decreased equilibrium time to under 30 minutes. The rate appeared to decrease rapidly as initial nickel concentration rose from 1 to 10 g/L for 10% extractant concentration but the simultaneous fall in % extraction indicates that this is probably associated with decreased free reagent concentration.

**Stripping kinetics:** Ni loaded organic phases were stripped with varying concentrations of HCl between 2.04 and 8.22 M at 298, 313 and 328 K. Decreasing extractant concentration from 30% to 10% reduced equilibrium time from over 3 hours to under 30 minutes with increased recovery from 65% to over 90%. Increasing temperature led to an increase in stripping rate at all HCl concentrations with a fall in stripping time from over 3 hours at 298 K to below 30 minutes for 8.22 M HCl. The degree of stripping achieved was highly dependent on HCl concentration and greater than 90% recovery of Ni needed a minimum of 6.19 M HCl.

**Addition of modifiers: Effect on kinetics of loading and stripping:** 10 % v/v of various long-chain alcohols and TOPO were tested in 10% Cyanex 301 in Escaid 110, Increasing chain length from octanol to dodecanol and changing the OH position from 1-ol to 2-ol led to a marginal increase in the rate of loading with no change in the recovery of Ni at pH 4.0 or from 6.19 M HCl. Addition of TOPO resulted in achievement of equilibrium within an hour with a 5% decrease in % extraction of Ni. The addition of modifiers also led to a marked increase in the rate of stripping by 6.19 M HCl - with octan-1-ol showing the greatest effect and leading to over 90% recovery of Ni within 20 minutes. TOPO also had a very marked effect on stripping rate with over 95% recovery in 20 minutes. Increase in the octan-1-ol concentration from 8 to 20% had a marginal effect on loading rate but increased the rate of stripping of Ni with 6.19 M HCl.

**Equilibrium pH:** Concentrations of Cyanex 301 of 10, 20 and 30% (unmodified) resulted in  $pH_{0.5}$  values of -0.25, -0.7 and -0.8 respectively after 24 hours contact. They clearly indicate that this extractant works very well in acidic media but that stripping would require very acidic solutions. The % Ni extraction for 30% Cyanex 301 ranged from 95% in 2 M HCl to 20% in 10 M HCl whereas 10% Cyanex 301 gave < 20% extraction above 4 M HCl.

**Magnesium co-extraction** from 2 g/L solution was less than 10% at  $pH < 1.5$  and the Ni/Mg separation factor ranged from a maximum of 5000 in 1 M  $MgCl_2$  to 1000 in 3 M solution which is encouraging for the application of this reagent to the leach liquors.

**Equilibrium Isotherms:** A feed of 5 g/L Ni gave loadings of 19 g/L, 12 g/L and 6.3 g/L Ni for 10, 20 and 30% reagent, respectively with a very steep initial rise at equilibrium pH values from 0.7 to 0.85 (for each extractant concentration).

**Stripping isotherms** were also obtained for 2, 4, 6 and 8 M HCl from organic phases loaded to 5.6 g/L, 9.2 g/L and 10.7 g/L for each respective extractant concentration. The plots for 2 and 4 M HCl showed the characteristics of good loading rather than stripping isotherms and only that for 8 M indicated efficient stripping. Even then a useful concentration factor for Ni would not be achieved unless a high metal recycle concentration were used. Thus Cyanex 301 would be very effective if it could be stripped. However stripping with strong acids is not likely to result in an aqueous phase of any use for further processing except by crystallisation (Wigstol and Froyland 1972) as other methods of Ni recovery from solution requires pH values of 4 or more (Boldt 1967).

**Alternative Stripping Agents:** Pressure reduction of Ni is usually done in ammoniacal media (Habashi 1993) and Ni can easily be precipitated from ammonium carbonate media by steam stripping of  $NH_3$  and  $CO_2$ , which can then be recombined and recirculated (Boldt 1967). Thus stripping with 1, 2 and 3 M ammonium sulphate or saturated ammonium carbonate was studied from 10% Cyanex 301 loaded with 6.3 g/L Ni.  $(NH_4)_2CO_3$  was totally ineffective but 3 M  $(NH_4)_2SO_4$  stripped about 33% Ni in 2 successive contacts and about 80% Ni in 6 contacts. However, there were problems with crud formation however and further work was discontinued.

## Cyanex 302

**Kinetics:** Preliminary testwork with very dilute Ni solutions indicated that extraction with Ni was complete within ½ hour but it was not possible to carry out tests on the rate of extraction of Ni by Cyanex 302 at appreciable loadings and constant pH owing to the change in pH caused by the  $H^+$  ion exchange in the extraction mechanism.

**Equilibrium pH** Varying concentrations of Cyanex 302 (10, 20 and 30%) resulted in  $pH_{0.5}$  values of 4.8, 5.05 and 5.4 respectively from a solution containing 2 g/L Ni initially in 2 M NaCl. The  $pH_{0.5}$  values obtained are somewhat lower than those reported by Tait (1993b) for Cyanex 302 in Shellsol AB modified by 10% isodecanol. This difference may be due to the use of largely aliphatic Escaid 100 as diluent.

**Separation from magnesium:** Similar tests on 2 g/L Mg in 2 M NaCl gave respective  $pH_{0.5}$  values of 5.8, 6.1 and 6.45. This difference of 1 pH unit gave a useful separation factor of 100 though values were higher for 3 M Mg. More Mg appears to be co-extracted with Ni at higher temperatures. Co-extracted Mg is easily scrubbed from Ni loaded Cyanex 302 with water.

**Extraction Isotherms:** Shake out tests with a feed of 50 g/L Ni at constant equilibrium pH values of 4.0, 5.2 and 6.5, for each extractant concentration, and equilibrium aqueous concentrations of 40 - 50 g/L Ni gave the maximum loadings shown in table 1.

TABLE 1.

Equilibrium Ni Loadings of Cyanex 302 at Various Concentrations and Equilibrium pH Values

Extractant Conc.v/v	Organic Loading (g/L Ni)		
	pH = 4.0	pH = 5.2	pH = 6.5
10	0.7	1.8	4.3
20	1.6	3.1	9.4
30	2.5	5.0	15.4

A McCabe-Thiele diagram for stripping of 20% Cyanex 302 loaded to 4.3 g/L Ni by 6 M HCl indicated that the strip product would contain 18 g/L Ni after 2 counter-current stages at an A/O volume ratio of 1:4. The problem of recovering Ni from 6 M HCl remains. However, the shapes of the loading isotherms summarized in Table 1 indicate that high acidity might not be necessary for the stripping of Cyanex 302. That for pH 4 suggested that this pH could be used for stripping 10% extractant rather than for extraction. Further testwork to check this possibility has shown that a higher acidity is necessary to allow for the exchange of H<sup>+</sup> for Ni<sup>2+</sup> ions. Nickel can be stripped from 30% Cyanex 302 loaded with up to 8.5 g/L Ni in 2 or 3 stages using 2 M H<sub>2</sub>SO<sub>4</sub> giving up to 60 g/L Ni in the strip liquor. About 1 g/L Ni remains unstripped. Optimisation of the stripping acid concentration is continuing and 1 M HCl or H<sub>2</sub>SO<sub>4</sub> can also be used for more dilute extractant.

**General Discussion**

The results indicate that although Cyanex 301 could be used with no pH adjustment as an extractant for recovering nickel from the leach liquor after the extraction of cobalt and iron the subsequent stripping would not yield a solution from which the metal could be recovered easily by conventional techniques. Crystallisation of NiCl<sub>2</sub>·2H<sub>2</sub>O might be possible as in the Falconbridge process otherwise MgO could be used to raise the pH of the strip liquor for either electrowinning or Ni(OH)<sub>2</sub> slurry pressure reduction, but this would increase the complexity and energy requirements for recycling the HCl and lead to losses of Ni. A better method would be to use 10 or 20% Cyanex 302 to extract nickel at pH 5.5 - 6, still giving good separation from Mg. Stripping with dilute HCl or H<sub>2</sub>SO<sub>4</sub> to give a final equilibrium pH range 3 - 4 would provide a suitable medium for electrowinning of Ni and the spent electrolyte could be recycled at about 0.1 - 1 M acid. The Ni distribution ratio in the pH range 3 - 4 for 10 % Cyanex 301 is < 0.1. Tait (1993b) used a pH of 3.3 to scrub Ni from a Co/Ni extract of Cyanex 302 and then stripped Co with advance electrolyte containing 18.7 g/L Co and 24 g/L H<sub>2</sub>SO<sub>4</sub>. Further work is required to define the flowsheet parameters but the system seems to be the most promising studied to date for concentrating Ni. Once the whole Leach/SX/recovery flowsheet has been defined it will be possible to estimate an energy balance for the route and to check how it compares with "conventional" technology for the processing of lateritic nickel ores (Taylor 1995).

**CONCLUSIONS**

Cyanex 302 is a very promising reagent for the recovery of Ni from the HCl leaching of lateritic ores thus "adding value through solvent extraction". Cyanex 301 is a powerful extractant for Ni from acidic chloride media but the need to use very high acid concentrations for stripping would lead to problems in its application.

**ACKNOWLEDGMENTS**

The authors acknowledge the contributions of all previous workers in this area at Leeds University and thank Dr W.A.Rickelton of Cytec for supplying the Cyanex reagents, Esso Europe for the diluent and all companies who provided samples of ores. RWG thanks the Isle of Man Government for a studentship and the Institution of Mining and Metallurgy for a Bosworth Smith award.

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## Application of the PHASE TRANSFER CATALYSIS in RARE EARTH SOLVENT EXTRACTION

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### ABSTRACT

In order to overcome the stripping difficulty and reduce the equilibrium time in heavy rare earth separation with acidic organophosphorous extractants, the phase transfer catalysis (PTC) technique was introduced to the solvent extraction process. It was especially applied to the stripping section, which was called phase transfer catalysis stripping (PTCS) process. In the PTCS process, an acidic phosphorous extractant was mixed with another extractant which could transfer hydrogen ion from aqueous phase to organic phase and almost did not extract rare earth ions, so that the stripping efficiency could be improved and the stripping extraction equilibrium be accelerated. The reaction mechanism of the PTCS and the requisite properties for a feasible PTCS catalyst in the rare earth extraction were studied. We selected D2EHPA as the extractant, Alamine 336 as the PTCS catalyst and mixed rare earth chlorides as the feed to test the PTCS phenomenon. Based on the experimental data, the possibility of applying the PTCS technique in rare earth solvent extraction was discussed.

### INTRODUCTION

Some acid organophosphorous extractants, such as D2EHPA (di-2-ethylhexyl phosphoric acid) and HEH(EHP) (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester), are excellent rare earth extractants used in rare earth separation industry. However, because of their acidities, it is very difficult to strip the loaded heavy rare earth ions from the organic phase completely. On the other hand, the stripping equilibrium is too slow to be undertaken in the heavy rare earth separation process. Therefore, we introduced the phase transfer catalysis (PTC) technique to the stripping extraction process.

The term "PTC" was proposed by C. M. Starks and first used in his patent in 1968, and was generally accepted since 1971. Because of high selectivity, yield, and efficiency of the PTC technique, it had been widely used and intensively studied in the latest two decades. Of course, the technique was brought into solvent extraction process. Yu *et al.* used it to reduce the stripping acidity of D2EHPA, when extracting iron sulfate. They obtained excellent effect. Based on the previous research work, we introduced this method to the rare earth solvent extraction process, especially to the stripping reaction. Referring to the PTC theory in other chemical fields, we suggested the phase transfer catalysis stripping (PTCS) theory.

In the PTCS process, an acidic organophosphorous extractant was mixed with a phase transfer catalyst which almost did not extract rare earth ions and could transfer hydrogen ion from the aqueous phase to the organic phase. In this paper, some concepts such as PTCS reaction, PTC factor, and the stripping reaction mechanism are presented. The selection and properties of a PTCS

catalyst are also discussed. In experiment, we selected D2EHPA as the rare earth extractant, Alamine 336 as the PTCS catalyst and mixed rare earth chlorides as the feed to confirm the PTCS phenomenon. On the basis of experimental data, we intensively studied the functions of the acidic extractant and the PTCS catalyst, and the application possibility of the PTCS technique in heavy rare earth solvent extraction industry.

## THEORETICAL

Referring to the PTC theory and method in catalysis chemistry(Dehmlow, *et al.*, 1993), we proposed the PTCS theory in the rare earth stripping extraction process.

### 2.1 Composition of organic phase

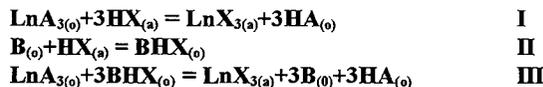
The organic phase is composed of two extractants and a diluting agent. One extractant is an acidic extractant which is used to extract the rare earth ions, the other is a PTCS catalyst which is used to transfer hydrogen ion from the aqueous phase to the organic phase.

### 2.2 Requisite properties of a PTCS catalyst

The requisite properties of a PTCS catalyst in the mixed extraction system comprises the nine points as follows: (1) the PTCS catalyst does not change the rare earth extraction sequence and the separation factor of the acidic extractant; (2) it can efficiently transfer hydrogen ions from the aqueous phase to organic phase; (3) it does not extract rare earth ions; (4) it is miscible with the acidic extractant and the diluting agent; (5) it is nearly insoluble in aqueous phase; (6) it is almost harmless; (7) it is difficult to be emulsified and to form the third phase; (8) it is produced with low cost, and (9) it can be easily applied into industry.

### 2.3 Reaction mechanism

If HA, B, and HX denote an acidic extractant, a PTCS catalyst, and an inorganic acid respectively, the extraction system can be simply expressed as  $[Ln^{3+} / HX / HA-B \text{ and solvent}]$ . Furthermore, if we neglect the association of the extractant itself and that between the extractant and the PTCS catalyst, the stripping extraction process can be described in the following reaction equilibrium equations:



The PTCS reaction process in the two phases can be simply shown in Fig. 1.

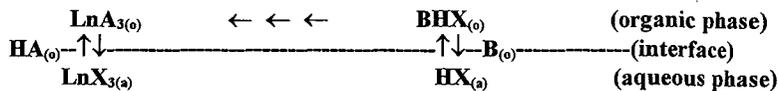


Figure 1. Diagram of the PTCS theory

In these three reactions, reaction I is a slow interface reaction, reaction II is a fast interface reaction, and reaction III is a slow homogenous reaction. Therefore, if we maintain enough inorganic acidity, the stripping reaction I and III will finish completely. Obviously, the reaction rate is much larger than that without the PTCS catalyst, due to the existence of the homogenous PTCS reaction. Before and after the PTCS reaction, the PTCS catalyst and its concentration do not change. This reaction

character is in agreement with the catalysis principle. However, the PTCS reaction process is much more complicated than we have expected.

#### 2.4 Concepts of PTCS reaction and factor

Based on the above PTCS reaction process, we define two important concepts in the PTCS process.

##### 2.4.1 PTCS reaction

The PTCS reaction explicitly indicates the homogenous reaction between the stripping agent and the extraction complex in the existence of the PTCS catalyst. Its character is that it develops in the organic phase instead of on the interface or in the aqueous phase.

##### 2.4.2 PTCS factor

If the extraction system excludes the PTCS catalyst, only the slow reaction I is present, which is the reaction-rate-controlling step. If the reaction is a first order reaction with respect to  $\text{LnA}_{3(o)}$ , a third order to  $\text{HX}_{(a)}$ , then, the reaction's kinetic rate equation can be written as:

$$v = -d[\text{LnA}_{3(o)}]/dt = k [\text{LnA}_{3(o)}] [\text{HX}_{(a)}]^3 \quad (1)$$

where,  $k$  is the rate constant.

Because of continuous addition of the stripping agent,  $[\text{HX}_{(a)}] = C_{\text{HX}}$ ,  $C_{\text{HX}}$  is the initial concentration of HX. If

$$k_{\text{obs}} = k [\text{HX}_{(a)}]^3 \quad (2)$$

then

$$v = -d[\text{LnA}_{3(o)}]/dt = k_{\text{obs}} [\text{LnA}_{3(o)}] \quad (3)$$

and

$$-d[\text{LnA}_{3(o)}]/[\text{LnA}_{3(o)}] = k_{\text{obs}} dt \quad (4)$$

where,  $k_{\text{obs}}$  is the observed rate constant.

Then, through definite integral and the relation:

$$Es = [\text{LnA}_{3(o)}]/C_M \quad (5)$$

where,  $Es$  is the stripping extraction rate,  $C_M$  is the initial rare earth concentration of organic phase, we finally obtain (6)

$$\ln(1/1-Es) = k_{\text{obs}} t \quad (6)$$

If  $\ln(1/1-Es)$  vs. reaction time is plotted, we get a line passing the origin, whose slope is  $k_{\text{obs}}$ . The half stripping extraction time  $t_{1/2}$  can be calculated from (7)

$$t_{1/2} = \ln 2/k_{\text{obs}} = 0.6932/k_{\text{obs}} \quad (7)$$

According to (2), we can get

$$k = k_{\text{obs}} [\text{HX}_{(a)}]^3 \quad (8)$$

If the extraction system includes the PTCS catalyst, both reaction I and reaction III are present, which are parallel reactions. If reaction I is a first order reaction with respect to  $\text{LnA}_{3(o)}$ , a third order reaction to  $\text{HX}_{(a)}$ , and reaction III is a first order reaction with respect to  $\text{LnA}_{3(o)}$ , a third order to  $\text{BHX}_{(o)}$ , then, the reaction's kinetic rate equation can be written as:

$$v = -d[\text{LnA}_{3(o)}]/dt = k [\text{LnA}_{3(o)}] [\text{HX}_{(a)}]^3 + k_1 [\text{LnA}_{3(o)}] [\text{BHX}_{(o)}]^3 \quad (9)$$

where,  $k_1$  is the rate constant of the reaction III.

In the reaction process, because of  $[\text{HX}_{(a)}] = C_{\text{HX}}$  (the initial acidity of the stripping agent), and  $[\text{BHX}_{(o)}] = C_B$  (the initial concentration of B), through the same mathematical treating as above, we can get the following results:

$$k'_{\text{obs}} = k [\text{HX}_{(a)}]^3 + k_1 [\text{BHX}_{(o)}]^3 \quad (10)$$

$$\ln(1/1-Es) = k'_{\text{obs}} t \quad (11)$$

$$k_1 = (k'_{\text{obs}} - k [\text{HX}_{(a)}]^3) [\text{BHX}_{(o)}]^3 \quad (12)$$

$$t_{1/2} = \ln 2/k'_{\text{obs}} = 0.6932/k'_{\text{obs}} \quad (13)$$

where,  $k'_{\text{obs}}$  is the observed rate constant,  $t_{1/2}$  is the half stripping extraction time.

From the above deductions, the PTCS factor is defined as:

$$P = k_1 [BHX_{(o)}]^3 k^{-1}_{obs} \quad (14)$$

The larger  $P$  is, the more obvious is the effect of PTCS. Therefore,  $P$  is the parameter measuring the effect of PTCS. Through experiment, the above parameters  $k$ ,  $k_{obs}$ ,  $k_1$ ,  $k'_{obs}$ ,  $t_{1/2}$  can be obtained by the mathematical calculation method.

### 2.5 Functions of a PTCS catalyst

From the above descriptions, we can see that the PTCS catalyst chiefly has three functions in the PTCS process: (1) accelerating the speed of the PTCS reaction, (2) shortening the reaction's equilibrium time, and (3) reducing the stripping agent's acidity.

### 2.6 Possibility of fulfilling the PTCS technique

In order to fulfill the PTCS technique, the selections of extraction system and PTCS catalyst are most important. The character of an available PTCS catalyst demands that the catalyst should extract inorganic acid readily. So, the catalyst must contain protophilic function group atoms such as nitrogen, phosphorus, oxygen, or sulfur atom. Among all kinds of extractants, there are two kinds worth considering: one kind is neutral phosphorus extractants, and the other is amine extractants. Because the protophilic ability of phosphorus extractants is much weaker than that of amine extractants. We think amine extractants are preferable. However, there are four different kinds of amine extractants, which are primary, secondary, tertiary amines, and quaternary ammonium salts. Their  $H^+$  extraction capability sequence is  $RNH_2 > R_2NH > R_3N > R_4NX$  ( $R = \text{alkyl}$ ), but, the rare earth extraction capability sequence is  $RNH_2 < R_2NH < R_3N < R_4NX$ . Considering their properties both in industry extraction and the PTCS reaction, we decided to use tertiary amine as the catalyst to test its PTCS capability. In our experiment, trialkylamine (Alamine 336) was used in D2EHPA extraction system due to its low cost and other good physical and chemical properties.

## EXPERIMENTAL

D2EHPA (HA) was of CP grade, Alamine 336 (B) was of industry grade, and the mixed rare earth oxides were from ion absorptive ore (containing  $Y_2O_3$ : 25 wt.%;  $Eu_2O_3$ : 0.3 wt. % et al.). The rare earth concentrations in the organic and the aqueous phases, and the concentration of  $H^+$  in the aqueous phase were determined by the general titrimetric analysis. The volume ratio of two phases was  $O/A=1:1$ . In different organic compositions, HA concentration changed from 0 to 1.0 M, B concentration changed from 0 to 0.5 M, the feed concentration changed from 0.15 to 0.50 M ( $pH=3\sim 4$ ). The extraction experiment was carried out on an oscillator in a thermostat (temperature:  $25 \pm 1^\circ C$ ).

Fig. 2, Fig. 3, and Fig. 4-7 show the relationship between  $\ln D$  and the atomic number, the relationship between the stripping extraction rate and the acidity of stripping agent, and the relationship between the stripping extraction rate  $Es$  and the reaction time respectively. Table 1 lists the measured kinetic data of the PTCS reaction.

## RESULTS AND DISCUSSION

### 4.1 Thermodynamic extraction property

The experiment data shows that the Alamine 336 alone almost did not extract rare earth ions in HCl medium. However, with the addition of the PTCS catalyst, the rare earth concentration of organic phase decreased, because the free HA concentration was reduced by the strong association between

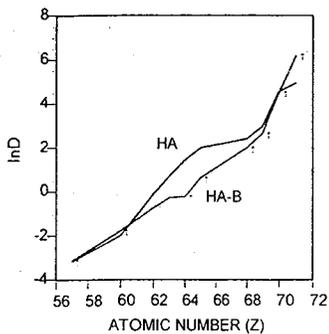


Figure 2. The rare earth extraction sequence of HA-B and HA

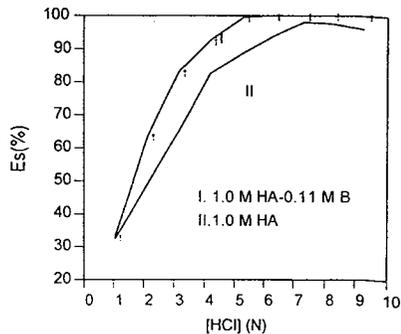


Figure 3. The isothermal diagram of stripping extraction

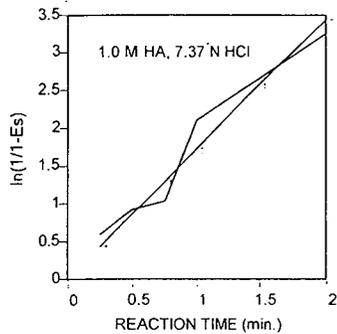


Figure 4. Relationship between  $\ln(1/1-E_s)$  and time

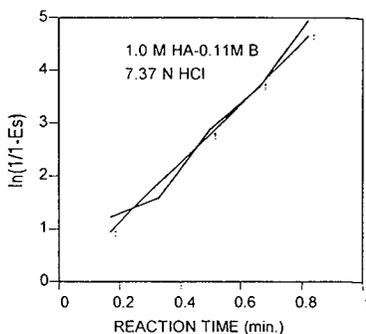


Figure 5. Relationship between  $\ln(1/1-E_s)$  and time

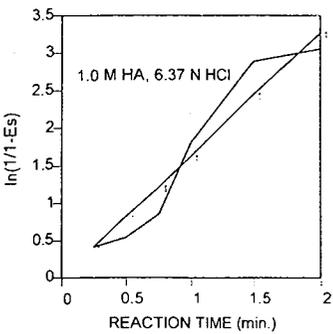


Figure 6. Relationship between  $\ln(1/1-E_s)$  and time

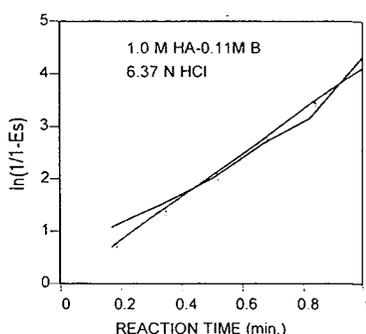


Figure 7. Relationship between  $\ln(1/1-E_s)$  and time

In Fig. 4-7, the solid line represents experimental data, the marked line represents calculated data.

HA and B. The association was confirmed by the IR spectroscopy. In the IR spectra of HA-B-CCl<sub>4</sub>,  $\nu_{P-O}$  shifted from 1228 cm<sup>-1</sup> of HA to 1221 cm<sup>-1</sup> of HA-B, and  $\nu_{P-O-C}(\nu_{P-O-H})$  shifted from 1035 cm<sup>-1</sup> of HA to 1047 cm<sup>-1</sup> of HA-B. Fig. 2 shows that the value of  $\ln D$  increased with the atomic number increasing, and appeared the "tetrad effect", so the rare earth extraction sequence of HA-B remained the same as that of HA. In other words, the PTCS catalyst B did not change the extraction sequence of HA.

TABLE 1  
The PTCS kinetic data

Extractant		1.0 M HA		1.0 M HA and 0.11 M B	
[HCl] (N)		6.37	6.37	7.37	6.37
Observed rate constant	$k_{obs}$	1.72	1.63	$k'_{obs}$ 5.56	4.11
Real rate constant	$k$	0.0050	0.0075	$k_1$ 2567	2066
$P$		0	0	0.61	0.67
$t_{1/2}$ (second)		24	26	8	10

#### 4.2 Thermodynamic and kinetic stripping extraction property

Fig. 3 shows that the minimum stripping acidity (when  $E_S=100\%$ ) was reduced from about 7.5 N to 5.5 N in the presence of the PTCS catalyst, because the effective concentration of the stripping agent  $H^+$  was greatly enhanced by B in the stripping process.

Fig. 4-7 show that  $\ln(1/1-E_S)$  was linear with time, so the stripping reaction seemed a first order reaction with respect to  $LnA_{3(a)}$ , a third order reaction to  $HX_{(a)}$ , and  $BHX_{(a)}$ . In Table 1,  $k'_{obs}$  in HA-B system was 5.56 ([HCl]=7.37 N) and 4.11 ([HCl]=6.37 N) min<sup>-1</sup>, and the PTCS reaction factor  $P$  was about 0.64. But,  $k'_{obs}$  in HA system was 1.72 ([HCl]=7.37 N) and 1.63 ([HCl]=6.37 N) min<sup>-1</sup>, and  $P$  was 0. Obviously, the results mean that PTCS reaction III was much faster than interface reaction I, and that the stripping extraction reaction was greatly accelerated and the equilibrium time was greatly reduced with the addition of the PTCS catalyst Alamine 336. Therefore, it confirmed the existence of the PTCS phenomenon in the HA-B extraction system, which basically agreed with the suggested theory.

From the above discussions, we can conclude that the PTCS phenomenon really exists in the HA-B extraction system, and the PTCS effect is very obvious, but the stripping agent acidity is not reduced too much. Therefore, the PTCS technique partially overcomes the difficulties of D2EHPA stripping extraction, and it may be used in heavy rare earth separation industry. However, the PTCS reaction process has been investigated insufficiently. In the future, there are three problems needed studying extensively, which are (1) how to get an excellent PTCS catalyst, (2) how to use the PTCS technique efficiently, and (3) how to obtain the real mechanism of the PTCS reaction.

#### ACKNOWLEDGMENTS

This work is supported by the National Key Project for Fundamental Research

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## THE STUDY OF SEPARATION OF COPPER AND ZINC IN AMMONICAL SOLUTION BY SOLVENT EXTRACTION WITH LIX84

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### ABSTRACT

Many materials in which copper and zinc coexist can be leached by ammonia-ammonium carbonate or sulphate, but it has been a difficult problem to separate copper and zinc effectively in the leach solution and then to produce pure products respectively. This paper describes the study that LIX84 is used to extract copper selectively and to separate copper and zinc effectively from the amine solution. As a result, 99.97% of copper but little zinc is extracted, and 99.42% of zinc goes into the raffinate, and the selectivity Cu/Zn reached  $1.08 \times 10^6$ . Finally First-class cathode copper ( $\text{Cu} > 99.97\%$ ) and activated ZnO with high quality are obtained.

### INTRODUCTION

Many materials such as copper-zinc complex ore, brass scrap, copper-zinc dross and all kinds of oxides residues bearing copper and zinc can be easily leached by ammonia-ammonium carbonate or sulphate. But it has been a problem to separate copper and zinc effectively from the ammonia leach solution and then to produce pure products respectively. Solvent extraction is a good approach for separation and purification. The extraction reagents used to extract copper selectively from ammonical solution are mainly LIX54, LIX860 and LIX84. LIX54 is specially used in extracting copper from ammonical solution, such as from copper-lead dross leach solution[1]. LIX860 was used in co-extracting copper and zinc from ammonical solution and then stripping them selectively with sulphuric acid in a US patent[2]. LIX84 was used in extracting copper in Arbiter Process[3] and in the recovery of copper from PCB etchant solution[4] and also in the separation of copper and nickel from ammonical leach solution of Ocean Nodules[5]. This paper describes the study in which LIX84 was used to extract copper selectively to separate copper and zinc effectively from amine solution.

### EXPERIMENTAL

Experimental feed solution was derived from the ammonia leaching of a copper-zinc complex ore. The composition is the following (g/L): Cu 7.35, Zn 25.85, total  $\text{NH}_3$  135.5. Extractant LIX84 used was commercial product of Henkel Corp and Diluent was commercial sulphonated kerosene. Condition tests were done in 500ml separation funnels and by a mechanical shaker. Continuous extraction test was done in perspex mixer-settlers with mixer size 60x60x60mm and settler size 60x140x80mm.

### RESULTS AND DISCUSSION

### $\text{NH}_3$ isotherms for LIX84:

Experiments conditions: total  $\text{NH}_3$  20-140g/L; 18% LIX84(v/v) + 82% (v/v) kerosene; phase ratio O/A=1; mix time 3min; room temperature. Fig.1 shows the results.

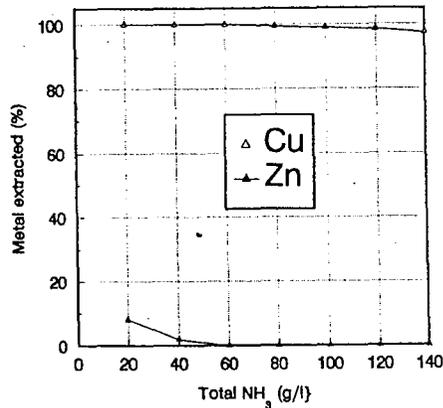


Fig.1  $\text{NH}_3$  Isotherms for LIX84

It indicates that copper extracted decrease slowly with the increasing total  $\text{NH}_3$ . For copper, the extraction recovery is still high (96%) even when the total  $\text{NH}_3$  reaches 140g/L, so LIX84 is suitable for copper extraction from ammine solution with high total  $\text{NH}_3$  concentration while LIX54 is not so. But for zinc, the extraction recovery is low in any total  $\text{NH}_3$  concentration that it's near to zero when total  $\text{NH}_3$  is more than 40g/L. It's the high selectivity of LIX84 to copper over zinc that makes it easy to separate copper and zinc from ammine solution.

### Condition tests:

First the Maximum copper loading was found to be 0.51g/L for 1%(v/v) LIX84 dissolved in kerosene extracting copper from ammine solution. Extraction kinetics is shown in Fig. 2 under the following experimental conditions: 20%(v/v) LIX84 + 80%(v/v) kerosene; phase ratio O/A=1; room temperature.

Fig.2 shows that it needs 2min. to reach extraction equilibrium while extraction recovery arrive at 98%.

Copper and zinc extraction results under various phase ratio see table 1. Copper extraction isotherm of LIX84 is drawn in Fig.3. Conditions are: 18%(v/v) LIX84 + 82%(v/v) kerosene; mix time 3min.; room temperature.

Fig.3 shows that by one stage extraction, copper can drop to 0.2g/L in the raffinate.

Considering the stage efficiency and the strict restriction to copper content in zinc products, two stages extraction would be better. Table 1 indicates that zinc is nearly extracted and can be separated well with copper and then recovered from raffinate as pure zinc products.

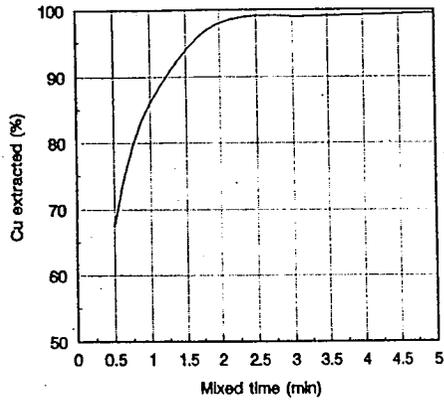


Fig.2 Extraction Kinetics

**Table 1**  
Extraction Results under Various Phase Ratio

O/A	Cu (g/l)		Zn (g/l)	
	Aqueous	Organic	Aqueous	Organic
3/1	< 0.001	2.40	24.80	0.26
2/1	0.0036	3.40	24.65	0.26
1.5/1	0.0036	4.60	25.15	0.28
1/1	0.0098	7.20	24.70	0.27
1/1.5	1.370	9.60	25.20	0.093
1/2	3.200	10.20	25.30	0.075
1/3	4.500	10.50	26.40	0.093

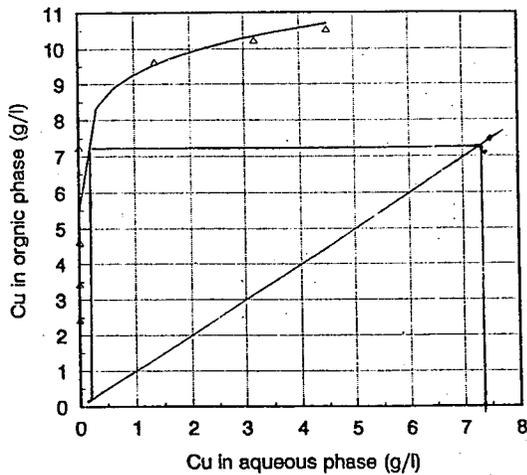


Fig.3 Copper Equilibrium Extraction Isotherm of LIX84

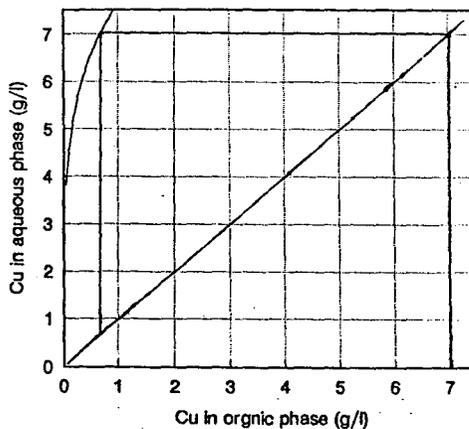
There will be a little amount of  $\text{NH}_3$  entrained into loaded organic while copper is extracted. It has to be scrubbed before copper stripping, otherwise it will go into the electrolyte and make bad effect on the quality of cathode copper. A typical loaded organic contains  $7.04\text{g/LCu}$ ;  $0.15\text{g/LZn}$  and  $1.58\text{g/L NH}_3$ . For the results of scrub tests see table 2. Test conditions: phase ratio  $O/A=3/1$ ; mix time 3min.

**Table 2**  
The effect of pH on the Scrub of  $\text{NH}_3$  In Loaded Organic

Equilibrium PH	Aqueous		Scrubed(%)			Scruber
	Cu	Zn	Total $\text{NH}_3$	Cu	Zn	
9.25	<0.001	0.048	95.57	0	32.00	Water
8.52	<0.001	0.052	97.47	0	34.67	Acid
7.96	<0.001	0.059	98.73	0	39.33	Acid
7.03	<0.001	0.065	100.00	0	43.33	Acid
6.05	<0.001	0.072	100.00	0	48.00	Acid

Table 2 indicates that  $\text{NH}_3$  in loaded organic can be easily scrubbed with water while copper will not scrubbed at all. A little amount of zinc in loaded organic can also be scrubbed partially and a little part of zinc remained in loaded organic will go into strong electrolyte by stripping and will build up for long-term recycle operation, then bleed will be necessary for zinc control in electrolyte.

Equilibrium strip isotherm of LIX84 is drawn in Fig. 4. Conditions are: organic  $7.04\text{g/LCu}$ ; aqueous  $170\text{g/L H}_2\text{SO}_4$ ; phase ratio  $O/A = 1$ ; mix time 3min.; room temperature.



**Fig.4 Equilibrium Strip Isotherm**

Fig.4 indicates that one stage strip will be enough.

**Simulation Experiments:**

After above condition experiments we can determine the extraction circuit and all the operation conditions as follows: organic:  $18\%(\text{v/v})\text{LIX84} + 82\%(\text{v/v})\text{kerosene}$ ; stages: 2 extraction, 1 scrub, 1

strip; retention time:3min.;phase ratio( O/A) : extraction 1/1,scrub 3/1,strip 1/1;scrubber:water;strip solution:170g/LH<sub>2</sub>SO<sub>4</sub> ; room temperature. In order to confirm the feasibility of the circuit to be commercialized, simulation experiment has been done and the results are shown in table 3.

**Table 3**  
Results of the Simulation Experiments

	Cu(g/L)	Zn(g/L)	Total NH <sub>3</sub> (g/L)	pH
Feed Solution	7.10	26.35	135.79	/
Raffinate	0.002	25.80	122.78	/
Loaded Organic	7.40	0.088	1.23	/
Scrubbing Solution	<0.001	0.14	3.68	9.25
Scrubbed Organic	7.40	0.040	0	/
Regenerated Organic	0.30	0	/	/
Strong Electrolyte	32.90	0.12	/	H <sub>2</sub> SO <sub>4</sub> 121g/L
Cu/Zn Selectivity		1.08x10 <sup>6</sup>		

Simulation continuous extraction operated for seven hours. Feed solution treated accounted for 8.81L and produced 9.104L raffinate solution(including start ammonia- ammonium carbonate solution for filling of the cells) and 1.72L strong electrolyte. The results conclude as follows:

.Through two stages extraction, 99.97% of the copper is extracted into organic while zinc is nearly extracted and 99.42% of the zinc goes into raffinate. So copper and zinc is separated nearly completely and the Cu/Zn selectivity is 1.08x10<sup>6</sup>. After stripping, pure copper strong electrolyte is produced and First-class cathode copper(Cu>99.97%) can be attained by electrowinning. From raffinate, zinc can be recovered as pure products such as activated ZnO.

. Little NH<sub>3</sub> entrainment in organic can be easily scrubbed by water and will not affect the quality of cathode copper.

### CONCLUSIONS

Copper and zinc in ammonical solution can be separated effectively by solvent extraction with LIX84, and the Cu/Zn selectivity reaches 1.08x10<sup>6</sup>. After separation, pure copper and zinc products can be easily obtained respectively with high recoveries. This study will be practical in the hydrometallurgy of complex ores in which copper and zinc co-exist and in the comprehensive utilization of other materials bearing copper and zinc.

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## SYNERGISTIC EXTRACTION OF RARE EARTHS BASED ON CYANEX 272

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### INTRODUCTION

Cyanex 272 is the trade name for bis(2,4,4-trimethylpentyl)phosphinic acid, a product of Cytec Industries, Ltd. As an extractant, Cyanex 272 has a series of technological advantages over other commercially available products due to the presence of two P-C bonds with bulky alkyl groups. The structural feature of this reagent makes the molecule higher chemical and thermal stability, better selectivity toward certain metal ions and easily to stripping during back extraction. Cyanex 272 is therefore used successfully for cobalt and nickel separation. Rickelton (1984). It is well supported by our theoretical calculation and prediction. Yuan (1988).

Nevertheless, the extraction behaviour of Cyanex 272 for rare earth separation has been reported by Freiser's group. Li (1986). But the practical application of this system was highly depressed by its insufficient extraction ability and low loading capacity of this reagent resulted from low lipophilicity of the coordination compound formed during the extraction process. In order to develop the field of application of Cyanex 272 in extractive separation of rare earths, it is necessary to overcome a lot of disadvantages of this extractant including the enhancement of extraction ability and separation factor in lanthanide extraction and to increase the lipophilicity of the rare earth complex formed. Our approach in these aspects is based on the establishment of synergistic extraction system by addition of various kinds of ligand to Cyanex 272. Several dozens of different types of ligands were examined for such purpose. The most successful example was described in this paper.

### EXPERIMENTAL

#### Reagents

Since Cyanex 272 supplied by Cytec Co. contains some acidic impurities as shown by silica-loaded paper chromatography and HPLC, pre-treatment of this reagent is therefore necessary. For this purpose, Cyanex 272 was diluted with equal volume of petroleum ether (b.p. 60~90°C) and then washed three times with equal volume of 2% NaHCO<sub>3</sub> solution. The organic solution was washed with water and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent on a rotatory

evaporator under reduced pressure, Cyanex 272 was obtained as colorless liquid. Potentiometric titration with Metrohm 636 Titroprocessor with 0.1M NaOH in 75% alcohol showed the purity of the pre-treated Cyanex 272 was 85.8%. As shown by  $^{31}\text{P}$ -NMR Spectrum (Bruker AM300MHz,  $\text{CDCl}_3$ , 85%  $\text{H}_3\text{PO}_4$  as external standard), the purified Cyanex 272 contains 93% dialkylphosphinic acid with minor amount of 1~2% dialkyl and trialkylphosphine oxide.

C274 is an organic mono-basic acid bearing stereospecific alkyl chains, which provide higher loading capacity and good extraction performance. C274 was synthesized with 94.7% purity in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The average molecular weight was determined to be 293.

### Extraction Equilibrium Procedure

Organic phase: 1.0 or 1.5M Cyanex 272 + C274 (equal molar solution) in n-dodecane was used.

Aqueous phase: (a) 0.1M rare earth chloride solution was prepared from corresponding oxide with purity >99.95% from Yue Long Nonferrous Metals Co., Shanghai, China. (b) For the evaluation of the stripping properties of loaded organic phase, various molarities of aqueous HCl were prepared.

Extraction equilibrium: In a 10ml separatory funnel, equal volumes (2ml) of organic phase and aqueous phase was mixed thoroughly in a mechanical shaker at  $25 \pm 1^\circ\text{C}$  for 30 min. The pH value of the aqueous phase measured after phase separation was taken as the equilibrium pH value. The phase separation behaviour in 1min. was recorded. The rare earth concentration in the aqueous phase was determined by standard complex titration with EDTA using xylenol orange as indicator and the rare earth concentration in the organic phase was estimated by difference  $D = [\text{RE}]_{\text{org}} / [\text{RE}]_{\text{aq}}$ . All of the extraction data were checked by three parallel experiments.

Separation factor in rare earth separation: Separation factor  $\beta$  is the ratio of D values between two rare earth metals.

## RESULTS AND DISCUSSION

1. Synergistic extraction system was established based on the examination of extraction behaviours of related extractants.

**TABLE 1**  
Distribution ratio of rare earths by various extractants

Extractants	D			
	Er	Tm	Yb	Lu
Cyanex 272	0.15	0.43	0.91	1.27
C274	1.81	10.2	31.2	49.2
Cyanex 272 + C274	2.82	11.9	37.2	52.1

The extraction ability as represented by distribution ratio of rare earth by Cyanex 272 extraction are very low (line 1 in Table 1). Surprisingly, upon addition of C274 to Cyanex 272, a dramatic

increase of the extraction ability for rare earth was observed. (line 3 in Table 1). Although C274 provides comparatively high D values in rare earth extraction (line 2 in Table 1), they are still low than that of mixture with Cyanex 272. Consequently, the extractant mixture composed from Cyanex 272 and C274 can be regarded as synergistic extraction system for rare earths.

2. Separation factor of heavy rare earths by Cyanex 272 + C274 system was shown in Table 2.

**TABLE 2**  
Separation factor of heavy rare earths by Cyanex 272 + C274 system

[Extractants] total, (M)	Molar Ratio (%)		$\beta$		
	Cyanex 272	C274	Lu/Yb	Yb/Tm	Tm/Er
1.0	70	30	-	3.55	3.29
1.0	60	40	-	3.76	3.63
1.0	50	50	1.63	3.32	4.29
1.5	50	50	1.61	3.98	4.41
1.0	100	0	1.40	2.10	2.95

3. The loading capacity is the major factor, governing the applicability of the extraction system. Table 3 showed the results of our investigation.

**TABLE 3**  
The extraction loading capacity of Cyanex 272 + C274 system  
Organic phase: 50% Cyanex 272 + 50% C274 in dodecane.  
Aqueous phase: 0.071M or 0.10M Yb, pH=3, ionic strength=1.0M (NaCl).

[Extractants] (M)	[Yb] <sub>aq</sub> (M)	Phase ratio (ml : ml)	[Yb] <sub>org</sub> (M)
1.0	0.071	1.0 : 1.8	0.116
1.2	0.10	1.0 : 1.8	0.123
1.5	0.10	1.0 : 2.0	0.161
1.5	0.10	1.0 : 3.0	0.200

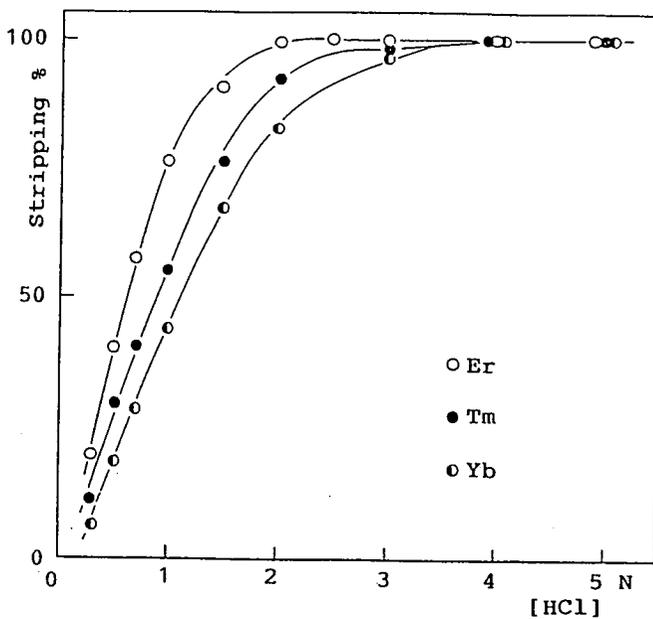
As illustrated in Table 3, the maximum loading capacity of Cyanex 272 + C274 was reached as high as 0.20M in which the phase separation was achieved rather fast and both layers were clear. It seems that the present system exhibits better behaviour in these aspects than that of HEHEPA or P507, a phosphorus-based extractant applied in rare earth separation in commercial scale, which has loading capacity only around 0.17M even at such concentration, formation of turbid organic phase was observed. In the meantime, the loading capacity for Cyanex 272 alone is only 0.08M.

4. The stripping property of an extraction system determines its practical value in metal separation. The percentages of stripping for Er, Yb and Lu were shown in Table 4,5 for 1.5M organic extractants and illustrated on Figure 1 and 2 for 1.0M organic extractants.

**TABLE 4**

The stripping behaviour of Er, Tm, Yb, Lu loaded organic phase (1.5M)  
 Organic phase: 1.5M [Cyanex 272 + C274] in dodecane loaded with Er,  
 Tm, Yb, Lu (0.1M).  
 Aqueous phase: Various concentration of aqueous HCl.

[HCl] (M)	Stripping %			
	Er	Tm	Yb	Lu
0.3	6.25	-	-	-
0.5	21.5	11.4	4.62	-
0.7	36.8	22.6	10.5	-
1.0	56.7	34.3	21.6	-
1.5	75.6	50.1	37.6	-
2.0	89.3	67.7	52.6	-
2.5	96.8	84.4	-	-
3.0	96.5	95.1	84.7	-
4.0	99.8	101.1	95.4	67.0
5.0	-	-	97.3	75.6
6.0	-	-	97.9	74.4

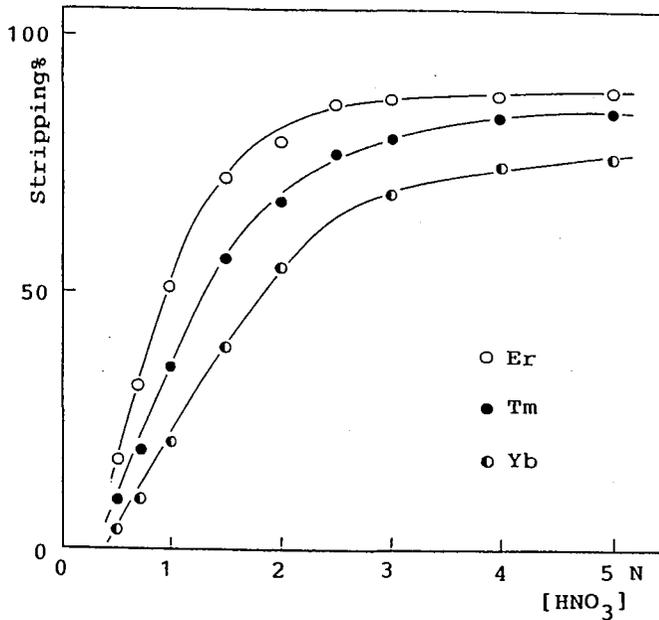


**Figure 1.** Stripping properties of Er, Tm, Yb-loaded 1.0M  
 Cyanex 272 + C274 as the function of aqueous HCl.

**TABLE 5**

The Stripping ability of  $\text{HNO}_3$  for Er, Tm, Yb, Lu-loaded organic phase  
 Organic phase: 1.5M [Cyanex 272 + C274] in dodecane loaded with Er, Tm, Yb, Lu (0.1M).  
 Aqueous phase: Various concentration of aqueous  $\text{HNO}_3$ .

[ $\text{HNO}_3$ ] (M)	Stripping %		
	Er	Tm	Yb
0.5	17.5	9.5	3.69
0.7	31.5	18.9	9.36
1.0	50.8	32.0	20.7
1.5	72.3	48.5	36.4
2.0	79.1	66.5	51.3
2.5	86.4	77.0	-
3.0	85.8	80.3	69.0
4.0	86.5	84.1	74.9
5.0	87.8	85.3	75.7
6.0	-	-	74.3



**Figure 2.** Stripping properties of Er, Tm, Yb-loaded 1.0M Cyanex 272 + C274 as the function of aqueous  $\text{HNO}_3$ .

The unique stripping properties of Cyanex 272 + C274 in  $\text{HNO}_3$  are very attractive, since it established a new method for the production of rare earth free from chloride contamination.

### CONCLUSION

A synergistic extraction system for rare earth separation based on Cyanex 272 is reported. A mixture composed from equimolar Cyanex 272 and C274 was found to be an unique extraction system which exhibits a series of technological advantages over parent components as well as HEHEHPA or P507, a commercial available extractant used in rare earth separation in industrial scale. The Cyanex 272 + C274 system possesses higher extraction ability, huge separation factor, larger loading capacity as well as excellent stripping behaviours. Its good stripping performance toward aqueous nitric acid provides promising possibility to produce high purity rare earth free from chloride ion.

### ACKNOWLEDGMENT

This project was supported partially by the State Committee on Science and Technology of China under Program "Basic Research of Rare Earths".

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# SLURRY EXTRACTION OF RARE EARTHS FROM BASTNASITE IN THE PRESENCE OF ALUMINIUM SALT

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## ABSTRACT

Bastnasite  $\text{RfCO}_3$  contains rare earths (R) and fluorine. Based on the fact that  $\text{F}^-$  ion can be complexed with aluminum ion, we used  $\text{HNO}_3$  and  $\text{Al}(\text{NO}_3)_3$  aqueous solution to decompose bastnasite at  $100^\circ\text{C}$  and used tri-*n*-butyl phosphate (TBP) as the extractant. Rare earths can be extracted directly from acid leach slurries. Under suitable conditions, the yield and purity of rare earths reach 90% and 97-98% respectively.

## INTRODUCTION

Slurry extraction has been used to treat uranium ore [Grinstead (1955)], but slurry extraction of rare earths minerals, which were decomposed with  $\text{Al}(\text{NO}_3)_3$ , has not been investigated. Bastnasite  $\text{RfCO}_3$  is an important industrial mineral containing rare earths (R) and fluorine. When it is decomposed with acids such as  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  by heating, poison gas containing F will be evolved. This gas contaminates the environment and corrodes the apparatus. In order to overcome these shortcomings, based on the fact that  $\text{F}^-$  can be complexed with  $\text{Al}^{3+}$ , we used  $\text{Al}(\text{NO}_3)_3$  containing  $\text{HNO}_3$  aqueous solution to decompose bastnasite at  $100^\circ\text{C}$  with TBP as extractant. Rare earths can be extracted directly from acid leach slurries. The yield and purity of rare earths reach 90% and 97-98% respectively.

The advantages of this slurry extraction method are: (1) the flowsheet can be shortened by combination of decomposition and extraction in one procedure; (2) temperature for decomposition and acidity of the aqueous phase (2N  $\text{HNO}_3$ ) are low; (3) addition of  $\text{Al}^{3+}$  can raise the yield of rare earths due to the fact that it can complex with  $\text{F}^-$  during decomposition and acts as a salting out agent during extraction; (4) the raffinate containing  $\text{Al}^{3+}$  and TBP can be recycled; the rare earths in the strip solution can conveniently be used as starting material for separation of individual rare earths; (5) problem of pollution and corrosion can be reduced.

## RESULTS AND DISCUSSION

### 1. Effect of Aluminum Salt

The composition of bastnasite is shown in table 1. 130ml aqueous solution containing  $\text{Al}(\text{NO}_3)_3$  and  $\text{HNO}_3$  were added into 10.00g bastnasite. The mixture was stirred and heated at  $100^\circ\text{C}$  about for 1 hr.. The slurry was cooled until  $80^\circ\text{C}$ , then 50ml TBP were added into the slurry. It was then stirred about 1 hr. for extraction rare earths. After the stirring was stopped, the organic phase separated

quickly ( about 0.5-1 minutes ). Then the organic phase was decanted and stripped with water, the content of rare earths in the stripping aqueous solution was analyzed. The slurry was filtered, the content of rare earths in the filtrate and solid residue were determined. The percentage of leaching and the extraction yield of rare earths were calculated.

The effect of the content of  $Al^{3+}$  ion in  $HNO_3$  solution on leaching and extraction is shown in table 2. If the bastnasite was decomposed only with  $HNO_3$  containing no  $Al(NO_3)_3$ , the percentages of leaching were low, it was 21.96% - 50.55% with 1.90N - 11.28N  $HNO_3$ . When the  $Al(NO_3)_3$  was added into the 2N  $HNO_3$  solution and used to decompose bastnasite, the percentage of leaching was increased from 21.96% to 91.72%, the extraction yields were increased from 7.43%-62.41%. This fact indicated that  $Al^{3+}$  ion complexes with  $F^-$  during decomposition, and the  $Al(NO_3)_3$  acts as a salting out agent during extraction.

If the  $Al^{3+}$  ion reacts with  $F^-$  ion to form  $AlF_3$  complex, the calculated amount of  $Al^{3+}$  is 0.35g which is enough to complex the content of  $F^-$  in 10g bastnasite. But in practice the amount of  $Al^{3+}$  must be many times greater than the calculated value in order to make the percentage of leaching of rare earths higher than 90%.

**TABLE 1**  
The composition of bastnasite

Composition	$R_2O_3$	$Nb_2O_5$	$ThO_2$	F	CaO	SrO	BaO	$SiO_2$
Content (%)	45.0	0.10	0.22	8.39	9.93	0.13	8.01	0.1

**TABLE 2**  
The effect of aluminum salt

No.	Conc. of $Al(NO_3)_3$ (M)	Content of $Al^{3+}$ (g)	Conc. of $HNO_3$ (N)	Percentage of leaching of RE. (%)	Extraction yield of RE (%)
1	0	0	11.28	50.55	14.23
2	0	0	1.90	21.96	7.43
3	0.10	0.35	1.90	45.51	9.17
4	0.21	0.74	1.90	64.56	10.52
5	0.50	1.75	1.90	87.29	18.17
6	1.00	3.51	2.05	90.37	30.13
7	2.28	8.00	2.05	91.72	55.16
8	3.20	11.22	1.90	89.43	62.41

## 2. Effect of $HNO_3$ Concentration

The effect of different  $HNO_3$  concentrations in  $Al(NO_3)_3$  solution on the percentage of leaching and the extraction yield of rare earths is shown in table 3. The result of experiment No.1 indicated that bastnasite can be decomposed directly by  $Al(NO_3)_3$  solution without any acid. Its percentage of leaching and the extraction yield of rare earths were 86.75% and 89.97% respectively. But when the

acidity of  $\text{HNO}_3$  is  $<1\text{N}$ , the time needed for settlement was very long. When the concentration of  $\text{HNO}_3$  is  $>2\text{N}$ , the time needed for settlement is  $<30$  seconds. The percentage of leaching of rare earths increased with increasing acidity, but the extraction yield of rare earths decreased.

**TABLE 3**  
The effect of  $\text{HNO}_3$  concentration

No.	Conc. of $\text{HNO}_3$ (N)	Conc. of $\text{Al}(\text{NO}_3)_3$ (M)	Percentage of leaching of RE. (%)	Extraction yield of RE (%)
1	0	2.94	86.75	89.97
2	0.38	2.82	87.88	91.12
3	1.06	2.61	90.13	90.65
4	2.05	2.28	91.72	55.16
5	2.37	2.47	91.00	37.65
6	3.40	1.83	91.78	19.88
7	6.19	2.11	89.20	15.97
8	8.96	1.80	87.77	16.53

### 3. Effect of the Ratio Between Aqueous Solution and Bastnasite

Different volumes of aqueous solutions containing  $\text{HNO}_3$  and  $\text{Al}(\text{NO}_3)_3$  were added into 10g bastnasite. The other procedures were the same as stated above. The effect of the ratio between aqueous solution and bastnasite on the percentage of leaching and the extraction yield of rare earths was shown in table 4. When the concentrations of  $\text{Al}(\text{NO}_3)_3$  and  $\text{HNO}_3$  in aqueous solution keep constant, the total content of  $\text{Al}^{3+}$  increased with increasing the volume of aqueous solution used, thus, the percentage of leaching increased; but the extraction yield of rare earths decreased with increasing volume of aqueous solution. When the content of  $\text{Al}(\text{NO}_3)_3$  and the concentrations of  $\text{HNO}_3$  in the aqueous solution remain constant, the percentage of leaching decreased slightly and the extraction yield of rare earths increased with decreasing volume of aqueous solution.

### 4. Effect of Leaching Time and Temperature

When the ratio of bastnasite, aqueous solution and TBP was 10g:80ml:50ml, the concentration of  $\text{Al}(\text{NO}_3)_3$  and  $\text{HNO}_3$  were 0.812M and 2.05N respectively, the effect of leaching time and temperature is as shown in table 5. The percentage of leaching increased with increasing leaching time until 2.0 hr. The optimum temperature was  $100^\circ\text{C}$ .

### 5. Recycle of Filtrate and Organic Phase

When the slurry was batch extracted with TBP about 3-4 times, the total extraction yield of rare earths approached 100%. After the slurry was filtered, part of  $\text{Al}(\text{NO}_3)_3$  and  $\text{HNO}_3$  still left in the filtrate which can be recycled to decompose next batch of bastnasite, but it is necessary to supplement  $\text{Al}(\text{NO}_3)_3$  and  $\text{HNO}_3$ . The organic phase obtained above was stripped with water 4-5

**TABLE 4**  
The effect of the ratio between aqueous solution and bastnasite  
( Bastnasite: 10.00g, TBP: 50 ml )

No.	Volume of Aq. Solution (ml)	Conc. of Al(NO <sub>3</sub> ) <sub>3</sub> (M)	Content of Al <sup>3+</sup> (g)	Conc. of HNO <sub>3</sub> (N)	Percentage of leaching of RE. (%)	Extraction yield of RE (%)
1	50	0.50	0.67	2.05	47.0	48.63
2	80	0.50	1.08	2.05	72.72	30.25
3	130	0.50	1.75	1.90	87.29	18.17
4	80	0.81	1.75	2.05	85.74	43.13
5	50	1.30	1.75	2.05	82.29	88.44
6	50	1.30	1.75	5.33	90.31	42.08

**TABLE 5**  
The effect of leaching time and temperature

No	Leaching Time (hr.)	Leaching Temperature (°C)	Percentage of Leaching (%)	Extraction Yield (%)
1	0.5	100	83.65	42.59
2	1.0	100	85.74	43.13
3	2.0	100	90.45	45.76
4	3.0	100	89.65	40.29
5	4.0	100	90.56	47.02
6	2.0	25	42.57	39.64
7	2.0	55	65.88	41.63

times. The rare earth nitrate solution was obtained, the purity of rare earths reach 97-98%, and the TBP can be recycled to extract next batch slurry.

When 320ml recycle filtrate with 2.05N HNO<sub>3</sub> and 6.9g supplementary Al<sup>3+</sup> was used to treat 40g bastnasite, then the slurry was extracted by 200ml recycle TBP, the percentage of leaching of rare earths (88.5%), the yield of the 1st extraction of rare earths (49.7%) and the total yield after three times extraction (100%) are shown in column 2 of table 6.( cycle 1 )

In order to study the effect of supplementary amount of Al<sup>3+</sup> on the slurry extraction, the recycle filtrate from cycle 1 was divided into three parts, each of which was 80ml and adjusted to 2.05N HNO<sub>3</sub>, but 0, 0.35 and 0.43g Al<sup>3+</sup> were added respectively. They were used to treat bastnasite with such condition that the ratio of bastnasite : recycle filtrate : recycle TBP from cycle 1 equals 10g : 80ml : 50ml. As shown in column 3 of table 6 , no Al(NO<sub>3</sub>)<sub>3</sub> was supplemented to the recycle filtrate from cycle 1, the percentage of leaching of rare earths was only 56.08%. When 0.43g Al(NO<sub>3</sub>)<sub>3</sub> was supplemented to the recycle filtrate from cycle 1, the percentage leaching of rare earths can reach 89.2% (see column 5 of table 6 ). The yields of the 1st extraction of rare earths was also increased from 38.8% to 50.44%, the total yield of extraction of rare earths after three times extraction approached 100%.( cycle 2 )

When 160ml recycle filtrate from cycle 2 with 2.05N HNO<sub>3</sub> and 0.86g supplementary Al<sup>3+</sup> was

used to treat 19.99g bastnasite, then the slurry was extracted by 100ml recycle TBP from cycle 2, the percentage of leaching of rare earths (90.4%), the yield of the 1st extraction of rare earths (71.97%) and the total yield after three times extraction (100%) are shown in the last column of table 6.( cycle 3 )

**TABLE 6**  
Recycle of filtrate and Organic Phases

Bastnasite	(g)	40.00	10.04	10.03	10.14	19.99
No. of cycles		1	2	2	2	3
Volume of recycle filtrate (ml)		320	80	80	80	160
Conc. of HNO <sub>3</sub> in recycle filtrate (N)		2.05	2.05	2.05	2.05	2.05
Supplement of Al <sup>3+</sup> (g)		6.9	0	0.35	0.43	0.86
Volume of recycle TBP (ml)		200	50	50	50	100
Percentage of leaching (%)		88.5	56.08	86.80	89.22	90.44
Yield of the 1st extraction (%)		49.72	38.82	53.26	50.44	71.97
Total yield after three times extraction (%)		100	92.5	98.02	100	100

### CONCLUSIONS

1. Bastnasite can be decomposed directly by Al(NO<sub>3</sub>)<sub>3</sub> solution without any acid due to complex of Al<sup>3+</sup> and F<sup>-</sup>. The 2N HNO<sub>3</sub> in Al(NO<sub>3</sub>)<sub>3</sub> solution is needed for quick settlement.
2. We used Al(NO<sub>3</sub>)<sub>3</sub> solution containing 2N HNO<sub>3</sub> to decompose bastnasite at 100°C. Using TBP as extractant, rare earth can be extracted directly from slurry. The yield and purity of rare earths reach 90% and 97-98% respectively. This flow sheet is shortened by combination of decomposition and extraction in one procedure.
3. When the slurry after extraction was filtered, part of Al(NO<sub>3</sub>)<sub>3</sub> and HNO<sub>3</sub> still left in the filtrate, can be recycled to decompose the next batch of bastnasite. It is necessary however to supplement Al<sup>3+</sup>, which content is 4.3% of bastnasite by wt., and adjust the acidity to 2N HNO<sub>3</sub>. After the extractant is stripped with water 4-5 times, the TBP can be recycled to extract the next batch of slurry.

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## RECOVERY OF RARE METALS FROM SPENT HYDRODESULFURIZATION CATALYSTS BY MEANS OF SOLVENT EXTRACTION

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### ABSTRACT

The sulfuric acid leaching of spent hydrodesulfurization catalysts yields an acidic solution rich in rare metals such as molybdenum, vanadium, cobalt, and nickel in addition to aluminum. For the purpose of separating and recovering the rare metals from the solution, basic solvent extraction characteristics of the metals involved with commercially available acidic organophosphorus reagents such as TR-83, PC-88A, PIA-8 and CYANEX 272 from sulfuric acid media were investigated in the present work. It was elucidated that PIA-8 and CYANEX 272 possessed excellent selectivity for molybdenum and vanadium over the other metals at comparatively low pH. Further, the recovery of molybdenum and vanadium from the actual sulfate liquor by extraction with PIA-8 and CYANEX 272 was discussed. In addition, a systematic investigation was conducted on synergistic extraction by the mixtures of LIX 63, an aliphatic alpha-hydroxyoxime, in combination with a series of acidic extractants like PIA-8, CYANEX 272, PC-88A, D<sub>2</sub>EHPA, TR-83 and OPEHPA for cobalt, nickel and aluminum in order to selectively separate and recover cobalt and nickel from the raffinate obtained earlier containing an appreciable amount of aluminum. It was demonstrated that effective extraction of cobalt and nickel away from aluminum could be achieved from the sulfate solution at low pH (1.0 - 2.5) with the mixtures. Particularly, the mixtures consisting of LIX 63 and CYANEX 272 or PIA-8 appeared to be the most feasible and economic from a practical point of view, yielding acceptable separation efficiency for cobalt and nickel over aluminum and a low acidity requirement for stripping cobalt and nickel as well as negligible degradation of LIX 63. Aluminum left in the raffinate obtained above after recovering molybdenum, vanadium, cobalt and nickel can be easily recovered as sulfate salt by conventional crystallization method.

### INTRODUCTION

Since the early 1950s much of the world's crude oil and heavy fractions have been desulfurized by a catalytic process known as "Hydrodesulfurization"(HDS). A molybdenum trioxide catalyst promoted with cobalt and nickel oxide on a carrier of gamma-alumina has been generally used for this purpose. During the desulfurization process, such metals as nickel and vanadium present in crude oil are deposited on the catalyst together with hydrocarbons, carbon and sulfur. After a number of recovery cycles of burning off the carbon, hydrocarbons and sulfur, the catalytic activity is eventually reduced to the extent that the catalyst has to be renewed. Consequently a great amount of spent HDS catalyst is issued from petroleum refiners. Molybdenum and vanadium are being recovered to a certain extent from the spent HDS catalysts by leaching with hot water after roasting together with sodium carbonate at above 650°C, and then precipitating vanadium as ammonium vanadate by adding ammonium chloride and subsequently molybdenum as hydroxide after pH adjustment. However, all of cobalt and nickel still remain in the alumina carrier in addition to small amounts of molybdenum and vanadium not leached by this method. The waste carrier contaminated with these metals has not found any other uses and is being dumped or stored in appropriate locations until a suitable high-tech treatment is developed. Recently, research activities on the recovery of metal values from spent HDS catalysts have been focused on selective and effective leaching of these metals keeping the dissolution

of alumina carriers into the liquor as low as possible. Unfortunately, these methods do not solve the problem of the waste aluminum oxide carriers because an unacceptable amount of the metals always remain in the carrier. The alternative treatment to avoid the problem of solid waste disposal is total leaching of the metals from the spent catalysts with sulfuric acid. According to this process, the crushed sample powder, with a composition (wt.%) of 12.26 MoO<sub>3</sub>, 4.04 V<sub>2</sub>O<sub>5</sub>, 3.52 CoO, 0.75 NiO and 64.17 Al<sub>2</sub>O<sub>3</sub> obtained after burning the spent catalysts to remove sulfur, hydrocarbons and carbon deposited on them, was roasted for 2 hr at 700°C and then it was suspended in 62.7% sulfuric acid solution and heated at 120 - 200°C for 3 hr for vaporization to dryness. Subsequently, it was dissolved in water and heated at 100°C for 1 hr. The final solution was filtered to eliminate a small amount of solid silica and the filtrate was further diluted with water. A typical solution yielded consisted of (ppm) 2600 Mo, 810 V, 1000 Co, 210 Ni, 40 Fe, 12410 Al and pH 1.2, from which metal values had to be selectively separated and recovered leaving aluminum free from metal contamination in the solution. The object of this work is to develop a basic extraction process route and to provide the equilibrium data necessary for separating and recovering the metal values from the total dissolution liquor.

A literature survey revealed only a little information with respect to the separation and recovery of rare metals from HDS catalysts by solvent extraction. From the solution yielded from alkaline leaching of spent alumina-based catalysts, molybdenum and vanadium were isolated and recovered by quantitatively extracting molybdenum at pH < 1 with 0.1M Alamine 336 or by selectively extracting vanadium at 8 < pH < 9 with 0.1M Aliquat 336 after a small amount of aluminum was eliminated at pH 7-8 with 0.3% LIX 26 (Olazabal *et al.*, 1991; 1992). Concerned with cobalt and nickel, they were reported to be recovered from the acidic sulfate solution with CYANEX 272 after the removal of a small of aluminum with the same extractant (Orive *et al.*, 1992). It was also reported that vanadium and molybdenum were recovered from the ammoniacal liquor of spent HDS catalysts at pH 7.3 and pH 3.6, respectively using dialkylmono-thiophosphoric acid after nickel was extracted from the solution at pH 9.1 with the same extractant (Tsuboi *et al.*, 1992). However, no similar work to the present study has been found in literature.

## EXPERIMENTAL

### Chemical Reagents and Preparation of Solutions

Extractants used in this work were purchased or kindly donated from the following manufacturers, CYANEX 272, containing bis(2,4,4-tri-methylpentyl)phosphinic acid as the active components, from Cyanamid Canada Inc.; PIA-8, PC-88A, D<sub>2</sub>EHPA, TR-83, and OPEHPA, containing active component bis(2-ethylhexyl)phosphinic acid, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, bis(2-ethylhexyl)phosphoric acid and di[2-(1,3',3'-tri-methylbutyl)5,7,7-tri-methyloctyl]phosphoric acid, 4-(1,1,3,3,-tetramethylbutyl)phenyl-2-ethyl-hexyl phosphoric acid, respectively, from Daihachi Chemical Co. Ltd. and LIX 63, the active constituent, 5,8-diethyl-7-hydroxy-6-dodecanone oxime, from Henkel Corp.. The pK<sub>a</sub> values of these acidic organophosphorus reagents were determined at 298K by potentiometric titration (Preston, 1983), and shown in Table 1. All of these reagents were utilized as received without further purification after diluting in EXXSOL D80, an aliphatic commercial diluent. The concentration of the extractant in solvent is expressed by percentage of volume(v/v, %). Cobalt, nickel, aluminum, ferric and vanadyl sulfates as well as sodium molybdate were of analytical grade. The feed solutions of known composition were made up and pH was adjusted to the desired values by adding sulfuric acid or ammonia. The actual sulfate liquor was obtained according to the method described in Introduction. The synthetic aqueous solution containing the similar composition to the actual liquor was prepared as necessary.

### Experimental Procedure and Analysis

Solvent extraction tests were carried out batchwise by equilibrating equal volumes of aqueous and organic phases in flasks immersed in a thermostated air bath maintained at 313K. The metal contents in feed and aqueous solutions were determined by atomic absorption spectrophotometry for the individual element system except for molybdenum and vanadium or by ICP-AES for the multi-element system as well as those of molybdenum and vanadium in the single element system. The contents of metals in the organic phases were calculated based on mass balance.

TABLE 1  
The values of pKa of acidic extractants used in the present work

Extractant	CYANEX 272	PIA-8	PC-88A	TR-83	D2EHPA	OPEHPA
pKa	5.22	5.20	4.21	4.02	3.01	2.58

## RESULTS AND DISCUSSION

### Recovery of Molybdenum and Vanadium

The extraction of the metals with the organophosphorus acids are shown as a plot of % extraction of metals against equilibrium pH in Fig. 1. It can be clearly seen that nearly complete extraction of molybdenum occurs even at low pH with all of the extractants used. In particular, it can be highly selectively extracted away from other metals at ca. pH 0 with PIA-8 and CYANEX 272. Vanadium is also favored over aluminum with the two extractants. Thus it is concluded that CYANEX 272 and PIA-8 are likely to be the extractants suitable for the selective separation and recovery of molybdenum and vanadium from aluminum, cobalt and nickel from sulfuric acid media at low pH. A confirmatory test was conducted from the typical sulfate liquor of spent catalysts outlined earlier with 40% PIA-8 in EXXSOL D80. The results are shown in Table 2. As expected, aluminum is poorly transferred into organic solvent and cobalt and nickel are completely left in the raffinate. Similar results to PIA-8 system were also obtained for CYANEX 272 system. The increase of molybdenum extraction with decreasing pH is attributed to the formation of  $\text{MoO}_2^{2+}$  in the aqueous solution at low pH according to the reaction (Esnault *et al.*, 1974):  $\text{MoO}_4^{2-} + 4\text{H}^+ = \text{MoO}_2^{2+} + 2\text{H}_2\text{O}$ , which is a species extractable by the acidic extractants cited here in terms of the cation exchange mechanisms expressed as follows (Cao and Nakashio, 1989):  $\text{MoO}_2^{2+}(\text{aq}) + 2(\text{H}_2\text{R}_2)_{(\text{org})} = \text{MoO}_2\text{R}_2 \cdot 2\text{HR}_{(\text{org})} + 2\text{H}^+(\text{aq})$ . The molybdenum in the loaded solvent can be easily stripped and recovered as ammonium molybdate using 6.0%  $\text{NH}_4\text{OH}$  solution as a strip agent after scrubbing the coextracted elements such as vanadium, aluminum and iron with 2.15M sulfuric acid solution.

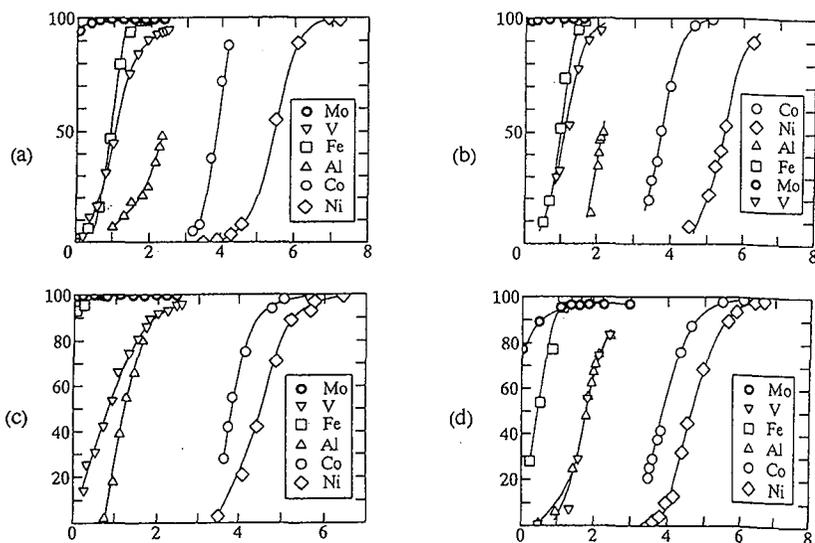


Figure 1 Percentage of extraction of metals from sulfate solutions as a function of equilibrium pH with 20% organophosphorus acids dissolved in EXXSOL D80 ((a) - CYANEX272; (b) - PIA-8; (c) - PC-88A; (d) - TR-83. X-axis represents equilibrium pH and Y-axis is percentage of extraction.).

**TABLE 2**  
Extraction of Mo and V from sulfate liquor with 40% PIA-8\*

pHeq	Extracted, %					
	Mo	V	Co	Ni	Al	Fe
1.44	65.5	92.0	0.2	0.4	2.2	100
1.36	82.4	91.1	0.0	0.0	0.9	100
1.20	91.1	80.5	0.0	0.0	0.7	97.7
1.00	96.1	71.7	-	-	0.2	94.9

\*The composition of feed (ppm): 2741 Mo, 859 V, 1066 Co, 226 Ni, 12990 Al, 38 Fe.

**TABLE 3**  
Recovery of vanadium from the sulfate scrub solution with 40% CYANEX 272\*

Extraction	
pHeq	1.52
Extracted, %	Mo 100 V 92.8 Fe 100**
Stripping	
Strip agent	6.0% NH <sub>4</sub> OH
Striped, %	V 96.2 Mo 100 Fe 0.0

\*Feed (ppm): 2 Mo, 430 V, 29 Fe, 32 Al, pH 1.56.

\*\*Al in the organic phase was not detected.

The vanadium in the sulfate scrub solution obtained above was further recovered by again extracting at pH 1.5 with 40% CYANEX 272 and by stripping with 6.0% NH<sub>4</sub>OH solution. The experimental results are presented in Table 3.

### Recovery of Cobalt and Nickel

(1) **Synergistic extraction of individual metals** Extraction of nickel, cobalt and aluminum was separately examined at various pH with organophosphorus acids(HR) such as CYANEX 272, PIA-8, PC-88A, TR-83, D<sub>2</sub>EHPA and OPEHPA alone and in admixture with LIX 63. Typical experimental results are shown in Fig. 2 (See Fig. 1 for the extraction of cobalt, nickel and aluminum with CYANEX 272, PIA-8, PC-88A, and TR-83 alone.). It can be clearly seen that the values of p*H*<sub>0.5</sub> (defined as the pH at which 50% extraction occurs.) for cobalt and nickel are markedly shifted to lower pH by adding LIX 63 to these organophosphorus acids, demonstrating the remarkable synergistic effect for cobalt and nickel in the mixed systems. Conversely, the extraction of aluminum is significantly depressed by adding LIX 63. Such results suggest that all of the synergistic systems exhibit good selectivity for cobalt and nickel over aluminum, making it possible to extract cobalt and nickel away from aluminum using these synergistic mixtures from sulfate solutions at low pH.

If a synergistic coefficient (SC) is defined according to Castresana (1988) as:  $SC \propto n \Delta pH_{0.5}$  (where n is the oxidation state of the metal and  $\Delta pH_{0.5}$  is the difference in p*H*<sub>0.5</sub> for the LIX 63 systems with and without the organophosphorus acids, i.e.,  $\Delta pH_{0.5} = pH_{0.5}^{LIX\ 63} - pH_{0.5}^{LIX\ 63 + HR}$ ), the relative values of the synergistic coefficients for cobalt and nickel in the systems studied can be calculated as shown in Table 4. It can be seen that the degree of the synergism decreases in the order: OPEHPA > D<sub>2</sub>EHPA > TR-83 > PC-88A > PIA-8 ~ CYANEX 272. This is consistent with the order of p*K*<sub>a</sub> of these extractants as shown in Table 1, i.e., the lower the p*K*<sub>a</sub>, the greater the synergism.

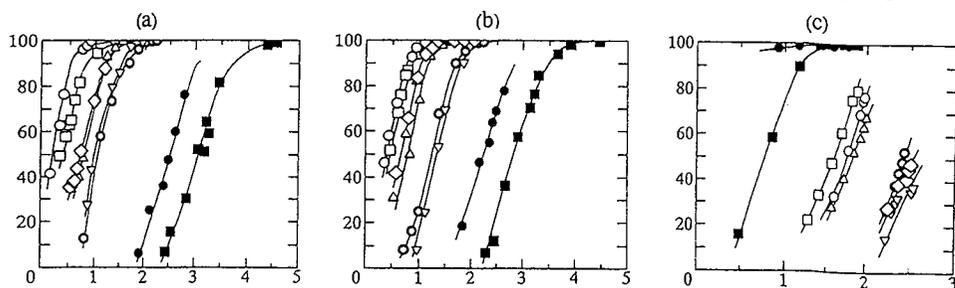


Figure 2 Extraction of nickel(a), cobalt(b) and aluminum(c) from sulfate solutions with mixtures of 20% LIX 63 and 7% various organophosphorus acids ((●) LIX 63+CYANEX 272; (▽) LIX 63+PIA-8; (Δ) LIX 63+PC-88A; (◇) LIX 63+TR-83; (□) LIX 63+D<sub>2</sub>EHPA; (○) LIX 63+OPEHPA; (■) 20% D<sub>2</sub>EHPA alone; (●) 20% OPEHPA alone. X-axis represents equilibrium pH and Y-axis is percentage of extraction of metals.)

**TABLE 4**  
pH<sub>0.5</sub> values and synergistic coefficients (SC) for extraction of cobalt and nickel by the mixtures of 20% LIX 63 and 7% organophosphorus acids in EXXSOL D80 at 40°C\*

Synergistic system	pH <sub>0.5</sub>		SC	
	Co <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>
CYANEX 272 - LIX 63	1.23	1.03	5.34	4.78
PIA-8 - LIX 63	1.31	1.00	5.18	4.87
PC-88A - LIX 63	0.69	0.80	6.42	5.24
TR-83 - LIX 63	0.65	0.72	6.50	5.40
D2EHPA - LIX 63	0.44	0.35	6.92	6.14
OPEHPA - LIX 63	0.37	0.24	7.06	6.36

\*The values of pH<sub>0.5</sub> with 20% LIX 63 alone were 3.90 for Co and 3.42 for Ni.

**TABLE 5**  
Extraction of metals with the mixtures of 10% HR and 30% LIX 63 in EXXSOL D80 from the multi-component sulfate solutions

No*	pH <sub>feed</sub>	Extracted, %		
		Co	Ni	Al
1	2.38	92.8	62.9	0.85
2	2.40	96.7	73.5	1.15
3	1.78	94.9	79.6	3.40
4	1.48	99.1	100	0.25
5	1.38	98.0	94.1	2.66
6	1.09	98.3	93.5	1.68

\*1 - CYANEX 272 - LIX 63, 2 - PIA-8 - LIX 63,  
3 - PC-88A - LIX 63, 4 - TR-83 - LIX 63,  
5 - D2EHPA - LIX 63, 6 - OPEHPA - LIX 63.

**TABLE 6**  
Scrubbing of aluminum from the loaded solvents of 10% HR and 30% LIX 63 in EXXSOL D80 by sulfuric acid solutions

No*	Loaded solvent, g/l			H <sub>2</sub> SO <sub>4</sub> (M)	Scrubbed, %		
	[Co]	[Ni]	[Al]		Co	Ni	Al
1	1.04	0.14	0.11	0.038	11.8	0.0	100
2	0.93	0.14	0.13	0.035	5.8	0.0	97.5
3	1.06	0.18	0.45	0.125	10.8	0.0	100
4	1.10	0.20	0.35	0.375	14.3	0.0	99.4
5	1.10	0.21	0.22	0.503	10.9	0.0	97.9

\*1 - CYANEX 272 - LIX 63, 2 - PIA-8 - LIX 63,  
3 - PC-88A - LIX 63, 4 - D2EHPA - LIX 63,  
5 - OPEHPA - LIX 63.

**TABLE 7**  
Stripping of cobalt from the scrubbed solvents of 10% HR and 30% LIX 63\*

No**	Strip agent (H <sub>2</sub> SO <sub>4</sub> , M)	Stripped, %	
		Co	Ni
1	0.25	89.5	0.0
2	0.25	82.9	0.0
3	0.74	86.2	0.0
4	1.40	82.1	1.7
5	2.53	84.7	1.0
6	3.60	93.4	4.7

\*The contents of Co and Ni in the scrubbed solvents were approx. (g/l): [Co] = 0.8-1.0, [Ni] = 0.14-0.2.

\*\*The compositions of the mixed extractants were the same as described under the Table 5.

**TABLE 8**  
Stripping of nickel from the scrubbed solvents of 10% HR and 30% LIX 63\*

No**	Strip agent (H <sub>2</sub> SO <sub>4</sub> , M)	Stripped, %
		Ni
1	1.03	67.3
2	1.04	68.7
3	3.54	61.6
4	4.45	70.4
5	4.59	71.1
6	4.74	74.1

\*The content of Ni in the organic solvents was approx. 0.14-0.2 g/l.

\*\*The compositions of the mixed extractants were the same as described under the Table 5.

(2) **Recovery of cobalt and nickel from the solution containing aluminum** Tests on recovery of cobalt and nickel were conducted from sulfate solutions containing approx. (g/l) 13.1 Al, 1.1 Co and 0.2 Ni. Table 5 shows that cobalt and nickel are extracted selectively over aluminum for all synergistic systems under the given conditions. Table 6 illustrates that the complete removal of

a small amount of aluminum coextracted with cobalt and nickel into the organic phase can be accomplished by contacting the loaded solvent with dilute sulfuric acid. Table 7 indicates that cobalt in the scrubbed solvent can be effectively stripped by moderate concentrations of sulfuric acid solutions. The stripping of nickel appears to be comparatively difficult and high concentrations of sulfuric acid have to be used to enhance the strip ratio of nickel, except for the mixtures of LIX 63 and CYANEX 272 or PIA-8 for which only relatively low acidities were required for stripping nickel (Table 8).

**(3) Degradation of LIX 63** Investigations indicated that the extractability for cobalt and nickel decreased to a greater or lesser extent with the mixtures comprising of LIX 63 and the relatively strongly acidic extractants like D<sub>2</sub>EHPA or OPEHPA after the mixtures had been aged for six months, whereas no obvious change in distribution ratios of cobalt and nickel was observed with those mixtures consisting of LIX 63 and the relatively weakly acidic extractants such as CYANEX 272 and PC-88A, in particular the mixture of CYANEX 272/LIX 63. Additional inspection of the color of the mixtures also revealed that the samples containing D<sub>2</sub>EHPA or OPEHPA had gradually changed from light to heavy yellow with increasing aging time while those containing PC-88A and CYANEX 272 did not essentially change in color. Such results reflect that LIX 63 is degraded to varying degrees by the strongly acidic extractants while on the other hand, the degradation caused by the weakly acidic extractants seems to be negligible. The degradation of LIX 63 is considered to be via nitrogen atom in LIX 63 which forms an ammonium ion (NH<sub>4</sub><sup>+</sup>) and the C=N group is transformed into a C=O group as observed in the HCl-D<sub>2</sub>EHPA-EHO(2-ethylhexanal oxime) system reported by Groves and Redden (1990).

## CONCLUSIONS

An effort has been made to develop a recovery process for molybdenum, vanadium, cobalt and nickel from the acidic sulfate liquor of spent HDS catalysts by solvent extraction. The extraction process presented is composed of the recovery of molybdenum and vanadium using organophosphinic acid like CYANEX 272 or PIA-8, and that of cobalt and nickel using a mixture consisting of LIX 63 in combination with CYANEX 272 or PIA-8. The attractive features of the process mainly lie in:

1. CYANEX 272 or PIA-8 exhibits an excellent selectivity for molybdenum and vanadium over aluminum, cobalt and nickel at relatively low pH and provide high recovery yields for the two metals.
2. Although the mixtures of LIX 63 and CYANEX 272 or PIA-8 cause the weakest synergism for cobalt and nickel among all the mixtures studied in this work, both of the systems exhibit good selectivity for cobalt and nickel over aluminum at appropriately low pH. The acidities necessary for stripping cobalt and nickel from these loaded solvents are relatively mild and in addition, no marked degradation of LIX 63 is observed. Consequently, from the viewpoint of commercial application, the two mixtures are considered to be the most suitable for separating and recovering cobalt and nickel from the sulfate solutions in the presence of an appreciable amount of aluminum at low pH.
3. Aluminum can be readily recovered as sulfate salt by direct crystallization from the raffinate after recovering molybdenum, vanadium, cobalt and nickel in advance.

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## PHASE DISENGAGEMENT PROBLEMS IN SOLVENT EXTRACTION

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### ABSTRACT

The phase disengagement properties of several commonly used copper and uranium extractants in the presence of flocculating agents and materials known to cause phase disengagement problems were investigated. For all the extractants tested, the effect of flocculants was much more marked where the continuous phase was the aqueous medium. For the copper extractants, dissolved silica was found to be very detrimental to phase separation in the presence of flocculants, however, in many cases some improvement was achieved where solid silica was also present. The presence of silica was disastrous for the uranium extractants tested. Phase disengagement times were long and crud formation evident in all cases.

### INTRODUCTION

Poor phase disengagement during solvent extraction is a problem frequently encountered in the mining industry where leach solutions often contain particulate matter and other undesirable material. In the extreme case, these stable emulsions can result in the formation and/or accumulation of solid material, known as crud, at the interface.

Ritcey and Ashbrook (1979) cite the most commonly encountered causes of crud formation as the presence in the leach solution of suspended solids and colloids such as silica. However, they also point out that crud formation can result from the presence of soluble solvent extraction degradation products or indeed sparingly soluble compounds such as gypsum, provided sufficient shear is present in the mixing process. Sinegribova et al (1993) also describe problems in phase separation in the presence of dissolved silica. Guedon et al (1994) note in their investigation of zirconium precipitation with the degradation products of TBP that precipitates are mainly not effective in stabilising emulsions and cannot be the simple cause of crud.

McDonald et al (1981) note the problems associated with soluble silica and also report that significant increases in phase disengagement time can occur in solvent extraction procedures where flocculating agents are present and particularly where the aqueous phase is the continuous phase. The use of flocculating agents prior to solvent extraction may thus be counter productive in regard to the settling problems they may cause and Fisher and Notebaart (1983) advocate the testing of all such reagents for compatibility with the solvent extraction process.

In this work, the influence of suspect materials in the presence of flocculants on the phase disengagement properties of several solvent extractant/synthetic leach liquors was investigated.

### EXPERIMENTAL

The composition of the synthetic leach liquors used is shown in Table 1. Uranium and copper were present as their sulphates.

**TABLE 1**  
Synthetic Leach Liquors

Solution	pH	U, g/l	Cu, g/l	CaSO <sub>4</sub> , ppm	Silica, ppm	
					Soluble	Insol
A1	1.5	1.0	3.0	0	0	0
A2	1.5	1.0	3.0	860	320	1700
A3	1.5	1.0	3.0	860	0	0
A4	1.5	1.0	3.0	860	320	0

The polymeric flocculants used were Afloc 625 (anionic), Afloc 620 (nonionic) and Afloc 7145 (cationic). They were supplied by Nalco Australia. Test solutions containing flocculants were freshly prepared on the day of the test runs.

The solvent extractants investigated are given in Table 2. All were diluted with Shellsol 2046.

**TABLE 2**  
Solvent Extraction Reagents

Reagent	Application	Concentration, % v/v
LIX 622	Cu	10
LIX 84	Cu	10
LIX 860	Cu	10
Acorga P5100	Cu	10
Acorga M5640	Cu	10
DEHPA	U	10
DEHPA/isodecanol	U	10/5
Alamine 336	U	5
Alamine 336/isodecanol	U	5/2.5

The apparatus consisted of a tank of section 65mm x 65mm and 75mm deep. A perspex lid, slotted to allow passage of the stirrer motor shaft, fitted over the tank. Agitation of the contents was via an impeller and a conventional stirrer motor. The impeller was made of perspex and was 6mm thick and 30mm diameter. On the underside were six grooves, each of section 3mm x 3mm, radiating from the centre. The impeller was affixed to a 6mm diameter stainless steel drive shaft. Test speed used was 2000 rpm.

The organic phase (140 ml) and the aqueous phase (86 ml) to be tested were placed in the tank. The impeller was positioned in the middle of the organic phase when organic continuous was required and at the base of the aqueous phase when aqueous continuous was required. The mixture was stirred for two minutes at the cessation of which time the depth of the continuous phase was measured. This depth was then monitored at 10 second intervals till the phases coalesced or till eight minutes had elapsed, whichever was sooner. The % separation was taken as

$$\frac{\text{Depth of continuous phase at time } t \text{ after mixing terminated}}{\text{Depth of continuous phase prior to mixing}}$$

## RESULTS AND DISCUSSION

### Flocculants

The results of a brief study into the effects of flocculant on the phase disengagement times for LIX 622 against Solution A2 are summarised in Table 3.

**TABLE 3**  
Effect of Flocculants on Phase Disengagement  
(All flocculants at a concentration of 100 ppm each)

Flocculant	Time (s) for 50% Sepn		Time (s) for 100% Sepn	
	Aq cont	Org cont	Aq cont	Org cont
Nil	22	6	70	50
620	35	3	>480	30
625	28	3	360	20
7145	22	3	420	30
620+625	22	23	>480	100
620+7145	28	29	>480	140
625+7145	20	23	>480	90
620+625+7145	31	17	>480	150

From Table 3 it can be seen that small amounts of the three flocculants separately actually enhance the separation rate when the organic continuous configuration is used. However, the rate decreases somewhat when two or more flocculants are present.

The effect of flocculants in aqueous continuous mode was very much more marked. This confirms the findings of McDonald et al (1981) who tentatively attributed the effect to the fact that the flocculant is water soluble and so causes increased viscosity of the aqueous film. This increases viscosity will retard coalescence since the film is much more difficult to rupture.

As a result of these findings, the three flocculants were added to all synthetic leach liquors except solution A1 for further runs. The concentration of each flocculant was 100 ppm.

Further results are summarised in Tables 4 and 5.

**TABLE 4**  
Times for 50% Phase Disengagement (s)

Solution Continuous Phase	A1		A2+flocclulants		A3+flocclulants		A4+flocclulants	
	Aq	Org	Aq	Org	Aq	Org	Aq	Org
Extractant								
LIX 622	15	3	31	17	31	17	28	21
LIX 84	25	8	30	14	23	18	35	14
LIX 860	17	3	30	42	46	42	49	48
Acorga P5100	12	32	37	40	37	38	37	38
Acorga M5640	16	3	30	15	28	8	32	9
DEHPA	33	3	78	12	22	4	85	12
DEHPA/Iso	34	3	48	>480	23	14	64	43
Alamine 336	30	>480	150	70	45	>480	190	88
Alamine 336/Iso	33	27	110	58	38	40	120	69

**TABLE 5**  
Times for 100% Phase Disengagement(s)

Solution Continuous Phase	A1		A2+flocclulants		A3+flocclulants		A4+flocclulants	
	Aq	Org	Aq	Org	Aq	Org	Aq	Org
Extractant								
LIX 622	50	30	>480	150	>480	90	>480	130
LIX 84	70	70	>480	90	>480	120	>480	160
LIX 860	60	30	>480	120	>480	120	>480	160
Acorga P5100	40	100	480	240	360	180	>480	300
Acorga M5640	60	50	>480	70	480	80	>480	120
DEHPA	100	60	>480	>480	>480	40	>480	>480
DEHPA/Iso	90	40	>480	>480	>480	90	>480	>480
Alamine 336	60	>480	>480	>480	300	>480	>480	>480
Alamine 336/Iso	80	100	>480	>480	300	180	>480	>480

### Phase Continuity

As can be seen from Tables 4 and 5, in almost all cases, except for the Alamine combinations, organic continuous gives shorter settling times. For Alamine 336, with and without isodecanol, the aqueous continuous mode is superior unless silica is present. In this case, the organic continuous is better, but complete phase disengagement is still not achieved within the eight minute test time.

### Isodecanol

The presence of isodecanol does little for the phase disengagement characteristics of DEHPA. In fact, for 50% phase disengagement, organic continuous, the performance is worse than when it is absent.

The addition of isodecanol to Alamine 336 results in some improvement at the 50% level for all organic continuous and most of the aqueous continuous tests carried out. However, as noted above, Alamine 336 with and without isodecanol does not completely disengage within eight minutes when silica is present regardless of which phase is the continuous one.

### Silica

While Tables 4 and 5 indicate the superiority of Acorga M5640 over the other copper extractants as regards phase separation properties in the presence of silica, Figure 1 shows this more clearly. However, the other copper extractants all achieved 100% phase disengagement provided they were run organic continuous.

Formation of stable emulsions was not observed with any of the copper extractants run organic continuous. As Tables 4 and 5 show, the presence of soluble silica did in all cases cause a marked increase in the phase disengagement time, however, the further addition of solid silica did in all cases except for LIX 622 actually shorten the time for phase disengagement.

This could perhaps be ascribed to the fact that flocculants adsorb preferentially on solids which effectively lowers their concentration in the aqueous phase when solids are present. This may be sufficient to decrease their interaction with soluble silica and calcium sulphate and so give better phase disengagement properties.

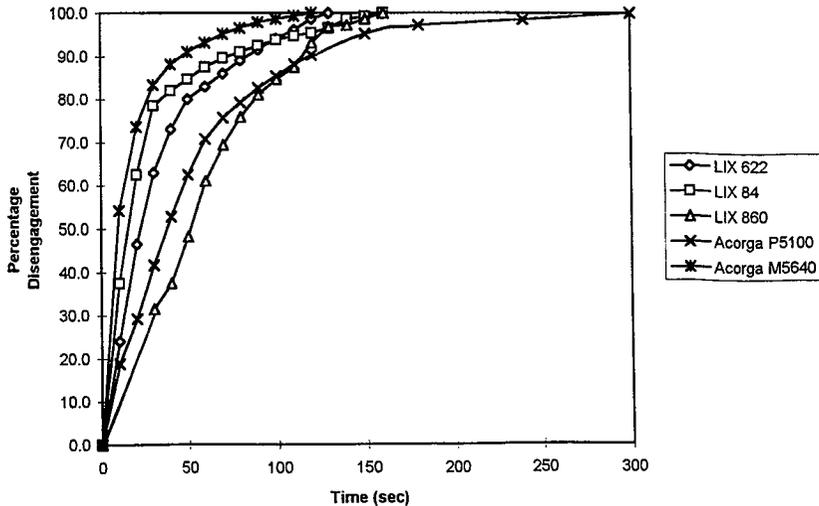


Figure 1: Phase Disengagement Profiles for Copper Extractants (Solution A4, Organic Continuous)

The phase disengagement curves for Acorga M5640 in the presence of silica are shown in Figure 2.

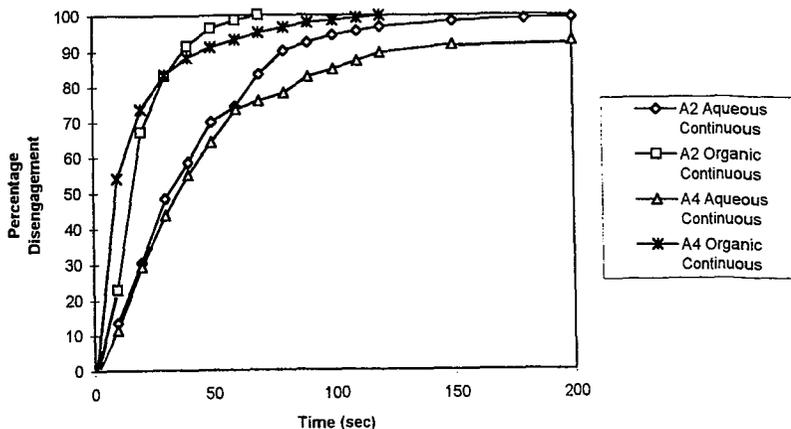


Figure 2: Phase Disengagement Profiles for Acorga M5640

From Table 5 it can be seen that none of the uranium extractants in the presence of silica achieved 100% phase disengagement with either organic or aqueous continuous. Worse, in all cases a solid white crud formed at the interface. As Table 4 shows, generally the presence of solid silica gave some improvement at the 50% level, although this was not the case for the DEHPA/isodecanol combination.

### Calcium Sulphate

With the exception of DEHPA run organic continuous, the simultaneous presence of dissolved gypsum and flocculants caused increased phase separation times. However, no crud formation was evident in any of the combinations tested.

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## RESEARCH CONCERNING THE DEVELOPMENT OF COPPER SOLVENT EXTRACTION TECHNOLOGIES IN ROMANIA

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### ABSTRACT

The modernization of the Romanian mining-metallurgical industry provides, as a priority, the implementation of hydrometallurgical technologies implying solvent extraction for copper recovery from raw materials, secondary materials, scraps and waste waters. The paper presents the results of solvent extraction research works for copper recovery from low grade ores, complex concentrates, flue dusts and spent electrolyte.

Discussions are presented regarding the intentions to promote the research results to industrial scale.

### INTRODUCTION

Copper mining and metallurgical industry are very old and have an extensive tradition in Romania.

It is established that the ore deposits having a copper content higher than 0.25% Cu are sufficient for covering the country requirements for a period of 100 years.

Copper ore deposits in Romania have certain special characteristics: most of them are complex ores having an average metal content of: 0.3-1.3% Cu; 1-3% Zn; 0.5-1.5% Pb; other are constituted of relatively pure copper ores: 0.3-1.4% Cu; 0.05-0.1% Zn; 0.01-0.06% Pb. The largest part of ore deposits are fine concrescent so, they are difficult to concentrate by classical flotation procedures. [2]

This is the reason why, during last years, there have been performed researches regarding promotion of new, hydrometallurgical technologies for copper recovery out of low grade ores, low grade complex concentrates, as well as mine waters and they have developed in an alert course with notable results.

The balance of copper reserves in Romania has not mentioned at their rightful place the sub-products of metallurgical and copper processing industry such as: fly ashes, skulls, impure spent electrolyte, gases scrubbing waters. These sub-products are resulting from: copper plants using Outokumpu process, ISP process for Zn and Pb processing (Cu-Pb scories), smelters (slags and ashes), processing industry (galvanizing slurries, leaching solutions).

This work presents the results of research aiming to copper recovery of products, sub-products, scraps and effluents resulted from mining and metallurgical industry that were mentioned above.

Table 1 shoes the main raw materials that were the object of researches done in IMNR for copper recovery using hydrometallurgical processes, that imply solvent extraction.

**TABLE 1**

Main raw materials, sub-products, scraps, waste waters processed by hydrometallurgical technologies that imply solvent extraction for copper recovery

Denomination	Average composition	Technology	Composition of the solution processed using SX	Extractant
<b>MINING INDUSTRY</b>				
Low grade ores, tailings	Cu: 0.05-0.3 % Fe: 3 - 4 % Zn: 0.01-0.1 % Pb: 0.01	dump bacterial leaching-SX-EW	Cu: 0.85-1.2 g/l Fe: 5 - 6 g/l pH: 1.8-2	Acorga M5640
Complex low grade concentrates	Cu: 8.5-10.5 % Zn: 27-29 % Pb: 9-13 %	roasting -H <sub>2</sub> SO <sub>4</sub> leaching-SX-EW	Cu: 9-14 g/l Fe: 20-40 % Zn: 30-80 g/l pH: 1.9-2	Acorga M5615 M5640
Complex concentrates	Cu: 10-12 % Zn: 29-31 % Pb: 10-15 %	pressure leaching-SX-EW	Cu: 10-14 g/l Zn: 35-45 g/l Fe: 2-4 g/l pH: 1.8-2	Acorga M5640 M5615
Mine waters	Cu: 0.6-0.8 g/l pH: 1.4	SX-CuSO <sub>4</sub> crystallization	Cu: 0.6-0.8 g/l pH: 1.4	Acorga M5640
Laterite ores	Ni: 1.8-2 % Cu: 1-1.2 % Co: 0.2	ammonia leaching SX-EW	Ni: 10 g/l Cu: 59 g/l Co: 0.8 g/l	LIX 64N
Mo-Cu concentrates	Mo: 10 % Cu: 12 %	acid leaching-SX - PP	Mo: 25 g/l Cu: 20 g/l Bi: 20 g/l	D2EHPA [1]
<b>PROCESSING INDUSTRY</b>				
Slags and smelting ashes	Cu: 32-50 % Zn: 17-21 % Pb: 1-3 % Sn: 1 % Fe: 4 %	ammonia leaching -SX-EW- (crystallization)	Cu: 50 g/l Zn: 10-15 g/l	LIX 64N Acorga M5640 LIX 54
Leaching solutions, galvanic slams	Fe: 10 % Cr: 10 % Cu: 1 - 2 % Ni: 0.5 %	ammonia leaching-SX-EW	Cu: 2.8 g/l Ni: 1.0 g/l Zn: 3.5 g/l	LIX 54 LIX 64N
<b>Cu, Pb, Zn METALLURGICAL INDUSTRY</b>				
Fly ashes, skulls	Cu: 3-12 % Zn: 6-12 % Pb: 7-16 % As: 2-3 %	acid leaching SX - EW	Cu: 12 g/l Fe: 10 g/l As: 3 g/l Cd: 0.3 g/l Zn: 3 g/l	Acorga M5640
Impure spent electrolyte	Cu: 35 g/l	SX - EW		
Gas scrubbing effluents	Cu: 1.3 g/l	SX - EW		
Pyrite cinders	Cu: 0.7 % Zn: 0.5 % Fe: 50 %	Kowa Seiko - SX - EW	Cu: 10 g/l Fe: 2 g/l	Acorga M5640 CLX 50
Cu-Pb scories	Zn: 1-5 % Cu: 20-40 % In: 10 <sup>-2</sup> %	acid leaching - SX - EW	Cu: 1.5 g/l Zn: 2 g/l pH: 2	Acorga M5640 D2EHPA

**DESCRIPTION OF THE BASIC FLOWSHEETS**  
**EXPERIMENTAL RESULTS**  
**Cu, Zn, Pb extraction of complex, low grade concentrates**

Complex concentrates obtained by collective flotation have the following average composition: 8.5-10.5% Cu; 27-29% Zn; 9-13% Pb; 12-14% Fe; 32-34% S and mineralogical composition as it follows (table 2):

**TABLE 2**  
 Mineralogical composition of complex concentrates

Ore	Formulae	%
Blenda	ZnS	42-43
Galena	PbS	15-16
Chalcopyrite	CuFeS <sub>2</sub>	24-25
Pyrite	FeS <sub>2</sub>	13-14
Quartz	SiO <sub>2</sub>	3-4

The experiments referring to the processing of these complex concentrates have used a technological flow sheet which consists of: leaching with water under high O<sub>2</sub> pressure, SX, EW.

The solutions that resulted from leaching with water under high oxygen pressure have the average composition: 9-14 g/l Cu; 35-45 g/l Zn; 0.01-0.02 g/l Pb; 2-4 g/l Fe and an adjusted pH of 1.9-2.

The experiments were carried out using ACORGA P5050, M5615, M5640 and LIX64N extractants. Taking into account the process kinetics, extractant resistance to hydrolysis, etc, the researches were developed at industrial scale, using ACORGA M5640 extractant. Figure 1 and figure 2 show the extraction, stripping isotherms and copper distribution in a continuous system having 3+2 contact stages (figure 3). Aqueous solution flow rate (9 g/l Cu) was 600 l/h. The organic phase has been constituted of a mixture: 30 % M5640 in kerosene. The stripping solution had the following composition: 30 g/l Cu; 180 g/l H<sub>2</sub>SO<sub>4</sub>. The continuous phase was the organic phase.

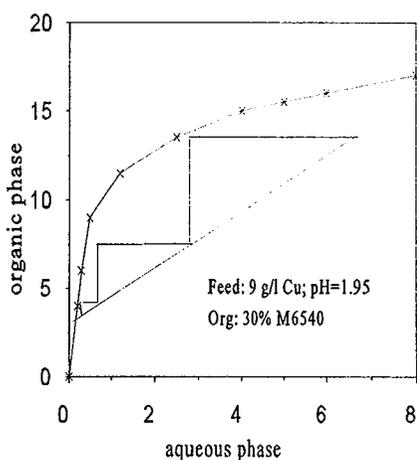


Figure 1 Extraction isotherm

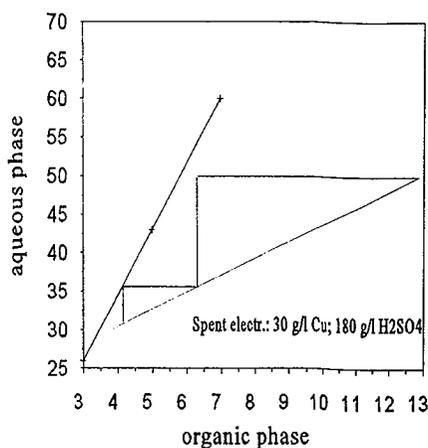


Figure 2 Stripping isotherm

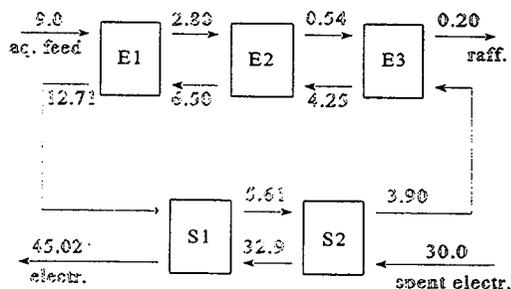


Figure 3 Copper distribution in the extraction circuit:  
9.0 g/l Cu, pH=1.95 vs 30vM5640

By analysing these results, it is noted that copper recovery efficiency are higher than 95 %. There were no emulsions in the system.

Another technological alternative for processing of complex concentrates, based on the concentrate roasting and leaching in sulphuric acid has lead to solutions being obtained. An organic solution 30% M5640 in ESCAID 100 was used. The pilot experimental plant had 3 + 2 contact stages. It is noticeable that copper extraction efficiency was of 96.48 %.

By the analysis of the organic phase (10.58 g/l Cu; 0.0018 g/l Fe) the selectivity of the extractant was determined and the value obtained was 5.878.

During this second technological alternative, technological difficulties were encountered when pH adjustment was made. Due to iron high concentration in solution precipitates formed and they were hard to re-dilute or to remove.

The research works are to be finalized in 1997 and an industrial plant will be accomplished in the next 3 - 4 years.

### Copper extraction of barings and low grade ores

The research performed in this field have aimed to process low grade ores from Rosia Poieni Mine. The ore deposit has an average content of 0.45 % Cu (maximum copper content is of 1.4 %) and 4 - 6 million tons of low grade ores produced every year. The average composition of low grade ores is: 0.24% Cu; 5.5% Fe; 6.2% S; 0.05% Zn; 0.07% MgO; 0.3% CaO; 61% SiO<sub>2</sub>; 16% Al<sub>2</sub>O<sub>3</sub>. There is a natural culture of Thiobacillus Ferrooxidans.

The experiments were carried out by processing a quantity of 70,000 t low grade ore in a dump consisting of:

- oxidated ores 12% : carbonates, malachite
- secondary sulphides 58% : covellite, chalcosine
- primary sulphides 30% : chalcopyrite, bornite.

The bacterial leaching in the dump has taken place for approximative 1.7 years when 65% of the copper existing in the ores has passed into solution. The composition of these solutions was: 0.9-1.2 g/l Cu; 4-6 g/l Fe; 0.1-0.2 g/l Zn; pH 1.6-2. The solvent extraction plant, consisting of 2 + 1 or 2 + 2 stages has enabled the processing of approximative 1000 l/hr of aqueous solution. The composition of the organic phase was: 4.0 % ACORGA M5640. The obtained results are shown in figure 4, 5 and 6.

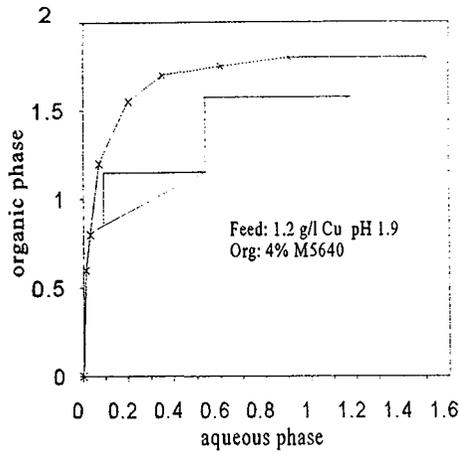


Figure 4 Extraction isotherm

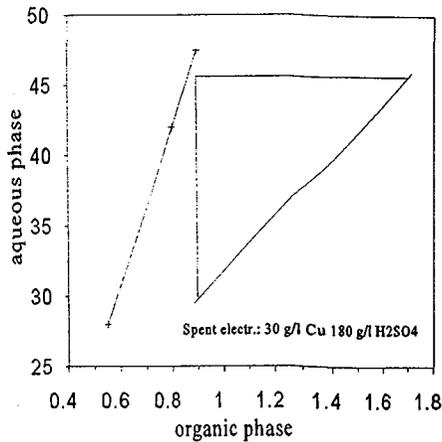


Figure 5 Stripping isotherm

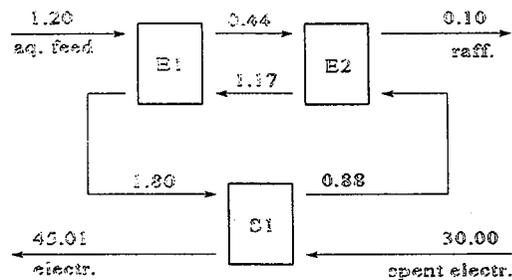


Figure 6 Copper distribution in the extraction circuit: 1.2 g/l Cu, pH 1.9 vs 4% M5640

An important chapter of the research has aimed to identify the controversial influence of the organic phase on the activity of bacterial culture. Somehow surprising, a slight beneficial effect of the organic phase on the bacterial culture was noticed and in no situation no inhibition of bacterial activity was noticed.

A bacterial leaching - solvent extraction plant having 4,000 - 5,000 t Cu/yr capacity is going to be built in 1996 - 1997.

### Copper recovery from sub-products of Outokumpu process

In Romania there are two plants using Outokumpu technology to process copper concentrates. A complex hydrometallurgical technology enables the recovery of Cu, Zn, Pb, Cd while the effluents resulting from the process are recirculated mostly to the H<sub>2</sub>SO<sub>4</sub> obtaining plant. Copper recovery using organic solvents was performed by processing the solution having the following composition: 12.5 g/l Cu; 10.7 g/l Fe; 3.2 g/l As; 0.3 g/l Cd; 3 g/l Zn.

Copper distribution on contact stages is shown in figure 7.

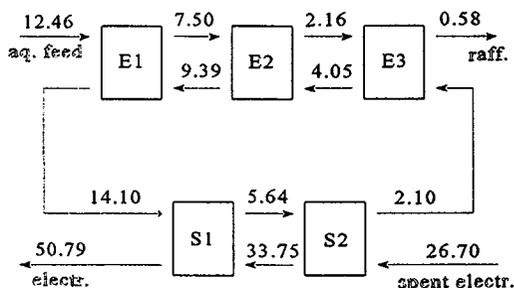


Figure 7 Copper distribution in the extraction circuit:  
12.46 g/l Cu, pH=1.9 vs 30vM5640

An industrial experimental plant having a capacity of approx. 6,000 t  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$  per year is scheduled to be put in operation in 1996 at PHOENIX SA plant in Baia Mare.

### CONCLUSIONS

Applications in Romania of hydrometallurgical technologies implying solvent extraction for copper recovery or primary and secondary resources represent a component part of the strategy for industrial development in the near future.

The significant results of the research works that were carried out will allow the development in the next 3 - 4 years of industrial plants for copper recovery from low grade ores and mine waters, sub-products and effluents from copper plants as well as machine construction plants. It is certain that applications of solvent extraction will constitute an assurance that the romanian copper industry will be modernized.

### ACKNOWLEDGEMENTS

The authors wish to express their thanks to ZENECA Company and mostly to Mr. Brian Townson as well as Dr. Raymond Dalton and Terry Conniffe for the very professional technical and technological assistance they provided as well as for their friendship.

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## SOLVENT EXTRACTION IN AUSTRALIA - A REVIEW

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### ABSTRACT

This paper reports on the development of solvent extraction in Australia. While most of the copper and uranium solvent extraction technologies were imported from the USA, new or modified processes were developed in Australia in the copper, arsenic, rare earth and nickel industries. These will be briefly described to show the increasing range and application of solvent extraction. There are currently seven copper mines operating nationwide which use solvent extraction in their process plants.

### INTRODUCTION

Solvent extraction (SX) was first introduced in Australia in 1960 at the El Sherena uranium mine, and rapidly established itself in the uranium industry. Due to government policy restrictions, at present, there are only two operating uranium mines (Ranger and Olympic Dam) using SX.

The copper industry has been slow to adopt SX. In 1979, Pasminco introduced the first copper SX plant, at the Imperial Smelting Furnace plant (NSW) to process copper dross. In 1984, the same company incorporated a SX/electrowinning (EW) plant at its lead smelter at Port Pirie, SA. By 1988, Western Mining Corporation had developed the huge Olympic Dam copper/uranium deposit, which includes a SX circuit for copper and uranium. In 1990, Mount Isa Ltd followed by Gunpowder Copper Ltd, started copper heap leach/SX-EW operations. Two more copper SX/EW operations: Girilambone Mine and Nifty Mine were commissioned in late 1993.

However the total copper metal produced by these plants (51,400t) represent only 10% of the national production. This is probably due to:

- 1) The lack of very large acid-soluble copper deposits in this country.
- 2) There are no sulfuric acid production facilities close to the acid-soluble copper deposits.
- 3) Electric power is not readily available from grid supply in many of the geographically favourable areas.

Nickel and arsenic are two other metals which are solvent extracted in Australia. Vanadium and cerium may be added to the list in mid 1996. Tantalum and niobium were solvent extracted at Greenbushes Mine (WA), before the plant shut down in 1991. Further details on the operations described in this paper have been reviewed by Lallene (1993).

## URANIUM

Uranium leach liquors in early plants were extracted with D2EHPA and later with secondary and tertiary amines which proved superior because they are kinetically faster and are more selective for U(VI) in the presence of Fe(III), Th(IV),  $PO_4^{3-}$ , and rare earth elements. Higher loadings are also obtained with tertiary amines in particular.

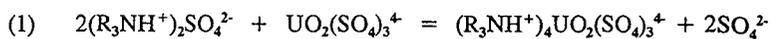
Ranger Uranium Mines, Northern Territory (Roberts, 1991)

Mining commenced at an annual rate of  $1.15 \times 10^6$  t of ore. The treatment plant is designed to produce 3000 tpa of  $U_3O_8$  in yellow cake. The ore is leached with sulfuric acid at controlled Eh under the condition shown in Table 1 and the pregnant leach solution (PLS), is fed to a SX circuit consisting of 4 counter-current SX/stripping stages.

Table 1: Australian Uranium Production from SX Plants

Mines	Location	Leaching		Conditions		Production	Extractants
		mV	pH	T°C	hr		
Ranger	Alligator Rivers	450	1.8	50	29	3000 $U_3O_8$	Alamine 336
Olympic Dam	Roxby Downs	440	<1	60	12	1900 $U_3O_8$	Alamine 336

The extraction of the Uranium (VI) from the PLS containing 1.0 g/L uranium is achieved by contacting the liquor for 50 sec. with Alamine 336 (3% v/v), diluted with Shellsol 2046. The extractant selectively extracts the uranium complex as follows:



The loaded solvent is stripped by addition of ammonia which increases the pH from 1.8 to 3.5. The ammonium sulfate strip solution is pumped directly into a precipitation tank, where further ammonia and air are added to raise pH to 6.9-7.2. Uranium precipitates as ammonium diuranate  $((NH_4)_2UO_2(SO_4)_2)$ , yellow cake.

The Uranium concentration in the raffinate has increased from 1ppm to 5ppm due to contamination and degradation of the extractant. Various modifications have been considered such as changing the wetting properties of the baffles material to enhance phase disengagement due to solvent degradation and the addition of an acidic regeneration stage of the organic to increase the stripping efficiency. (Ritcey, 1994)

Olympic Dam Operations, South Australia (Roberts, 1992)

The Olympic Dam Operations (ODO) comprises a concentrator, hydrometallurgical plant, copper smelter and copper refinery. The treatment plant is designed to treat about 360 t/h of ore and has a capacity to produce 1,900 tpa of  $U_3O_8$  as yellow cake. The principle ore minerals are chalcocite, chalcopyrite, bornite and pitchblende.

Once the sulfide copper has been floated, the non-sulfide particles, which contain most of the uranium bearing particles, are drawn off as "tailings". This tailing is leached (Table 1) and the PLS fed to the copper SX plant. The copper raffinate is then contacted in 3 stages with 4% Alamine 336 in Shellsol 2046. The loaded solvent is scrubbed (3 stages) by acidified water and the uranium is stripped into aqueous ammonium sulfate solution, held at pH 3-4 by the injection of gaseous ammonia. Stripped solvent is regenerated with a caustic carbonate solution before recycling to extraction.

Like Ranger, ammonia and air are added to the strip solution to raise pH to 6.6 - 7.0 and precipitate yellow cake over a period of 1.5 hours. In this operation, cruds form throughout the settlers due to dissolved silica from the leach. With time, poisoning of the solvent leads to lower loading efficiency thus a solvent regeneration step was required. It is believed that isodecanol slowly oxidises to carboxylic acids (Ritcey, 1994).

## COPPER

Most copper plants, in Australia (Table 2), use sulfuric acid as lixiviant for copper leaching. However Pasmaenco-BHAS oxygen leach a copper-lead matte with a mixed sulfuric acid chloride solution whilst Pasmaenco Metals Sulfide leach the copper dross with an oxygenated solution of ammonium carbonate.

The copper minerals leached from Nifty, Mt Isa, Gunpowder and Girilambone ores are mostly chalcocite and/or malachite. Bacterial leaching of the copper sulfide minerals using thiobacillus ferrooxidans produces a range of acidic copper solutions enriched with iron (II) and iron (III) to different levels depending on the ore. Thus different solvent extractant systems have been employed around Australia to extract copper from various types of leach liquors.

Table 2. Australian Copper Production from SX-EW Plants.

Plant	Location	Leaching	Production	Extractants
Girilambone	Nyngan NSW	Heap	14,000	LIX 984
Gunpowder	120 km NS Mt Isa	In place/ heap	7,300	Acorga M5640
Mt Isa Mines	Mt Isa QLD	Heap	3,650	LIX 984
Nifty	Near Telfer WA	Heap	16,500	Acorga M5640
Olympic Dam	Roxby Downs SA	Tailings	5,000	Acorga M5640
Pasmaenco-BHAS	Port Pirie SA	Cu/Pb Matte	3,650	Acorga M5640
Pasmaenco Metals	Cockle Creek NSW	Cu/Pb Dross	1,300	LIX 54

Pasmaenco - Cockle Creek (Tyson, 1993)

In 1979, Pasmaenco Metals-Sulfide Pty Limited, introduced a dross leaching/SX plant, at the Imperial Smelting Furnace plant at Cockle Creek. The plant is capable of treating 3000tpa of copper-lead dross producing 5000tpa of copper sulfate pentahydrate (99.7% pure).

The copper-lead dross is leached with an oxygenated solution of ammonium carbonate to produce  $\text{Cu}(\text{NH}_3)_4^{2+}$  at pH 10.

The clarified loaded liquor is contacted in one stage with a diketone extractant LIX54 dissolved as a 2:1 solution in Shellsol 2046. The strip aqueous phase is recycled for further leaching. The loaded organic is stripped of its copper with sulfuric acid (90 g/L) and this strip solution transferred to an adiabatic crystalliser, operating at 5kPa pressure absolute. Ammonia leaching also extracts some zinc and lead which reports to the solvent. Thus scrubbing with dilute  $\text{H}_2\text{SO}_4$  at pH5 was found necessary to remove these impurities along with entrained ammonia.

#### Pasminco Metals - BHAS, Port Pirie (Johns, 1991)

The Pasminco lead smelter produces in excess of 3600tpa of copper cathode from its copper-lead matte (35% Cu, 38% Pb and 12% S). The matte is leached by  $O_2/H_2SO_4$  catalysed by 20 g/L Cl at 85°C, and the residue containing 32% Pb and Ag is recycled to the smelter. The clarified copper pregnant leach liquor (40 g/L Cu, pH 1.5) is contacted in two stages with Acorga M5640 (30% v/v in Shellsol 2046), which is a strong aldoxime reagent exhibiting fast extraction kinetics. The raffinate is returned to the leaching section. About 75% copper is extracted in this manner. The loaded solvent is washed to remove chloride impurities and stripped by 2 stage contact with spent electrolyte (33 g/L Cu, 180 g/L  $H_2SO_4$ ).

In this plant the electrolyte is cooled by heat exchange to minimise degradation of the organic caused by excessive temperatures.

#### Olympic Dam Operations (Roberts, 1992)

Copper leached from the flotation tailings (2.5 g/L Cu) is solvent extracted prior to uranium in one extraction stage. The loaded solvent is scrubbed to remove chloride before stripping and electrowinning. In this plant the chosen solvent was Acorga M5640 (9%) in Shellsol 2046 diluent. Spent electrolyte from the EW stage strips copper from the loaded solvent in one stage. The copper raffinate passes to a holding tank which serves as a surge feed vessel for uranium solvent extraction.

The main problem is solution clarification due to the presence of solids. Some 3.5 tons/week of fine solids find their way into the PLS which lead to some cruds in the SX circuit. (Ritcey, 1994).

#### Girilambone Copper Company (Basden, 1993)

The Girilambone project is a good example of the SX/EW success in copper mining. Mining started in 1994 and the project produces 14,000tpa of grades A copper cathodes using a relatively low cost plant. The ore is about 30% copper oxide and 70% chalcocite. Heap leaching produces pregnant solutions containing 1.6-3.6 g/L copper which is pumped to SX. The raffinate is recycled to the heaps and acidified to repeat the leaching process. The strip solution (45 g/L Cu) is pumped to the EW tankhouse.

When the plant started high solvent losses were experienced due to the apparent degradation of the solvent by permanganates in the leachate. This leads to the introduction of bentonite clay filters to regenerate the organic extractants (Malnic, 1995).

#### Gunpowder Copper Operation (Middlin, 1993)

Prior to the commencement of production in 1990 a major dewatering program was necessary to re-establish access to the old workings. The mine workings were flooded to within 135 m of the surface with approximately 300 M litres of water containing up to 3 g/L Cu. The recovery of Cu from this liquor provided an early cash flow for the project. Otherwise the heaped ore is irrigated with mine water, raffinate from the plant and fresh water.

The PLS fed to the SX/EW plant contains about 5 g/L Cu and 18 g/L Fe at pH 1.5. No liquor clarification is used but settling in the feed ponds is usually sufficient to keep suspended solids below 50 ppm. The SX circuit consists of two mixer-settlers followed by two stripping stages. The extractant chosen was Acorga M5640 diluted with Shellsol 2046 which extract about 94% of Cu. Spent electrolyte containing 185 g/L sulfuric acid and 35 g/L Cu is used to strip the solvent (O/A = 1:1). The enriched strip solution (50 g/L Cu) is filtered to remove any entrained organic and then mixed with spent electrolyte to produce the cellhouse feed with a copper tenor of 38 g/L.

It has been reported that occasional crud problems occur, particularly following heavy rain when suspended solids in feed liquor exceed design levels. Also entrainment of aqueous into the organic during the extraction stages results in a build up of iron in the advance electrolyte which is detrimental to EW process. The iron concentration is then controlled by periodical bleeding (Ritcey, 1994).

#### Mount Isa Mines (Miller, 1992)

MIM commissioned a SX/EW plant at the Isa mine in April 1990 to recover oxidised copper sulfide in 20 year-old dumps from the Black Rock orebody. The heaped ore is sprayed with a ferric/sulfuric acid solution (pH 2.3) and raffinate from the plant. The PLS solution (1.5-1.9 g/L Cu) is then collected into a large evaporating pond and eventually the Cu concentration is expected to build up to 3.5 g/L. The PLS is then pumped into the SX system at a rate of 70-100 m<sup>3</sup>/h, where it is contacted in a two-stage mixer with LIX 984, (10% v/v) diluted into Shellsol 2046. Over 90% extraction is achieved, with O/A of 1.4:1. The raffinate is recycled to the heap whilst the loaded solvent is stripped with spent electrolyte (45 g/L Cu, 170 g/L H<sub>2</sub>SO<sub>4</sub>) in two stages. A particular feature of this plant is the recovery of entrained organic from electrolyte using a Jameson Cell which is a new application for this type of flotation cell (Readett, 1993).

As it is often the case, seasonal rain lead to clays entrainment in the feed and eventually form cruds in the SX circuit (Ritcey, 1994).

#### Nifty Mines

Nifty was commissioned late 1993. Production rates initially were less than 50% of the actual design (16,500 tpa), but it is now approaching capacity. The copper oxide ore is heap leached with sulfuric acid to produce a PLS containing 7.8 g/L Cu, which is fed to the SX/EW plant. The SX circuit consists of two extraction stages, a wash and two stripping stages (Krebs mixer-settlers). The organic phase includes an Acorga M5640 extractant (23% v/v) diluted with Shellsol 2046. Early problems were experienced with emulsions, cruds and slow phase disengagement. Manganese oxidation to permanganate during electrowinning was a problem during start up. Cruds are attributed to clay carry over from the ore and dissolved silica. Phase disengagement problems disappeared when treating different heaps. Possible reasons and the underlying chemistry are currently being evaluated to avoid future problems (Ritcey, 1994).

### SOLVENT EXTRACTION OF OTHER METALS

#### Niobium/Tantalum - Greenbushes Tin, WA.

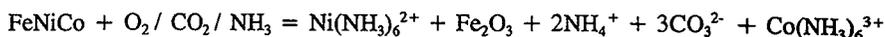
For several years between 1980 - 1990, Greenbushes operated a small SX plant to produce high purity niobium and tantalum oxides from its tantalite concentrate. This concentrate was leached with HF and the complex fluorides H<sub>2</sub>Nb<sub>2</sub>F<sub>7</sub>/H<sub>2</sub>TaF<sub>7</sub> extracted into pure MIBK. Selective stripping of these complexes was achieved by first hydrolysing and precipitating Nb(OH)<sub>5</sub> using water followed by Ta<sub>2</sub>(OH)<sub>5</sub> using aqueous NH<sub>3</sub>.

#### Arsenic Removal - Copper Refineries Pty Ltd, Townsville, QLD (Hoey, 1993)

Arsenic impurities have been solvent extracted from copper electrolyte since 1984, to maintain an arsenic concentration below 10 g/L. The primary liberation electrolyte bled from the Tank House is contacted in four stages with tributyl phosphate (TBP) dissolved in Shellsol 2046. Arsenic acid (H<sub>3</sub>AsO<sub>4</sub>) is transferred into this solvating solvent then stripped with ammonium sulfate solution recycled from the copper arsenate plant, resulting in a solution containing 30 g/L arsenic. This liquor is then mixed with a copper sulfate solution and neutralised with ammonia to produce a bicupric arsenate (BCA) precipitate which is used as a feedstock in the production of chrome copper arsenate, a timber preservative.

Nickel Laterite - Queensland Nickel Pty Ltd (Reid, 1993)

Queensland Nickel operates a hydrometallurgical plant at Yabula, QLD, to treat lateritic nickel ore. The roasted reduced ore is leached with ammonia-ammonium carbonate solution according to the following equation:



The SX process installed in 1989, separates nickel from cobalt from an entirely ammoniacal system in a novel way. The key step requires Co (II) to be oxidised to Co (III) by  $\text{H}_2\text{O}_2$  before SX, to prevent cobalt extraction and lock-up in the organic phase. The PLS (13 g/L Ni, 0.5 g/L Co) is then passed through a series of 3 mixer-settlers where the nickel is preferentially extracted into a modified ketoxime extractant LIX 84 in Escaid 110. The loaded organic is stripped by an ammonium carbonate solution (280 g/L  $\text{NH}_3$ ). The stripped liquor contains about 80 g/L Ni which precipitates as nickel carbonate (99.6%Ni). Plant experience highlighted the need to address reagent degradation and reagent poisoning by Co.

Rare Earths - Ashton Rare Earths (Ring, 1993)

A commercial rare earths operation was under evaluation in mid 1994 at Mount Weld near Laverton, WA. It is proposed to mine 50,000 tpa of ore containing 20% rare earths oxides (REO) to produce 10,000 tpa of a monazite concentrate containing 50% REO. After fluxing the concentrate with NaOH calcining at 650°C and acid leaching, it is proposed to separate and extract cerium with D2EHPA. The rare earth chloride raffinate will then be processed by a SX circuit being developed by ANSTO in Sydney.

Vanadium - Clough Resources, Perth, WA

The SX of vanadium from a Bayer liquor has been patented by Clough (1994). The ore is roasted and digested under pressure with a caustic solution to leach the alumina and the vanadium (as  $\text{Na}_3\text{VO}_4$ ). A bleed is pumped to the SX circuit where the vanadium is extracted in 4 stages, using Aliquat 336 (20% w/v) in a high flash point diluent. The organic is washed to remove any entrained impurities and stripped with an ammonium chloride solution (2.5M) in a 3 phase-separator. Ammonium meta vanadate is precipitated (99.9%) and the stripped organic is regenerated via a pulse column.

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## A COMPREHENSIVE APPROACH TO IMPROVE EXTRACTOR OPERATIONS AND REDUCE WASTEWATER TREATMENT COSTS FROM A MANUFACTURING FACILITY

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### ABSTRACT

A multi-faceted approach involving computer simulation, pilot plant experimentation, and plant operations was initiated to study ways to improve extractor operations and reduce overall wastewater treatment costs for a manufacturing facility. A number of potential opportunities were identified and evaluated. They were: 1) add stages to achieve the desired separation, 2) reduce residual solute levels in the returned solvent, 3) optimize the temperature of the feed and solvent, and 4) evaluate the impact of impurities in the feed material. This integrated approach allowed for independent examination of each of the factors and under conditions not normally seen in production. It also allowed for verification of the computer model in predicting effects of different operating conditions in the plant. The benefits that could be expected from such a detailed study of an already existing operation include improved operations, decreased wastewater treatment cost, minimized impact on downstream operations, and overall reduced operating costs. In addition, future process changes can be implemented based on model predictions alone with a higher degree of confidence.

### BACKGROUND

**Process Description:** The process under study involves parallel operation of multiple extraction columns in similar service. These columns have diameters ranging between 1.8 and 3.8 m, and heights ranging from 30 - 45 m. The internal configurations for all columns are geometrically similar, and are non-agitated. The exact configurations are proprietary.

Previous attempts at process improvement had resulted in much needed capacity increases, but little enhancement in efficiencies. The process was modeled, however, the model used could not include hydraulic capabilities, and therefore, could only predict trends, at best. This extraction operation was previously piloted in a Karr reciprocating plate column, in hopes of combining a capacity increase per unit area with an improved solute recovery. However, repeated experiments did not demonstrate favorable results. Plant experiments were also initiated, but process conditions upstream of the extractors made it nearly impossible to isolate the effects of only one variable. Ever increasing wastewater treatment costs and the need for additional extraction capacity sparked new interest in improving the operations of the existing extractors.

The objective of this project, therefore, was to improve operations in existing facilities by using a combined approach including plant data, pilot plant data on both pure components and plant material, and computer simulations.

## PILOT PLANT PROGRAM

Extraction studies were conducted in the pilot facility, illustrated in Figure 1, using a 76 mm diameter rotating disk contactor, RDC, from the Otto H. York Co. This jacketed column was 4.3 m tall and consisted of 72 actual stages with a 44.5 mm plate spacing and 50% open area. The column, from the top down, consisted of a 432 mm disengagement region, an active section of 36 plates, a 305 mm open section, and another 36 plates. Solvent entered the bottom of the column through a sparger located 254 mm above the bottom flange and 76 mm below the lowest plate. The interface was maintained at the top of the column via a swing arm. Positive displacement pumps transported the feed and solvent through heat exchangers to the RDC. The flowrates and densities of these streams were measured by Micromotion D-12 mass flowmeters. The temperature of the feed and solvent were monitored on a Camile 2000, which was also the control system used for the pilot facility. Samples of the feed, solvent, extract, and raffinate were collected through Dopak in-line samplers. Solute and other component concentrations were quantified by a number of different analytical methods.

Eight independent variables were identified as having major impact on extractor performance in plant operations. All were analyzed in the pilot plant. These factors were: column flux, solvent and feed temperatures, solute concentrations in the feed and solvent, solvent-to-feed ratio, and solid or liquid additive concentrations. The dependent variable was the fraction of solute unextracted, expressed on a solute-free basis as  $X_n/X_f$ .

The experimental procedure consisted first of charging the column with the continuous phase. Next the solvent and feed streams were fed at the targeted temperatures and flowrates. At least five column turnovers were allowed prior to sampling all streams. Then, the variable under study would be changed. Total mass balance around the column closed within the 2-3% range recommended for reliable data by Pratt and Hanson (1983).

A single system with three different sources of feed and solvent material was examined: pure components, sales-grade chemicals; and two different plant materials, identified as Plant 1 and Plant 2. Plant 1 material had 10% higher levels of solute in the feed and ten times higher levels of solute in the solvent than Plant 2 material. There were also different trace impurities in the two plant materials. The interfacial tension was 0.51 mN/m at the top and 9.8 mN/m at the bottom for the pure components. The interfacial tension ranged from 0.86-0.89 mN/m at the top and 3.7-4.2 mN/m at the bottom for plant materials. Both phases offered significant resistance to mass transfer.

Figure 2 shows the fraction unextracted versus total column flux for actual Plant 1 operating data as well as pilot data for pure components, Plant 1 and Plant 2 material. Flooding was visually determined by noting the point where solvent or feed was rejected in the raffinate or extract, respectively. The flooding point was significantly different for all three systems: pure components at 31,000 l/hr/m<sup>2</sup>, Plant 1 at 28,000 l/hr/m<sup>2</sup>, and Plant 2 at 26,000 l/hr/m<sup>2</sup>. As noted previously, fluctuations in plant operations result in a lot of scatter in the Plant 1 operating data. The data from the pure component pilot experiments showed good agreement with the plant operating data. However, for both plant materials run in the pilot plant, the fraction unextracted was consistently about an order of magnitude higher than the pure component system. These results demonstrate the dramatic effect of different trace materials in the system on extractor performance. This effect of trace materials on mass transfer rates is documented by Davies (1972).

FIGURE 1. Extraction pilot plant flowsheet.

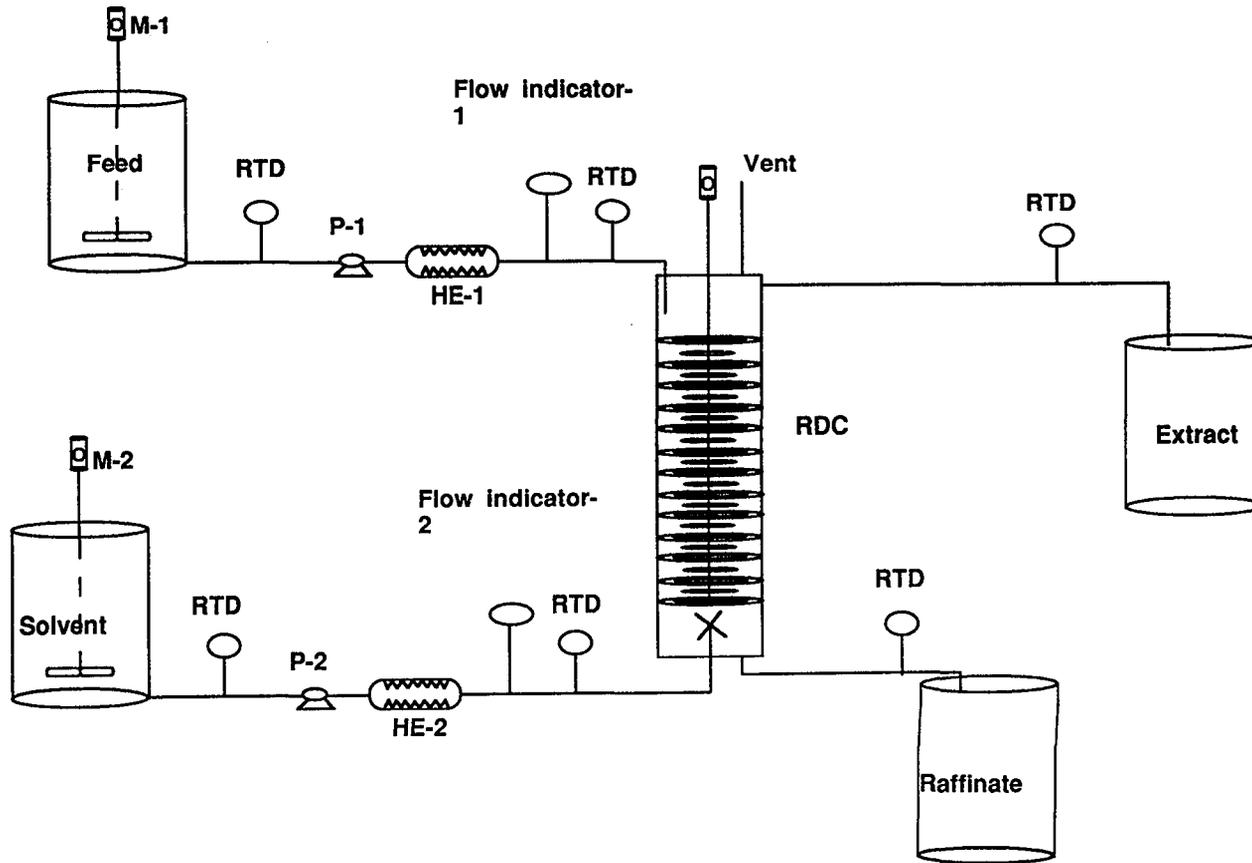


FIGURE 2. Effect of total flux on fraction unextracted.

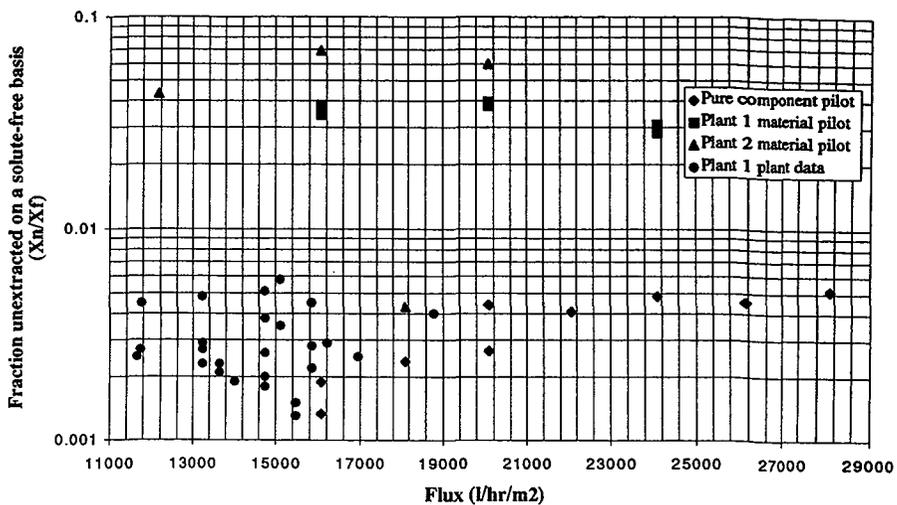
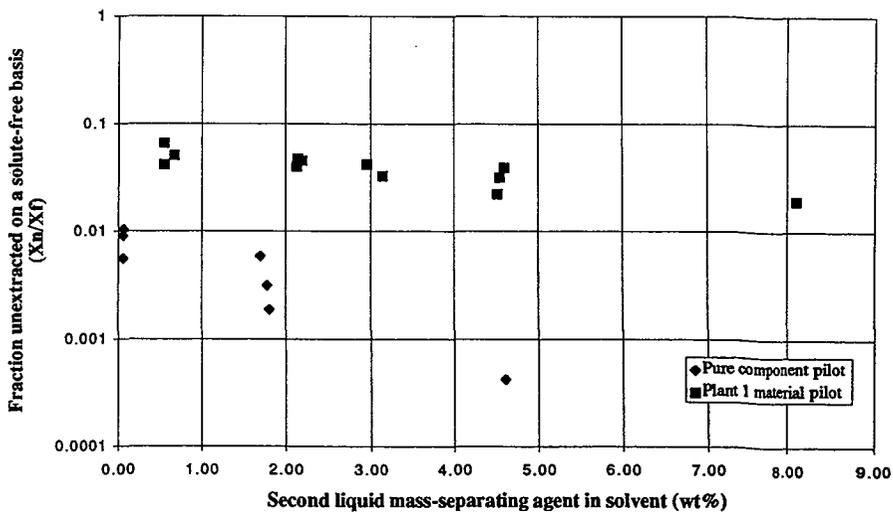


FIGURE 3. Effect of second liquid mass-separating agent on fraction unextracted.



The effects of feed and solvent temperature on the fraction unextracted are summarized in Table 1. Heating the feed to 40 °C and the solvent to 45 °C for both pure and Plant 1 material resulted in a statistically significant minimum in the fraction of solute unextracted at the 95% confidence level.

TABLE 1 Temperature Effects

FEED TEMP (°C)	SOLVENT TEMP (°C)	$X_n/X_f$ PURE COMP.	$X_n/X_f$ PLANT 1
25	25	0.0063	0.097
25	45	0.0070	0.080
25	60	0.0043	0.058
40	25	0.0049	0.068
40	45	0.0029	0.053
40	60	0.0032	0.056

As expected, the fraction unextracted increased with solute concentration in the solvent for both pure components and Plant 1 material. This effect was found to be significant in the pilot unit and in production and was more pronounced in the pure component system.

The solute concentration in the feed was varied from the production target by -20 to +13%. The solvent-to-feed mass ratio was held constant. Over this range, the solute concentration in the raffinate decreased smoothly by 70% for pure components and 17% for Plant 1 material. This difference in reduction in the solute losses between the two materials is largely due to impurities in the Plant 1 material and again underscores the need to pilot extraction with plant material, when available.

The solvent-to-feed ratio was varied  $\pm 30\%$  from the production target. Over this range, the concentration of solute in the raffinate decreased by a factor of 10 for Plant 1 material, and a factor of 100 for the pure components.

A second liquid mass-separating agent was investigated at the pilot scale. The effect of increasing its concentration in the solvent on the fraction of solute unextracted is shown in Figure 3. For both pure and Plant 1 materials, as the level of the agent was increased, extractor performance improved, largely due to increased interfacial area. Similar results were found when a solid mass-separating agent was introduced, and an increase in interfacial area was again observed.

### MODEL

A process simulator model was used to predict the separation in the plant extractors. The model used was initially a simple, 3-component model using UNIQUAC parameters for predicting the liquid-liquid equilibrium. Most of the equilibrium parameters were obtained from the Chemistry Data Series by Sorensen and Arlt. The rest were estimated using proprietary methods. Temperature profiles were based on molar flow from stage to stage. The model was used for staging calculations only, with the number of stages varied to meet measured endpoints. Searches in the literature yielded no model for predicting staging and hydrodynamic behavior combined for the type of contactor used in the plant operations. Prior to the pilot work, the model was only useful in

predicting trends. The pilot plant data verified the trends seen with the model - the effects of changing temperature of the feed and solvent, the effects of solute concentrations in the feed and solvent, and solvent-to-feed ratio variations.

Pilot and plant data were used to improve the predictive capabilities of the model. The difference between the pure component data and Plant 1 data on fraction solute unextracted, generally an order of magnitude, could not have been predicted with the model alone. Nor was the model able to predict the effects of changing flux. With plant data and pilot data collected using plant material, a model including hydrodynamic effects can now be developed. In addition, the current model was unable to predict the results of the mass separating agents as their effects appeared to be purely hydrodynamic in nature.

### CONCLUSIONS

The benefits of this multi-faceted approach are many. We now have a better understanding of our system which is already leading to improvements in operations. We have the potential for reducing solute losses at least by a factor of two with minimal capital expense, based on the results of the pilot work. We quantified the differences between the pure component and plant materials in operation, and know the benefits of further removing impurities in the system. We have developed a better process model, and will be able to better quantify effects of future changes in operating conditions. Most importantly, we have demonstrated that this combined approach, involving computer modeling, piloting, and operating data has the potential to reap similar benefits with other processes.

### NOMENCLATURE

$X_f$  - concentration of solute in the feed, mass basis  
 $X_n$  - concentration of solute in the raffinate, mass basis

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## Nickel Cobalt Separation by Ammoniacal Solvent Extraction: The Operating Experience

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### ABSTRACT

A solvent extraction process to separate nickel from cobalt in an ammoniacal environment was commissioned at Queensland Nickel Pty Ltd's Yabulu refinery, near Townsville in North Queensland, Australia, in early 1989. After three months of operation it became necessary to shut down the solvent extraction plant in order to resolve several operating problems. Flow sheet modifications were carried out, principally in surrounding plant, and a number of operating parameters were changed. The Ammoniacal Solvent Extraction (ASX) process was recommissioned in August 1989 and has operated continuously since that time.

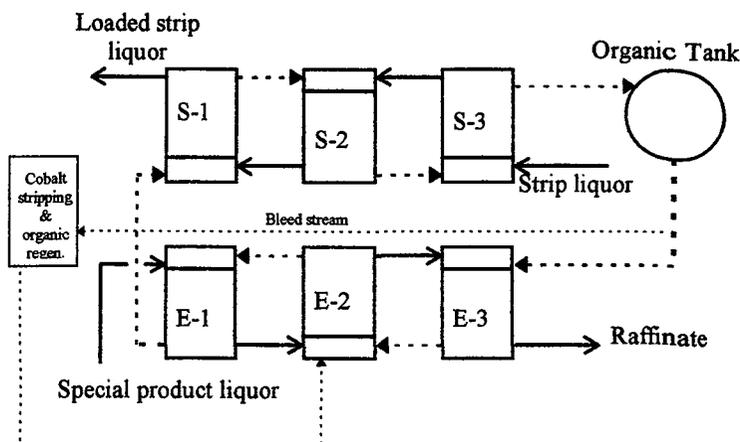
Problems encountered during the early stages of operation, and subsequently as nickel production through the ASX plant was increased from typically 21,000 tonnes to 28,000 tonnes per year, have included organic reagent degradation and slowed phase disengagement. Operational changes introduced to counter these and other problems are described in this paper.

Successful resolution of these problems has allowed Queensland Nickel Pty Ltd to develop and successfully introduce several new, higher value nickel products to the market. The ASX process has also provided the opportunity to pursue value added cobalt products.

### INTRODUCTION

Extensive laboratory and pilot plant test-work carried out at Queensland Nickel Pty Ltd's (QNPL) Yabulu refinery during the 1980's lead to the commissioning in January 1989 of a solvent extraction process to separate nickel from cobalt in a wholly ammoniacal system. Development of the process, which involves extraction of nickel from ammoniacal solution using a reagent mixture based on Henkel's LIX 84I (2-hydroxy-5-nonyl acetophenone oxime) in Escaid 110 aliphatic solvent followed by stripping into high strength ammoniacal ammonium carbonate, has been described by Price and Reid (1993). Details of the process and the changes required in the Yabulu flow sheet of QNPL are described in detail by Reid and Price (1993) and Reid (1994). The ASX circuit, which comprises three extract and three strip stages and utilises conventional mixer settlers, is shown in Figure 1.

Initial commissioning of the ASX plant proceeded smoothly, with the process being brought on line with minimal disruption to QNPL's production schedule. Over the subsequent three months, however, a number of problems developed which ultimately required that the ASX process be shut down and QNPL revert to pre-ASX operations while various modifications were carried out. The problems which brought this about were primarily associated with surrounding plant. In particular, difficulties in cooling special product liquor prior to presentation to solvent extraction prevented effective oxidation of  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$ , a necessary precursor to satisfactory Ni - Co



**Figure 1: ASX Circuit Flow Sheet**

separation; surfactants from the liquid polyelectrolyte flocculants used elsewhere on the plant caused phase disengagement problems; while organic reagent degradation associated with high cobalt loading reduced nickel transfer capacity.

Flow sheet modifications were carried out in the special product liquor clarification and cooling circuit; liquid flocculants were replaced with solid polyelectrolytes and an organic reagent regeneration plant based on a process developed at Yabulu was constructed over a five month period. The ASX plant was recommissioned in August 1989.

Since recommissioning the process has operated continuously, while nickel throughput has been progressively increased from around 21,000 tonnes in 1989-90 to over 28,000 tonnes in 1994-95. Current indications are that circuit production capacity has not yet been reached.

### ORGANIC REGENERATION

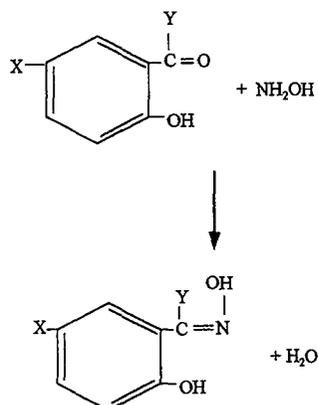
Separation of nickel from cobalt in the ASX process relies on prior oxidation of cobalt in the special product liquor to the trivalent state. Residual  $\text{Co}^{2+}$  loads onto the organic reagent along with  $\text{Ni}^{2+}$ . Once loaded, it is prone to oxidation and will not strip in the strong ammoniacal strip liquor used in the ASX plant. A bleed stream treatment process to remove this cobalt from the organic reagent is therefore required. One consequence of the cobalt removal process is the degradation of oxime extractant to ketone, resulting in a loss in nickel transfer capacity. The re-oxidation process developed at Yabulu to combat this effect has been of fundamental importance to the economical operation of the circuit.

**TABLE 1**  
**Metal contents of main ASX circuit streams**

Stream	Ni	Co
Special Product Liquor	11 - 14 kg.m <sup>-3</sup>	0.5 - 1 kg.m <sup>-3</sup>
Raffinate	10 - 50 g.m <sup>-3</sup>	0.5 - 1 kg.m <sup>-3</sup>
Loaded Strip Liquor	70 - 85 kg.m <sup>-3</sup>	15 - 25 g.m <sup>-3</sup>
Stripped Organic	1.5 - 2 kg.m <sup>-3</sup>	1.5 - 2 kg.m <sup>-3</sup>
Loaded Organic	10 - 11 kg.m <sup>-3</sup>	1.5 - 2 kg.m <sup>-3</sup>
Cleaned Regenerated Organic	0.1 kg.m <sup>-3</sup>	0.15 - 0.3 kg.m <sup>-3</sup>

### The Regeneration Process

The regeneration, or re-oximation, process used is described by Ferguson, Price and Reid (1988). The process involves reaction of a bleed stream of stripped organic reagent containing ketone at generally 15 - 25 kg.m<sup>-3</sup> with an aqueous ammoniacal solution of hydroxylamine sulphate. The process can be described by the following equation:



X = CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub> -- CH<sub>2</sub> --, CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub> -- CH<sub>2</sub> -- or branched isomers

Y = H, CH<sub>3</sub>, 

### Regeneration Operation

Regeneration is carried out at 70°C in a heated, agitated vessel fed by a bleed stream of organic reagent containing ketone and an aqueous stream containing hydroxylamine and ammonia. A reaction time of between 12 and 20 hours is required, and conversion in excess of 80% is achieved. The dispersed phases discharging from the reaction tank pass to a settler where the phases disengage. The regenerated organic reagent, now containing typically less than 5 kg.m<sup>-3</sup> ketone,

returns to the main ASX circuit, while the aqueous phase is recycled. Using this process, oxime can be produced from ketone at a cost of around 10% of that of fresh reagent.

When initially commissioned, the concentration of aqueous reactants was maintained by adding concentrated make-up streams of ammonium hydroxide and hydroxylamine sulphate. The hydroxylamine sulphate concentrate was prepared in a bleed from the aqueous recycle stream. Work in the early period of operation, however, showed that over 30% of the hydroxylamine was being lost by reaction with other soluble species in the aqueous stream. Laboratory studies demonstrated that the process was equally effective when the necessary hydroxylamine sulphate was added as a solid direct to the reaction tank by means of a volumetric feeder rather than pre-dissolved in an aqueous phase, with the prospect of reduced hydroxylamine wastage. Plant trials subsequently confirmed this, and the regeneration process is now carried out in this manner.

### PHASE DISENGAGEMENT

On commissioning, the ASX circuit was operated with aqueous continuous dispersions at O:A=50:50 in both extract and strip mixers. Pilot plant work had shown this to provide optimum phase disengagement and nickel transfer kinetics. Phase separation rates have subsequently required a change to organic continuous operation on the strip side, while modifications to the organic inlet configuration have been required to ensure stable aqueous continuous operation of the E-3 mixer.

#### Strip Side Operation

For reasons still not fully defined, the phase separation rate of strip side dispersions slowed over the initial three month operating period, giving rise to widening dispersion bands. As a result, aqueous-free organic advances across the strip side became almost impossible to achieve, to the detriment of stripping performance.

Laboratory work at the time showed that separation rates of organic continuous dispersions were even slower to separate. However, the separation profile and the lower total volume of an organic continuous dispersion in the 80:20 - 70:30 organic:aqueous phase ratio region had a greater possibility of yielding a clear organic advance. Thus, on recommissioning in August 1989 the plant was brought on line with strip mixers operating organic continuous. The penalty has been some loss in stage efficiency associated with the organic-rich dispersion but largely aqueous-free organic advances have resulted.

Residual dispersion in the settlers has also resulted in some problems with organic entrainment in aqueous advance, particularly from S-1. Reagent entrained from the circuit in S-1 aqueous advance is extraordinarily slow to coalesce; dispersions prepared in the laboratory have remained uncoalesced after 24 hours. Clay contacts and other treatments have not yielded any improvement. No surfactants or other degradation products have as yet been identified. Indications are that the reagent contains ultra fine iron oxide precipitate, probably resulting from contact between loaded organic containing iron at up to 150 ppm (incoming special product liquor contains iron at 1 - 2 ppm) with the ammonia rich nickel loaded strip liquor. Filtration of the entrained organic at sub-micron levels in the laboratory has had some beneficial impact on coalescence rates.

#### Extract Side Operation

Early in the operation of the plant an anomaly was noted in the phase continuity of the dispersion produced in the E-3 mixer. While operating aqueous continuous, small aqueous droplets were noted

to be present within a proportion of the organic droplets. Thus the aqueous continuous mixture also effectively contained a component of organic continuous dispersion. On coalescence this left an organic continuous dispersion band in the settler.

Of greater concern was the fact that under some circumstances the proportion of organic continuous mixture was sufficiently high that the dispersion became unstable and would readily flip to organic continuous. Coalescence rates were sufficiently slow under such circumstances that massive entrainment of organic reagent from the circuit occurred. (As the circuit was constructed with organic recovery after-settlers on both raffinate and loaded strip liquor streams this fortunately did not result in serious reagent losses.)

A considerable number of plant trials were carried out in an attempt to overcome this problem, which became more serious as flows were increased to raise nickel throughput. Adjustments were made to the height, speed and direction of rotation of the primary pump - mix agitator, to no avail.

In early work the most effective means of stabilising aqueous continuous phase continuity was found to be simply to increase the proportion of aqueous phase present. Thus mixer ratios, set at 50:50 O:A on commissioning, were progressively pushed to 45:55, 40:60 then 35:65 by increasing aqueous recycle flow. Phase stability generally improved but the total volume of dispersion passing through the settler also increased considerably.

As no similar problems were encountered in other extract side mixers and E-3 was the only mixer into which organic reagent was pumped, attention was turned to the reagent inlet geometry. A number of energy dispersing baffle configurations within the mixer inlet plenum were tried without success, before an experiment to introduce the organic stream via a dip pipe above the agitator was tried. This resulted in a considerable improvement in the stability of the aqueous continuous dispersion, and this configuration has been retained.

Operating observations over more recent times have shown that the presence of fine aqueous droplets entrained in the stripped organic feed to E-3 mixer is a potent cause of E-3 dispersion instability. Thus moves to reduce strip side entrainment have had an impact on E-3 stability.

### INCREASED NICKEL THROUGHPUT

As noted previously, nickel production at QNPL's Yabulu refinery has increased from around 21,000 tonnes per year to 28,000 tonnes per year since commissioning the ASX plant. Recently, annualised production rates well in excess of 30,000 tonnes per year have been sustained over periods of weeks at a time. This has been achieved with no increase in the size or number of mixer settler units in the circuit. Several factors have contributed to the achievement of this outcome - both within and beyond the ASX circuit. Within the circuit two factors have been critical: increased reagent inventory and the development of an on-line analytical capability.

#### Reagent inventory

Circuit design was based on an organic flow of  $330 \text{ m}^3 \cdot \text{hr}^{-1}$ . At a loaded organic nickel concentration of around  $10 \text{ kg} \cdot \text{m}^{-3}$  and a stripped organic of  $2 \text{ kg} \cdot \text{m}^{-3}$ , this equated to a capacity of around 63 tonnes per day. To achieve the daily nickel throughputs of 90 - 95 tonnes now being obtained, organic reagent flow has been increased to  $450 \text{ m}^3 \cdot \text{hr}^{-1}$ . In terms of unit settler throughput, design extract side rates of  $4.4 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$  have been increased to around  $7.5 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$ .

Early operation of the circuit was based partly on a minimum reagent inventory philosophy; organic reagent depths as low as 150 mm (or even lower on occasions) were used. As organic reagent flows were raised, linear flow velocities in the settlers increased. This combined with the high interfacial

velocity differential obtained with low organic reagent depths made it increasingly difficult to obtain aqueous-free organic advances between stages. The result was impaired loading and stripping.

As changes occurred in the surrounding plant making it clear that higher nickel throughput was a requirement, a decision was made to invest in a quantum increase in organic reagent inventory. Reagent depths of at least 300 mm were established in all settlers, with the result that the necessary flow increases could be sustained without incurring an entrainment penalty.

#### **On-line analysis**

To maximise production in the ASX circuit it has been necessary to fully utilise the transfer capacity of the organic reagent. Thus loaded organic reagent ex E-1 is operating close to its theoretical loading capacity. The implication of this is that any marginal increase in the nickel concentration in the incoming liquor has the potential to result in an immediate loss of nickel to raffinate.

Control strategies based on sampling and conventional analyses required that a margin of capacity had to be retained in order to accommodate swings such as these. However the in-house development of an absorbance based on-line analytical technique using an LED light source has allowed the circuit to be safely operated at capacity at all times.

### **CONCLUSIONS**

Development, commissioning and successful operation of the ASX process has been critical to the recent large increases in nickel and cobalt production and reductions in operating costs of QNPL. The process strategy adopted, whereby the major constituent is transferred through the organic reagent, has resulted in a marked improvement in the purity of nickel products produced (Reid, 1994, 1995). This, in turn, has provided the basis for development of a new range of products. Similarly, the reduced nickel content of the cobalt product has presented opportunities for further value adding.

The ASX circuit itself has been remarkably robust. Successful resolution of the problems described in this paper has enabled refinery output to be increased by a factor approaching 50% with minimal capital outlay, a circumstance which has had a marked impact on the cost of production.

### **ACKNOWLEDGMENTS**

The authors thank QNI management for permission to publish this paper.

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## OPERATING EXPERIENCE OF THE SOLVENT EXTRACTION PROCESSES IN THE THERMAL OXIDE REPROCESSING PLANT

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### INTRODUCTION

The Thermal Oxide Reprocessing Plant (THORP) at the Sellafield, UK site of British Nuclear Fuels Plc reprocesses irradiated oxide nuclear fuel from British, Japanese and European Light Water and Gas Cooled Reactors. In the Head End section irradiated fuel is received, stored under water, sheared and dissolved in nitric acid, whilst in the Chemical Plant the PUREX solvent extraction process using tri-butyl phosphate in kerosene as solvent is used to separate uranium, plutonium and fission products. There are further facilities for the conversion of plutonium and uranium nitrate to the oxide products and for treating highly active and medium active liquid wastes.

The capacity of THORP is 1200 tonnes irradiated fuel per year and, during the first 10 years of operation, there is a committed throughput of 7,000 tonnes at irradiations up to 40 GW days per tonne and out-of-reactor cooling time of 5 years. Subsequently, more highly irradiated fuels will be reprocessed including mixed uranium and plutonium oxide fuels. A full account of the development, design and construction of THORP is given elsewhere - Phillips (1993), Phillips (1989), Harrop and Phillips (1992). With some 15,000 process vessels, 300,000 metres of pipe, 3 million metres of electrical and instrument cabling and 14,000 instrument loops contained in a building 500m long, 150 m wide and 50 m high, THORP is one of the biggest and most complex chemical plants in the world.

Construction was completed on time in 1992, and commissioning with water, acid and uranium was finished during 1994. Irradiated fuel was introduced into the Head End in early 1994 and into Chemical Plants a year later. This paper describes the initial performance of the Chemical Plant Solvent Extraction Processes with a radioactive feed.

### SOLVENT EXTRACTION FLOWSHEET AND EQUIPMENT

#### Design Principles

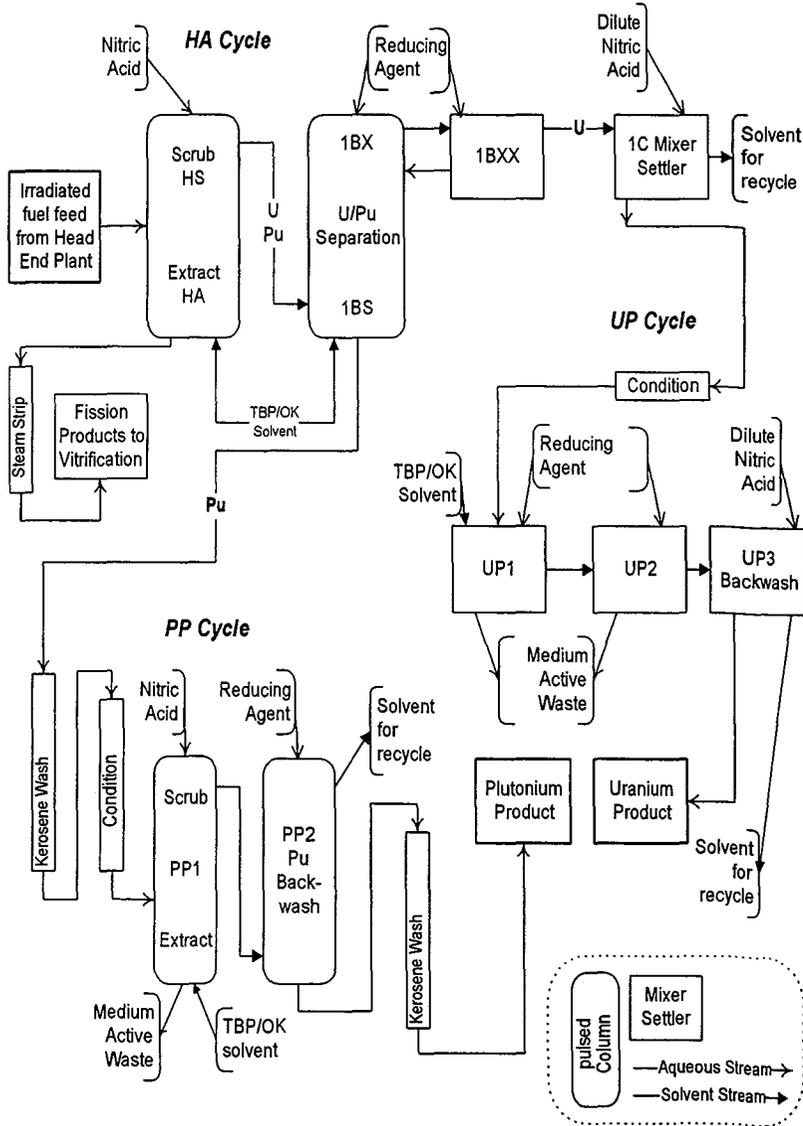
Three main principles governed the design of the solvent extraction cycles:-

- a) In order to minimise the amount of activity discharged in liquid wastes, the chemical reagents fed to the process to adjust valency states are "salt-free" so that they do not restrict the ability to concentrate and encapsulate waste streams.
- b) It was required to minimise the extent, size and complexity of the process equipment in contact with radioactive material, so as to minimise operator radiation dose and reduce capital and operating costs. This was achieved by using an "early-split" flowsheet with U-Pu separation in the first solvent extraction cycle, followed by single cycles for uranium and plutonium purification.
- c) Pulsed, perforated plate columns are used as the solvent extraction contactors in the Highly Active (HA) and Plutonium Purification (PP) cycles to allow critically safe operation with the higher plutonium concentrations of oxide fuel. Their relatively short aqueous-solvent contact time also minimises solvent degradation from the increased amounts of fission products in oxide fuel.

**Flowsheet**

The three-cycle PUREX flowsheet is shown in Figure 1. The HA and HS columns in the HA cycle extract the uranium and plutonium from the nitric acid solution of the fuel into the 30% TBP in kerosene solvent, leaving almost all the fission products in the acid aqueous phase, which flows to the Vitrification Plant. The uranium and plutonium are then separated in the 1BX and 1BS columns by chemically reducing the plutonium using salt-free uranium IV produced on site from uranium VI.

**FIGURE 1**  
THREE CYCLE PUREX FLOWSHEET

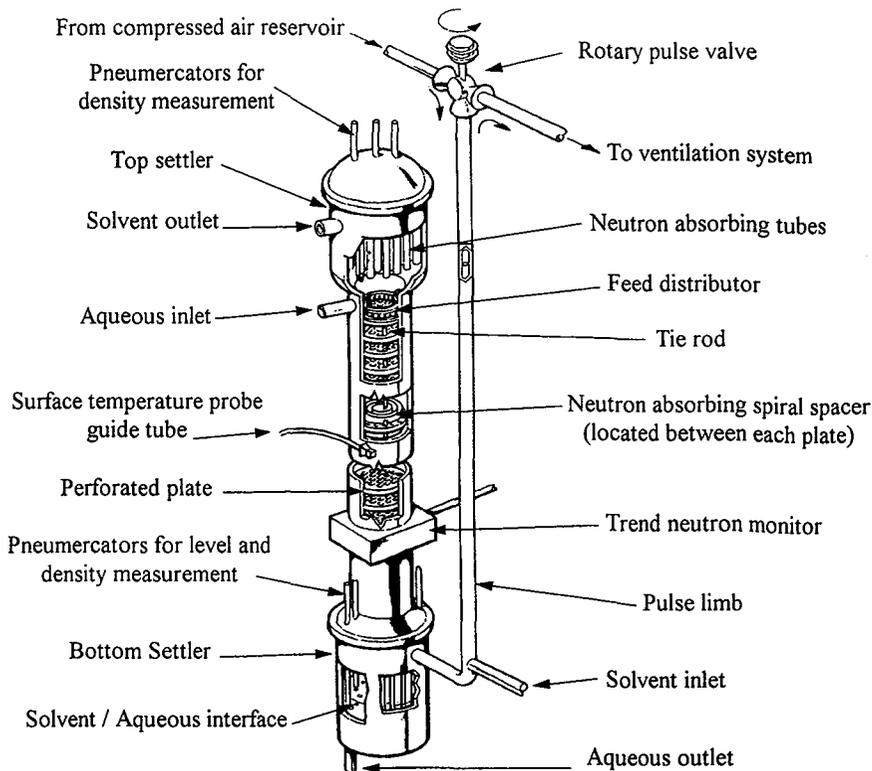


The plutonium stream passes to the single PP cycle where pulsed columns and 30% TBP/kerosene are again used to purify the plutonium product from the principal contaminant technetium and residual uranium, ruthenium, caesium and cerium. The single UP cycle uses 20% TBP/kerosene and mixer settlers to remove neptunium, plutonium, ruthenium, caesium and cerium from the uranium product. Careful valency conditioning of the neptunium and plutonium prior to solvent extraction, and the use of hydroxylamine nitrate reductant, achieves high simultaneous neptunium and plutonium decontamination - Dennis, Phillips, 1992 - in a single solvent extraction cycle.

### Pulsed Columns

The pulsed columns used in the HA cycle are illustrated in Figure 2. They consist of stainless steel tubes, typically 300 mm in diameter and 6-10 metres in height filled with stainless steel perforated plates which are spaced by a series of spiral stainless steel or hafnium spacers. The phase disengagement sections or settlers at top and bottom of the column are filled with stainless steel tubes containing boron carbide to provide criticality poisoning. The column illustrated has a phase interface in the bottom settler, with droplets of aqueous phase falling through the rising continuous phase to coalesce at the interface. The opposite arrangement of rising solvent drops in a continuous aqueous phase is also used. The columns have facilities for the measurement and control of the interface and for the measurement of neutron and temperature profiles. Pulsing is provided by alternately admitting and exhausting compressed air to the solvent-filled pulse limb.

FIGURE 2



## COMMISSIONING OF SOLVENT EXTRACTION PROCESSES

Commissioning of the solvent extraction processes followed a logical sequence with four stages - Phillips, Hamilton, 1993:-

1. Water commissioning to set equipment to work, check liquid pumping devices and calibrate vessels.
2. Nitric acid and TBP/kerosene solvent commissioning to set up and test 2-phase equipment, and initially set up instrumentation and control devices.
3. Uranium, nitric acid and TBP/kerosene commissioning to obtain pulsed column and mixer settler mass transfer and maximum throughput data, and refine instrumentation and control.
4. Irradiated fuel, nitric acid and TBP/kerosene commissioning to prove the chemical flowsheet with different fuels and to verify that product quality is achieved.

The commissioning work was straightforward and successful with plant operation and performance following closely that predicted from the pilot plant development trials. Irradiated fuel commissioning is now in progress using fuel of progressively increasing irradiation and decreasing cooling time.

## OPERATION OF SOLVENT EXTRACTION PROCESSES

Irradiated fuel commissioning of the solvent extraction processes commenced with the processing of 27 te fuel from UK advanced gas-cooled reactors (AGR) and 15 te fuel from a Japanese boiling water reactor (BWR). A comparison of these fuels with the design reference fuel is given in Table 1.

TABLE 1

Comparison of Fuel Processed with Design Reference

	Design Reference	AGR Fuel	BWR Fuel
Irradiation GWD/te	40	10	15
Cooling Time Years	5	5-8	15
Plutonium Content %	100	30	50
Neptunium Content %	100	23	30
Fission Product Content %			
Tc 99	100	23	25
Ru 106	100	2	1
Cs 134	100	2	0.5
Cs 137	100	20	27
Ce 144	100	1	0.3

The plant was operated at a throughput of 4 te U/day and was chemically and hydraulically stable throughout, showing the value of the extensive development work carried out on both the chemistry and engineering of the solvent extraction processes. The performance of the plant was studied by looking at fission product separation efficiency, uranium-plutonium separation efficiency, amounts of uranium and plutonium in waste streams and, where available, the response of neutron monitors measuring plutonium.

### Fission Product Separation Efficiency

Table 2 illustrates typical fission product decontamination factors (DF's) across the HA and HS pulsed columns for ruthenium, caesium and cerium, compared with THORP reference flowsheet.

**TABLE 2**

Comparison of Observed Fission Product DF's with Flowsheet

Fission Product	Ref Flowsheet DF (HA & HS)	AGR Fuel DF (HA & HS)	BWR Fuel DF (HA & HS)
Ruthenium	$1.0 \times 10^3$	$0.9 \times 10^3$	$5.0 \times 10^3$
Caesium 134+137	$4.5 \times 10^3$	$6.75 \times 10^4$	$4.2 \times 10^4$
Cerium	$3.3 \times 10^3$	$1.1 \times 10^5$	$6.5 \times 10^4$

DF is Concentration of FP in Feed per g of Uranium  
Concentration of FP in Product per g Uranium

**Uranium - Plutonium Separation Performance**

Table 3 shows typical uranium-plutonium separation performance of the 1B(1BX, 1BXX, 1BS) system compared with reference flowsheet expectations.

**TABLE 3**

Comparison of Observed U-Pu Separation Performance with Flowsheet

	Ref Flowsheet DF	AGR Fuel DF	BWR Fuel DF
Removal of Pu from U product	$3.3 \times 10^3$	$2.2 - 4.8 \times 10^4$	$1.3 \times 10^4$
Removal of U from Pu product	$2.1 \times 10^3$	$1.6 - 10 \times 10^4$	$2.5 \times 10^4$

**Amounts of Uranium and Plutonium In Waste Streams**

Table 4 shows the percentage of the expected flowsheet quantities of uranium and plutonium found in waste streams from the solvent extraction contactors. These amounts are also expressed as percentages of the feed quantities in the fuel being reprocessed. The waste streams are further treated to remove the uranium and plutonium, but the waste stream compositions are a good measure of extraction and backwash efficiency.

**TABLE 4**

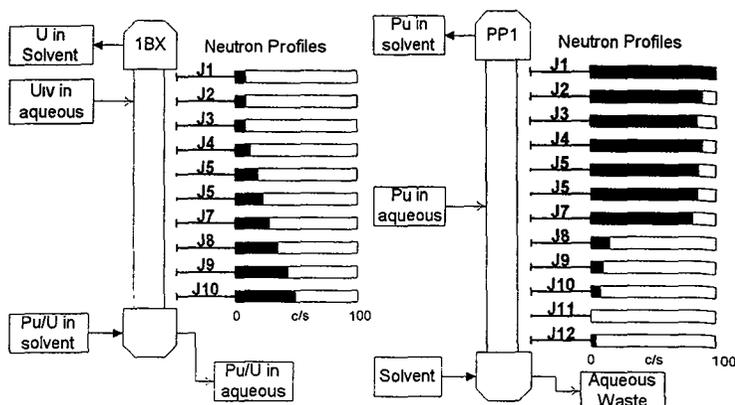
Uranium and Plutonium Content of Waste Streams

Waste Stream	U or Pu	AGR Fuel		BWR Fuel	
		% of Ref F/S	% of Feed	% of Ref F/S	% of Feed
Aqueous from HA Column	U	100	0.001	100	0.001
Aqueous from HA Column	Pu	0.1	0.0004	0.1	0.0002
Solvent from 1C M/Settler	Pu	25	0.002	13	0.0001
Aqueous from PP1 Column	Pu	24	0.03	25	0.02
Solvent From PP2 Column	Pu	3.2	0.003	7.2	0.003
Aqueous from UP1 M/Settler	U	187	0.003	-	-
Aqueous from UP2 M/Settler	U	5.8	0.00003	-	-

**Neutron Monitor Response**

The neutron profiles produced by plutonium in the 1BX and PP1 columns are shown in Figure 3. These profiles are from the "trend" neutron monitors positioned at 1m intervals up each column and show the plutonium concentration profiles. The high concentration at the base of 1BX, tapering off up the column, is typical and shows satisfactory backwashing of plutonium from the solvent into the aqueous, with very little penetrating to the top of the column. The PP1 column which has the main aqueous plutonium feed entering at approximately half of its height shows a characteristic extraction "front" with little or no plutonium penetrating down the column. This is consistent with the low amounts of plutonium in the aqueous waste from this column.

FIGURE 3



### Discussion of Solvent Extraction Performance

Performance of the solvent extraction processes was excellent with generally high fission product decontamination in the HA cycle and excellent removal of plutonium from the uranium stream in the 1BX/1BXX system. Uranium removal from the plutonium stream in the 1BS column was also extremely good, lessening the need for this removal in the PP cycle. It is recognised that this good performance is partly due to a lower than flowsheeted uranium IV content of the plutonium stream leaving 1BX, uranium IV being less extractable than uranium VI. The 1B system received extensive chemical and hydraulic development using a range of pilot plants - Phillips (1991) - and its satisfactory operation shows the value of this.

The uranium and plutonium content of waste streams was in all cases a very small percentage of that fed to the plant and, with one exception, was at or below flowsheet expectations. The exception was the waste from UP1 mixer settler which had a higher uranium content than expected. The reasons for this are unclear, but it is anticipated that adjustment of operating conditions will reduce it.

DF data for the PP and UP cycles is not available from the initial operation with low burn-up fuel. This is because the low fission product content of this fuel, together with the high efficiency of the HA cycle, mean that the concentrations of fission products entering the purification cycles are too small to measure reliably. This will be addressed as higher burn-up, shorter cooled fuel is reprocessed as the commissioning programme proceeds.

### CONCLUSIONS

The design, construction and commissioning of THORP has been the most challenging single project ever undertaken by BNFL. The solvent extraction plant uses well established reprocessing technology in an innovative way so as to minimise the number of solvent extraction cycles needed to meet product quality specifications, and the number of waste streams. The plant was commissioned and set to work without significant difficulty and this was due to extensive development work and close liaison between developers, designers and the commissioning teams during design, construction and commissioning.

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## ADVANCED SOLVENT MANAGEMENT IN REPROCESSING: 5 YEARS OF INDUSTRIAL EXPERIENCE

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### 1 INTRODUCTION

The La Hague UP3 plant commissioned in full active operation since 1990 has now reprocessed about 3000 tons of LWR fuels, with high and stable performances of extraction cycle.

The main breakthrough in extraction process is a new, global solvent management, which will be described hereafter. The same management is applied also in UP2-800, commissioned in 1994, and will be implemented in the Japanese reprocessing plant of Rokkasho.

### 2 SOLVENT MANAGEMENT IN PREVIOUS PLANTS

In previous French reprocessing plant Marcoule UP1, and La Hague UP2-400, solvent management was performed as follows:

- continuous treatment using alkaline washing at the outlet of each extraction cycles,
- variations of solvent stock due to losses by evaporation, addition of diluent for washing of aqueous raffinate, addition of TBP for continuous adjusting of TBP content of the solvent. It results in excess of solvent to be disposed,
- periodical circulation of solvent hold up from the less active cycle to the most active one,
- periodical discarding for disposal of solvent stock of the most active cycle, when operational difficulties appeared.

As a result a fairly large amount of contaminated solvent, with high content of degradation product had to be disposed.

Last, but not least, decontamination performances of extraction cycles were decreasing steadily as degradation product amount in solvent of the plant increase. In the same time ruthenium build-up in the solvent was observed, as well as accumulation of interfacial cruds.

### 3 SOLVENT MANAGEMENT IN UP3

#### 3.1 UP3 main extraction process

UP3 extraction process has already been described extensively [1], [2], [3].

Plutonium and uranium are codecontaminated and separated in the first cycle; plutonium is then concentrated and purified in two cycles, and uranium is further decontaminated in one extraction cycle. Thanks to the good performances of the extraction cycles, the third uranium cycle is seldom used.

All operations are performed in pulsed columns, annular or cylindrical, and in mixer-settler banks. All equipment is tight, and vented through process ventilation network, thus the evaporation rate of diluent is low.

### 3.2 Removal of TBP from aqueous phases

TBP has to be removed from aqueous phase leaving extraction equipment in order to:

- eliminate risks of sending TBP in evaporators, which could lead to formation of compounds with nitrate, some of them being explosive,
- ensure high purification factor in evaporators,
- minimise entrainment of solvent in downstream vessels, where evaporation of diluent could lead to formation of "heavy phase".

In UP3, TBP removal is performed by diluent washing of all acidic aqueous phases.

TBP dissolved or entrained in aqueous phases is extracted by diluent, which is then sent back to extraction cycles. In UP3, diluent flowrate and number of stages of diluent washing extractors are designed to ensure high efficiency of TBP removal.

The main disadvantage is the resulting decrease of TBP content in solvent.

Steam stripping is an interesting alternative to diluent washing to eliminate TBP from aqueous phase. It avoids the requirement of diluting the solvent of the plant with diluent, but it presents also the main disadvantage of generating large amount of low active aqueous streams, saturated with TBP and difficult to release without any further treatment.

### 3.3 Solvent regeneration

At the outlet of each extraction cycle, solvent is regenerated by successive washing using sodium carbonate, nitric acid and caustic soda, followed by a filtration [4]. Compared with previous plants, improvement results from with increased number of stages, counter current operation and increased mixing and settling time.

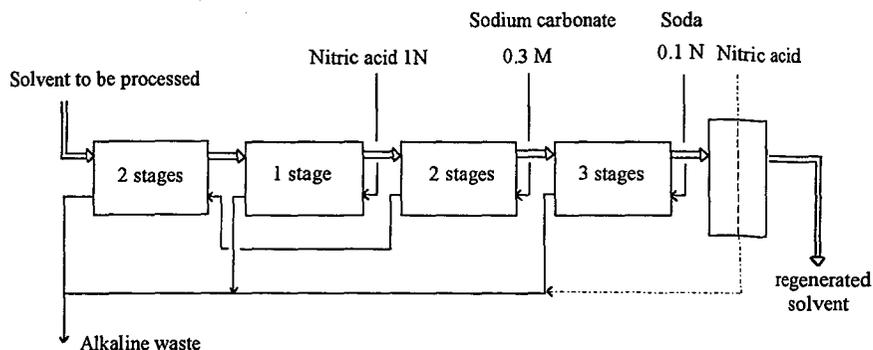


Figure 1 : solvent regeneration

### 3.4 Adjustment of TBP content

The recycling of diluent from diluent washing in extraction cycles results in decrease of TBP content of the solvent. Therefore concentrated TBP is continuously fed in solvent regeneration unit in order to maintain TBP content at 30 %. The excess solvent resulting from this adjustment is sent to the organic waste treatment unit.

### 3.5 Organic waste treatment [5]

The excess solvent is treated by distillation, primarily to recover pure diluent and concentrated TBP for recycling purposes. In addition distillation ensures the decontamination of the processed solvent, as well as elimination of heavy degradation products of the solvent, which are at least partly responsible of the loss of selectivity of the irradiated solvent.

This process is operated at reduced pressure to keep the solvent at moderate temperature, and with thin film evaporators in order to limit the residence time. These operating conditions were selected to avoid any significant degradation of the solvent and fouling of the evaporator.

The equipment includes:

- dehydration by distillation under reduced pressure,
- an evaporation system which evaporates (and decontaminates) the solvent and produces an active residue. This residue is composed mainly of TBP and heavy degradation products.
- a rectification tower, which fractionates the organic vapours into two parts: pure diluent and concentrated TBP.

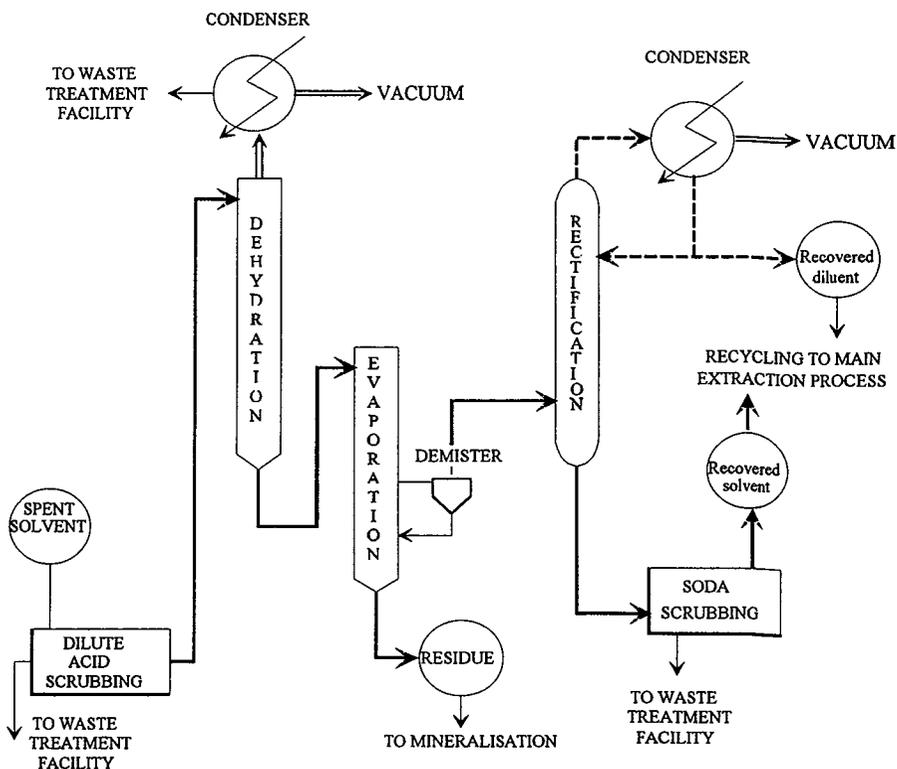


Figure 2 : organic waste treatment

### 3.6 Circulation of the solvent in the plant

The excess solvent from the less active extraction cycles (uranium and plutonium cycles) is sent to the first extraction cycle, in order to get the maximum renewal rate of the solvent in this cycle. Then the whole excess solvent from the plant is sent to organic waste treatment unit.

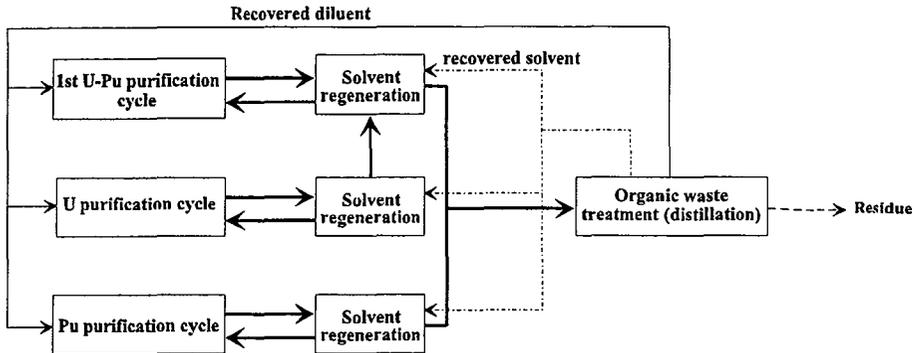


Figure 3 : solvent circulation in the plant

### 3.7 Mineralisation of solvent residue

The residue from the solvent distillation will be mineralised by pyrolysis process in the near future, and the resulting ashes will be embedded in concrete.

## 4 OPERATION RESULTS

The main results are as follows [6]:

- fissile material content in aqueous raffinates and in unloaded solvent are far lower than design values,
- very high decontamination factors achieved for  $\beta\gamma$  emitters
- high efficiency of U/Pu separation
- high efficiency of solvent regeneration unit
- very low residue rate in organic waste treatment unit (residue rate is the ratio between feeding flowrate and residue flowrate)
- very low activity of the solvent of the plant, and consequently low activity of residue
- recovered diluent free of TBP
- high TBP content of recovered solvent
- no significant accumulation of degradation products in the solvent

After more than five years of operation, and the processing of about 3000 tons of fuels, the efficiency of this advanced solvent management is clearly demonstrated. It plays a major role in the drastic reduction of long-lived waste volume, which has been made possible particularly due to the excellent performances of extraction process.

Process unit	Process item	Actual performance	Design value
1st purification and separation cycle	DF for fission products	Uranium : > 2 10 <sup>5</sup> Plutonium : > 8 10 <sup>4</sup>	2500 1250
	U-Pu separation	< 10 µgPu/kg U	1 mgPu.kg U
uranium cycle (only one cycle in operation most of the time)	DF for neptunium DF for plutonium	100 to 250 non significant	specifications : α activity (others than U): < 15000 dpm/gU βγ < 25 µCi/kgU
	βγ activity in uranium	< 2 µCi/kg U	
plutonium cycles	DF for fission products	100 to 1600	specification
	βγ activity in plutonium	< 1 µCi/gPu	< 8 µCi/gPu
Organic waste treatment	residue rate	about 1 %	5 %
	βγ activity of residue	< 0,2 mCi/l	18 mCi/l
	TBP in recovered diluent	< 200 ppm	< 200 ppm
	recovered solvent	80 % TBP	60 % TBP

Table 1 : UP3 operation performances

## 5 APPLICATION TO OTHER PLANTS

The solvent management presented here above could be considered as very specific to nuclear reprocessing industry.

However, with increasing environmental and safety constraints, it could be applied also, at least partially, to other industries using TBP extraction.

Several types of problems can be encountered:

- limitation of organic content in aqueous waste released to the environment,
- formation of complexes between TBP and some nitrate in evaporators, some of them being explosive,
- decreasing of solvent quality, leading at first to poor separation efficiency and formation of interfacial cruds, and then to discard solvent stock totally or partially,
- difficulty to dispose of large volume of used solvent.

The application of the advanced solvent management used in La Hague, at least partially, could help to solve these problems.

The two main steps which could be applied are:

- diluent washing, in order to remove TBP from aqueous phases,
- implementation of an organic waste treatment, which could be fed with a small fraction of the solvent flow used in the plant: it eliminates continuously degradation products, and by recycling of diluent and solvent, it drastically reduces the amount of organic waste to be disposed.

It has to be stressed that organic waste treatment is a rather simple and small unit, with very few items of mechanical equipment, and very low energy demands. In a plant like UP3, where the total instantaneous flow of solvent in extraction cycles is in the range of 5 m<sup>3</sup>/h, the organic waste treatment receive only about 200 l/h. Moreover, this flowrate is linked to the implementation of diluent washing; from the view point of solvent purification, and especially in non-nuclear plant, where solvent degradation is less severe, a much smaller solvent flowrate would be sufficient.

## 6 CONCLUSION

After five years of operation and the reprocessing of more than 3000 tons of nuclear fuels, the advanced solvent management implemented in UP3 has proven its efficiency from the viewpoint of process performances and waste minimisation. It has also been adopted for UP2-800 and new Japanese reprocessing plant.

Some steps of this management could also be used in non nuclear industry using TBP to solve environmental, safety and process difficulties. In particular the organic waste treatment process could be implemented at low cost to keep constant the solvent quality.

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## ENTRAINMENT COALESCING IN COPPER SX CIRCUITS

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### ABSTRACT

The volumetric capacity of many copper SX circuits is set by the ability of the settler to separate the two phases, and the effect that the residual entrainments have on down stream operations. Many plants suffer reduced throughputs when adverse conditions affect the separation, eg temperature, % reagent, pls suspended solids etc. Attempts to improve settler performance by use of in-situ and stream specific coalescing media have met with mixed success, as have flowing film bulk coalescent systems.

This paper discusses the testing and implementation of both insitu and stream specific coalescent materials in an Australian copper SX circuit. These low cost modifications have led to substantial improvement in plant performance and allowed higher flow rates to be processed during periods of adverse conditions. The media selected has been tolerant to crud both in the settlers and discharge streams, and has successfully removed polymerising silica from both aqueous and organic phases. This experience has been transferred to another operation suffering similar process conditions. The results from stream and insitu coalescing have confirmed the applicability of the media and flow selections to other operations.

### INTRODUCTION

The use of static mechanical coalescing medium in SX circuits has been the subject of much work over many years. Ritcey (1979) has a good summary of the state of the art on in-settler use, including multi tray Luigi settler, segmented circular settler (Davy design) with knitted mesh medium, inclined plate (IMI) design, baffles to CRA design. Other materials have been proposed including structured woven packing, Kimre (1993), interceptor plates, Spintek (1993), and strips of HDPE, Farias (1993); for removal of entrainment from advance streams.

The use of these techniques in the copper SX industry is very small, the major area being for the removal of organic from advance electrolyte to prevent organic burn in the EW cell house. Ritcey (1984) describes the use of a random packing for recovery of organic from a uranium raffinate stream. Other than the CRA baffles, used in the small Cockle Creek plant, and extra rows of picket fences, Hopkins (1994), there appears to be little documented use of mechanical coalescing within the SX settlers.

An operational review, Miller (1991) of both North and South American practice, showed that many operators utilised some mechanical improvement to their settlers. These included rows of inclined floor grating, nets and meshes strung across the settlers, extra rows of picket fences and other home made vertical baffles. All were required due to adverse operating conditions outside

the design criteria. These conditions have encompassed low temperatures, high reagent concentrations, high pls suspended solids, high levels of "dissolved" silica, Readett (1995), and degradation of the organic by manganese/permanaganate oxidation, Miller (1995).

### COALESCING REQUIREMENTS

The primary effect of poor settler performance is the appearance of a dispersion band of significant thickness at the settler discharge. This leads to high and highly erratic levels of entrainments in the streams advancing from the settlers, which in turn leads to effects such as high organic in raffinate and advance electrolyte, high pls entrainment in loaded organic, and high electrolyte entrainment in stripped organic. These situations can become unstable and require reduced volumetric throughputs to stabilise the operation satisfactorily.

The requirements for coalescing are different for in-settler and stream specific uses. Insettler coalescing aims primarily to **stabilise** the entrainment levels at around 500-1000 ppm; which is the normal design criteria for copper circuits. The elimination of shock loads due to entrainment of the dispersion band is important. Stream specific coalescing aims to **reduce** entrainment levels to 50-200 ppm in order to reduce costs (organic loss) or improve downstream process effectiveness (reduce organic burn and minimise pls to electrolyte).

There is thus an order of magnitude difference between the success criteria for the two different styles of operation which leads to two different sets of design criteria, and solutions for the problems.

### IN-SETTLER COALESCING

The observation of settler operations, at the two locations studied, showed similar gross effects; despite the fact that one was a conventional plant and the other was a Krebs design. There was a significant depth of dispersion band at the discharge end of the settler leading to uncontrolled carryover in advance streams. Initially, suspended nets were used in the conventional plant to help reduce entrainments but these become badly blocked by crud and tended to perform poorly after the first 1-2 weeks.

The selection of a permanent coalescing medium required the following criteria to be met:

Cheap, easy to make, materials readily available, have intermediate surface tension (so that both continuities could be treated successfully), chemically compatible, require simple installation, density greater than electrolyte to prevent floating, sufficient open area to allow crud to pass through unhindered.

One of the problems in media selection is that testing is not readily done, except in the industrial plant or a large pilot unit. Even on a large pilot unit full hydraulic similarity is not achievable. For this reason a scale up factor was used based on the stream coalescer specific flow rate,  $\text{m}^3/\text{hr}/\text{m}^2$  of media surface, and the target level of entrainment. A 1:4 ratio was used as the basis.

A packing type having the following feature was selected: random type packing, available in various sizes, made from a commercial plastic and readily available. The size of the packing was

selected based on the size of the openings available for crud passage. For the conventional settler this allowed a large size to be used, which occupied less than 40% of the settler volume. However with the Krebs unit a smaller packing size was necessary to preserve some clear space at the discharge for crud removal. In both cases the packing was contained in coarse mesh bags, manufactured from a 'solution' resistant material to prevent escape and blockage of pumps and valves.

## **STREAM SPECIFIC COALESCING**

Stream coalescing has been practised intensively on the aqueous streams from solvent extraction mainly to recover organic for economic reasons, and to prevent organic burn in the EW cell house. Coalescing of aqueous from the recirculating organic stream has however not found wide acceptance. Traditionally, a practice of having a large organic surge volume has been used to remove the aqueous. With highly adverse conditions this strategy has proved to be inadequate.

The starting point for selection of the medium for the loaded organic coalescor was that of removal of the organic from the electrolyte stream. Here the target of 10 ppm feed to the tank house is usually achieved by coalescing on an anthracite medium. To achieve 100 ppm of aqueous in the loaded organic a 1:10 scale up was used from the basis of the normal industry specific flowrate ( $\text{m}^3/\text{hr}/\text{m}^2$  of coalescing surface). This was tested in full scale columns to confirm design criteria and performance. Selection of the media size was referred to a successful operation described by Ritcey (1984), and the subsequent geometries developed for testing.

## **TESTWORK & DESIGN**

No preliminary testing or specific design work was required for the in-settler media. The loaded organic coalescing media was extensively tested at both plant sites prior to equipment design. Testwork indicated that both loaded organic streams responded well to the selected packing and specific flow rate. However the superficial velocity was found to be different to achieve the same success criteria. The h/d ratio required for the Krebs plant was twice that in the conventional process plant. This highlights the necessity of confirmatory testwork prior to implementation.

Engineering design was based on an upflow separator with aqueous trickling downward to the vessel bottom. Feed and overflow distribution was arranged to minimise short circuiting and hydraulic dead zones evident in other arrangements, Farias (1993). Aqueous removal was done below the feed distributor. Medium was contained within coarse mesh bags to allow ease of handling and prevent their escape into downstream equipment.

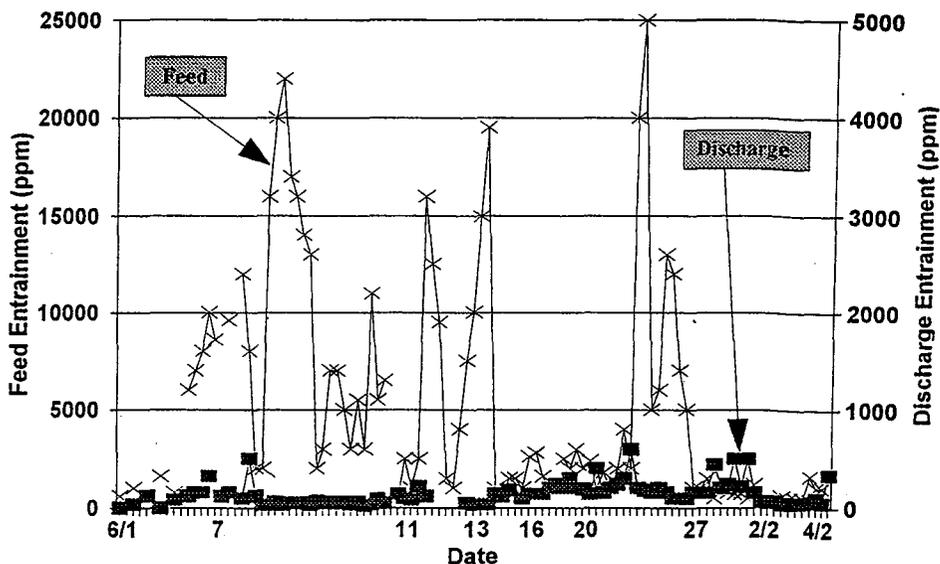
## **OPERATING RESULTS**

### **Stream Specific Coalescing**

Only one of these units has been installed to date. (The use of in-settler coalescing and a wash stage has reduced the urgency for this unit for the Krebs plant.) Figure 1 shows the results for the coalescor for the first two months of operation. The feed entrainments have been high with very wide fluctuations. The unit has proved consistent with an average 200 ppm aqueous in the loaded

organic, with a maximum of 400 ppm. Backwashing has been required on a four weekly cycle and has been integrated with the maintenance schedule. The high feed entrainment levels have resulted from the operation of the E1 mixer settler in organic continuity, to minimise crud and silica gel formation, Readett (1995). When coalescing aqueous from this settler's organic, when operating in aqueous continuity, the test unit media had become clogged with large jelly structures of silica gel. Farias (1993) also recommends operation of E1 in organic continuity for crud control but does not mention any blockages from an aqueous continuous operation.

**Figure 1 - Loaded Organic Coalescer  
Aq Entrainment in Feed & Discharge**



**In-settler Coalescing**

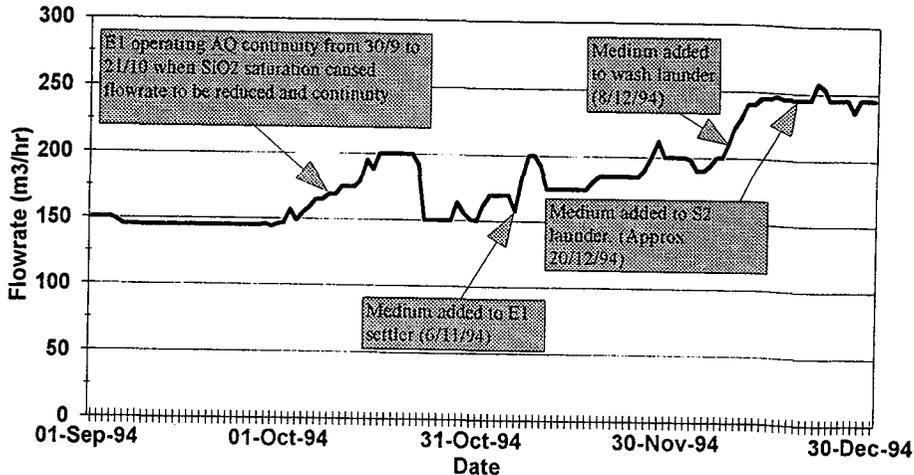
In-settler coalescing has been successfully implemented in two operations. One with conventional and the other with the Krebs technology. In the conventional plant, media was initially placed in E1 settler and the benefits were immediately obvious, with reduced entrainments and a more stable operation. The volumetric throughput was able to be maintained at design, despite the pls temperature being 10°C below design, and reagent concentrations 2-3% above design. Subsequently medium was added to E2 and the single strip stage. These served to reduce organic losses to raffinate and electrolyte.

A further benefit was the ability to operate in any continuity without excessive entrainments. E1 could be aqueous continuous without silica gel blocking the loaded organic coalescor. The gels were formed within the settler and were carried through to raffinate via E2. E2 was often operated aqueous continuous at very low temperatures, as this was more stable than organic continuous. The raffinate losses were controlled to acceptable levels by the medium.

The Krebs technology plant was limited, to 50% of pls throughput, by the appearance of large dispersion bands and uncontrolled entrainments from both E1 and the wash stage. Carryover of

manganese and chloride was having deleterious effects in the EW tankhouse. Medium was added in successive steps to various stages of the SX circuit. Figure 2 shows the pls throughput as affected by the action of the medium.

Figure 2 - Plant Throughput Increase With Media Addition



The full quantity of medium was added to E1 initially; which fully stabilised its operation. Aqueous entrainments dropped from +20,000 ppm to average 500 ppm with long periods of unmeasurable levels (using site techniques).

The organic phase in this operation exhibited a long 'induction period' before any visible phase separation occurred, which was combined with long break times. Because this induction period was longer than the residence time of the emulsion in the Krebs lauder, it was thought that little or no separation was occurring here. As a result the settler was having to perform as a "conventional" unit giving rise to the throughput limitations.

The wash stage Krebs lauder was partially filled with medium, which showed immediate benefits. There was a visually obvious phase separation at the end of the lauder where none had been previously, and the dispersion layer disappeared from the settler. Aqueous entrainments fell to acceptable levels. The wash stage began to remove entrained dissolved solids and electrolyte contamination fell to below target levels, particularly for Mn and CL. Iron control bleed was stopped to preserve a minimum chloride level for growth morphology control. A similar addition of media to the S2 lauder enabled plant full hydraulic capacity to be obtained for the first time. Flows have however been reduced due to the launders flooding with the medium in place. With

the success of the in-settler coalescing combined with the wash stage, loaded organic coalescing has not proved necessary to date.

In neither operation has there been any difficulty with crud blockage of the medium. Crud production is reduced due to the ability to change continuity for crud control without suffering excess entrainments as a result. The medium is generally cleaned by hose down once every 6-12 months as part of the normal settler clean out programme.

## DISCUSSION

The operating results show that the initial aim to provide a cheap, readily available, low tech solution to high entrainments, which is easily implemented and reliable, has been met. Crud accumulation does not occur in the settler medium and performance targets can be met. A rational basis for media size selection and scale up has been established, which requires only short term confirmatory field testing to establish the individual optimum parameters.

The use of coalescing medium in settlers and advance streams has shown the benefits of this low cost field modification. Analysis of the conventional plant results has shown that achievement of 200 ppm of aqueous in loaded organic is consistently possible. At these levels the carryover of deleterious ions into the electrolyte is much reduced. In the case where high plis chlorides are present, up to 4 g/l can be treated by this method before consideration of a wash stage is necessary. In both operations it has been shown that the severe contamination is caused primarily by erratic entrainment levels with very high peaks. Use of coalescing medium eliminates these peaks and produces a far more consistent level of entrainment.

In a further case study the use of in-settler coalescing could be readily cost justified by the reduction in acid lost in the electrolyte iron control bleed. A payback of four months was indicated for this project.

## ACKNOWLEDGMENTS

The authors would like to thank the staff of Girilambone Copper Company and Nifty Copper Operations for permission to publish this paper. The view of the authors do not necessarily reflect those of the companies.

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## COPPER SOLVENT EXTRACTION PROCESS: OPTIMIZATION OF THE DESIGN AND OPERATION OF PUMPER AND AUXILIARY IMPELLERS

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### ABSTRACT

A new generation of hydraulic efficient pumper and auxiliary impeller designs is the result of an extensive research program focused on improving the overall performance of existing SX-plants. Combined with the proper scale-up, these optimized designs will greatly reduce aqueous and organic entrainment losses, reduce or eliminate air entrainment and crud formation, enhance mass-transfer and maximize the overall copper yield. Compared with conventional pumps, the R320-style pumps require less installed power and have fewer wetted surfaces. The A310 and A6000 auxiliary impellers require an order of magnitude less power than the pumps, representing the lowest installed power of any auxiliary impeller design available today. Both pumper and auxiliary designs can be fabricated into any material, including composites. Currently, these new pumper and auxiliary impellers are installed full-scale in many SX-installations ranging in flow rates from 20 to 3500 m<sup>3</sup>/hr (90 to 15000 G.P.M.) and developed heads up to 1.3 m (51 inches).

### INTRODUCTION

Over the last 25 years copper solvent extraction has seen many modifications to increase the overall mass transfer yield and quality of the copper and to reduce entrainment losses. Many of these enhancements dealt with the design of the settlers, internals or post-processing. Others are described as *new* technologies, departing in design greatly from the conventional SX-design. Interestingly, the mixing technology of pumper design has not been pursued. Specializing in the field of mixing, *LIGHTNIN's* approach to optimizing the SX-process is to first understand the process requirements of mixing two immiscible phases (Oldshue 1983). Then it is possible to determine the impact of impeller design on head, flow, droplet distributions, entrainment losses, air entrainment, phase stability, mass transfer and the copper yield.

The pumper impeller must satisfy the head and flow requirement of the SX-plant. If it fails this, all other advantages are futile. The pumper must also create a stable dispersion. If too little energy is applied, phase disengagement takes place. This greatly reduces the interfacial area for mass transfer and so reduces the copper yield. If too much mixer power is applied, surface splashing and air entrainment will occur, which will contribute to crud formation. Finally, optimized pumper designs minimize the creation of fines, thus reducing entrainment losses. Proving pumper scale-up is essential.

The auxiliary impeller is required to refresh the boundary layers between the dispersed droplets and the continuous phase to enhance the mass transfer and copper yield. This is ideally accomplished by rapidly mixing the phases without additional shear. Although this is physically impossible, auxiliary impellers with streamlined blade profiles like the A310 and A6000, impart very little shear, but generate 3-13 turnovers of the box volume per residence time (Olderstein and Preston, 1986). The required power is

an order of magnitude less than for the pumper. The optimum auxiliary design will allow for some coalescence to take place. This preconditions the dispersion before entering the settler.

### HEAD-FLOW CHARACTERIZATION OF PUMPER IMPELLERS

To understand how impeller design affects head and flow, more than 300 pumper designs and positions were tested at various impeller speeds (Giralico et al.(1995)). Comparing their characteristics in dimensionless terms is convenient. The head number is described by  $N_H$ , the flow number by  $N_Q$ , and the power number by  $N_P$  in equations 1-3.  $H$  is head [m],  $N$  is impeller rotational speed [ $s^{-1}$ ],  $D$  is impeller diameter [m],  $Q$  is flow rate [ $m^3/s$ ],  $P_{imp}$  is impeller power [kW],  $\rho$  is the dispersed density [ $kg/m^3$ ] and  $g$  is the gravitational constant= $9.81 m/s^2$ .

$$N_H = \frac{2gH}{TS^2} = \frac{2gH}{(\pi N D)^2} \quad (1), \quad N_Q = \frac{Q}{ND^3} \quad (2), \quad N_P = \frac{P_{imp}}{\rho N^3 D^5} \quad (3)$$

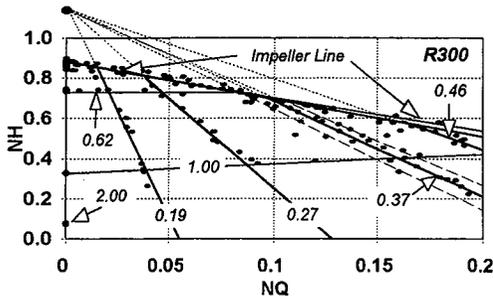


Figure 1: Head-Flow characteristics of a straight-bladed R300 pumper,  $D=152$  mm. The effect of the orifice size ratio (numbers in figure are  $D_0/D$  ratios) is quite pronounced.

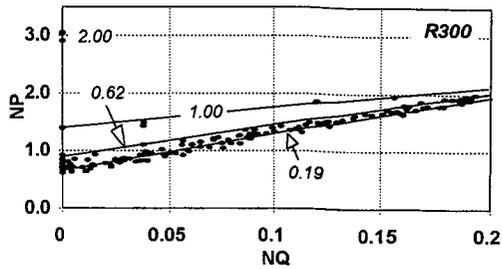


Figure 2: Power-Flow curve for the same data as in Figure 1. The power number is independent of  $D_0/D$  for  $D_0/D < 0.5$  over the entire range of  $N_q$ .

Figure 1 is illustrative of typical head-flow pumper curves, in this case a straight-bladed pumper,  $D=152$ mm (6"), with constant blade width,  $W/D=0.2$ , and off-bottom clearance,  $C/D=0.02$ . The maximum head numbers are described by the *Impeller Line*. The effect of the orifice to impeller diameter ratio ( $D_0/D$ ) is very pronounced. The slopes of the *Orifice Lines* (constant  $D_0$ ) are more negative than the impeller line. The resulting pumper curve is not really a curve, but the asymptote of these two intersecting lines. All pumps of the same design share the same impeller line. As  $N_Q$  increases beyond the *Intersecting Point*, the orifice line describes the departure from the impeller line, showing that the greater restriction to flow is in the orifice. For example, the intersecting point is at (0.1,0.7) for  $D_0/D=0.37$ . Note that the extrapolation of every orifice line toward  $N_Q=0$  merges at one point, the *Frictionless Impeller Point*. This point is always greater than the *Dead-Ended Point*, which is the intercept of the impeller line with the  $N_H$ -axis. The main restriction to flow left of the intersecting point is not the orifice, but the impeller design itself. Each impeller design has its own characteristic impeller line and slope. Above  $D_0/D$  ratios of 0.5, head decreases at low flow, until  $N_H$  reaches 0.08, which corresponds to a pump-box without a false bottom.

Figure 2 shows the power-flow characteristics of the same pumper. Orifice size has little influence on power if  $D_0/D < 0.5$ . Unlike open tank mixers that require no head, the power number of a pumper is not a constant in the turbulent regime. It is a direct function of the flow number.

## HYDRAULIC EFFICIENCY

From the Bernoulli equation, the hydraulic power (Equation 4) describes the power required to move the dispersion with a given density over a given height at a given flow rate. This hydraulic power,  $P_{Hyd}$ , is always less than the total amount of power dissipated,  $P_{Imp}$ , from the pumper to the fluid (Equation 3). The ratio of hydraulic to impeller power is defined as the hydraulic efficiency,  $\epsilon$  or Eff (Equation 5). The impeller design with the highest  $\epsilon$  can achieve the highest delivered head for the least amount of power. Based on Figures 1-2, the optimum R300 has an orifice size ratio of 37-46% for  $0.04 \leq N_Q \leq 0.095$ . For  $N_Q \geq 0.1$  the optimum orifice size is between 46-62%.

$$P_{Hyd} = \rho g H Q \quad (4), \quad \epsilon_{Hyd} = \frac{P_{Hyd}}{P_{Imp}} \quad (5)$$

## DROPLET SIZE DISTRIBUTIONS

Giralico et al.(1995) described the equipment and procedure to study droplet sizes. The video imaging technique, described by Dilley and Post(1995), was fully automatic. To study the drop breakup mechanism, a low concentration of organic was used to eliminate drop coalescence. This technique is best suited to determine the amount of fines generated. 1000-2000 droplets were counted and compared statistically per pumper design. Number ( $f_{n,i}$ ), area ( $f_{a,i}$ ), and volume ( $f_{v,i}$ ) fractions were determined over a wide range of tip speeds. The Sauter Mean diameter,  $d_{32}$ , is used when describing the interfacial area between two phases for mass transfer discussions.

$$f_{n,i} = \frac{n_i \cdot d_i}{\sum n_i \cdot d_i} \quad (6), \quad f_{a,i} = \frac{f_{n,i} \cdot d_{n,i}^2}{\sum f_{n,i} \cdot d_{n,i}^2} \quad (7), \quad f_{v,i} = \frac{f_{n,i} \cdot d_{n,i}^3}{\sum f_{n,i} \cdot d_{n,i}^3} \quad (8), \quad d_{32} = \frac{\sum f_{n,i} \cdot d_{n,i}^3}{\sum f_{n,i} \cdot d_{n,i}^2} \quad (9)$$

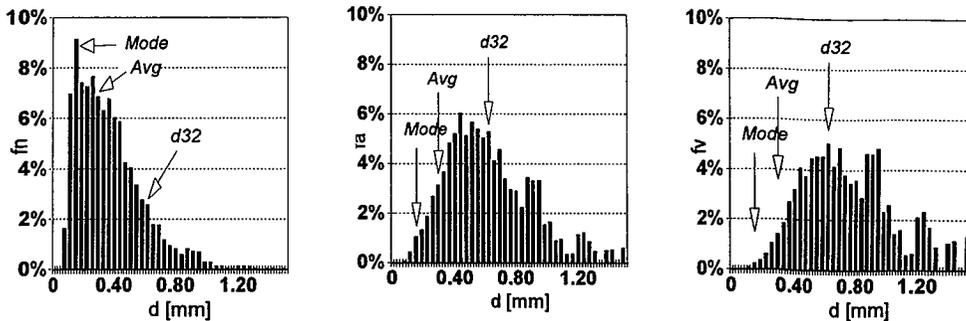


Figure 3: An example of the three types of droplet distributions generated when studying the effect of pumper design. This example is for a straight-bladed, 152 mm R301 pumper operating at 2 m/s with a  $D0/D=0.46$ .

Figure 3 shows an example of the three distributions, including the Mode (most prevalent fraction), Avg (number mean or avg), and  $d_{32}$  for a straight-bladed R301 at the low tip speed of just 2 m/s. While 9% of the total distribution has a drop size of 0.13 mm, only 1.3% of that fraction contributes to the total interfacial area for mass transfer, and less than 0.5% contributes to the total dispersed volume. Although  $d_{32}$  does not represent the average drop size on a number count basis, it is a good representation of the drop average, based on area and volume fractions. The  $f_n$  distributions exaggerate the fines production, and are used to characterize pumper design. The  $f_a$  distributions are useful for mass transfer

considerations, where the  $f_v$  distributions are used to compare relative entrainment losses. Entrainment is predictable when droplets are present under a certain droplet diameter.

Figure 4 is a composite of the results of many droplet experiments. Because of the wealth of information, the comparison is restricted to the number fraction mean or avg. The R320-style impellers and the Avendeno impeller generate the largest mean droplet sizes, because they minimize the formation of fines. The R301 always shows the smallest mean droplet size for any given tip speed.

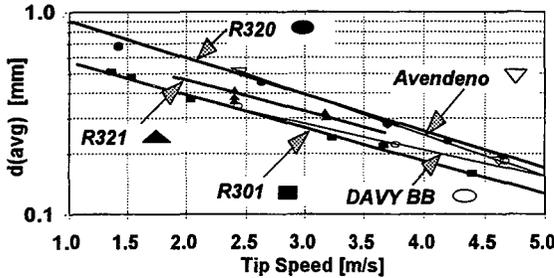


Figure 4: Effect of tip speed (TS) on the mean (avg) droplet size of five different basic pumper designs. In this comparison, only the R301 had straight blades. There is a significant spread in mean droplet sizes based on pumper design.

The R301, R321 and R320 impellers are positioned directly above the false bottom, whereas the Avendeno and Davy-BB pumps use draft tubes. At high enough tip speed, TS, the efficiency curves are parallel (Figure 6), like the semi-log lines in Figure 4. They also follow the same order. Thus, there is a very strong correlation between the hydraulic efficiency,  $\epsilon$ , and the mean droplet size of a given pumper design. Only the Avendeno pumper does not follow suit. Although it generates large droplets, it is apparent from Figure 5 that it cannot pump as much as other pumps, due to its low head and flow characteristics. This makes it ideal for pilot plants, but not for industrial large scale installations.

The data points in Figure 5 correspond to a tip speed of 3.8 m/s. Once again, except for the Avendeno pumper, the order from highest to lowest hydraulic efficiency matches the order from largest to smallest mean droplet size. Thus, a strong correlation between hydraulic efficiency and mean droplet size exists.

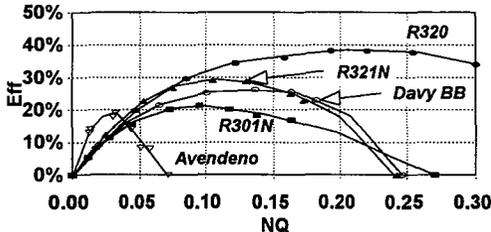


Figure 5: Hydraulic efficiency,  $\epsilon$  or Eff, as a function of  $Nq$  for the 5 pumper designs in Figure 4. The points represent  $TS=3.8$  m/s.

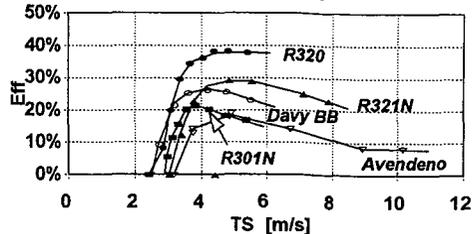


Figure 6: The hydraulic efficiency,  $\epsilon$  or Eff, as a function of impeller tip speed, TS.

### SHEAR GRADIENTS and TURBULENCE - LASER LAB STUDY

Shear and turbulence is caused by excess power. This excess is the difference between  $P_{Imp}$  and  $P_{Hyd}$ . Shear and turbulence is required to create a stable liquid-liquid dispersion. Too much shear and turbulence will cause excessive fines. Giralico et al. (1995) showed a comparison between the R320 and the R301 pumps by using laser Doppler velocimetry. The shear gradients of the R301 were shown to be much greater than the R320. This trend is the same as the trend in Figures 4-6. Again, these measurements support our claim that hydraulic efficient pumps generate fewer fines. The laser grams

also showed that the strong recirculation pattern under the Davy-BB is responsible for smaller droplets and its lower hydraulic efficiency.

### ENTRAINMENT LOSSES

DeVinney (1994) performed a large scale study to determine if a correlation existed between hydraulic efficiency and entrainment losses. He tested a curved-bladed R321N and a straight-bladed R301N. The pumper diameters were  $\approx 2.2$  m with tip speeds of  $\approx 5.2$  m/s. Figure 6 predicts a higher efficiency for the R321N, and therefore larger droplets. Lower entrainment values were expected. One S1 pump box was retrofitted with the R321N. The other S1 pump box in this parallel train had the R301N. Everything else was the same. They shared the same feed streams. S1 process conditions were organic continuous. Figure 7 confirms the prediction. Over this 3.5 month period from Winter to Spring, the entrainment losses of both aqueous in organic (530 - 294 ppm) and organic in aqueous (11 - 4 ppm) were cut in half with the R321N. High spikes were attributed to rain storms. Under the same process conditions ( $Q \approx 2000$  m<sup>3</sup>/hr  $\approx 9000$  G.P.M.) the R321N dissipated only 0.47 kW/m<sup>3</sup>, whereas the R301N dissipated 0.76 kW/m<sup>3</sup>. This is 38% less power for the same duty.

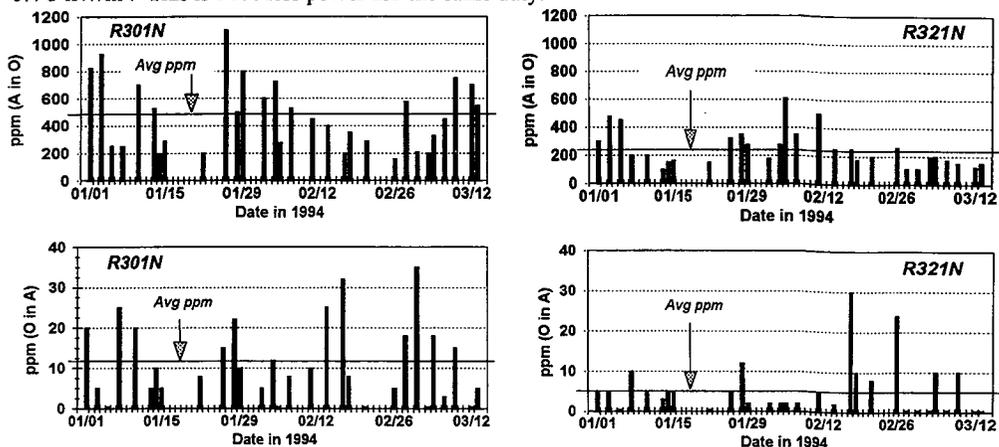


Figure 7: Comparison of entrainment losses between the R321N and the R301N in an existing industrial SX-plant for S1; organic continuous. Over a 3.5 month period a significant reduction in both aqueous in organic and organic in aqueous entrainment was observed.

### PHASE STABILITY and AIR ENTRAINMENT: THE POWER RANGES

To optimize mass transfer and the copper yield, phase disengagement must be avoided to obtain maximum interfacial area. Thus, a minimum degree of turbulence is required and is described by a minimum  $P_{imp}/V$ . Increasing  $P_{imp}/V$  increases mass transfer, but beyond a point, air entrainment is inevitable. This should be avoided to minimize the formation of crud. Thus, a maximum degree of turbulence should not be surpassed, which is described by a maximum  $P_{imp}/V$  and depends on baffle design and tank shape. Figures 8-9 show the optimum operating ranges for the R320 at liquid depth ratios of  $Z/T=0.5$  and 1.0. The limits depend on residence time and liquid depth. Almost twice the energy is needed for deep tanks. An optimum liquid depth ratio,  $Z/T$ , in the pump box will maximize hydraulic efficiency and satisfy all of the SX-specific process requirements. These considerations are important to know when designing a new SX-plant. To retrofit an existing plant, the head and flow requirements and the pump box dimensions will dictate the maximum hydraulic efficiency possible, while staying within these power ranges. For deep tanks, a dual impeller configuration is preferred.

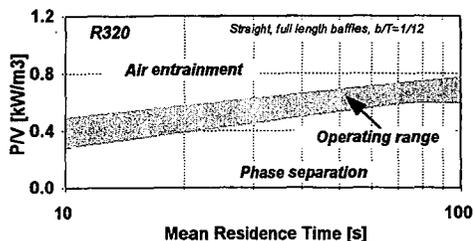


Figure 8: Optimum operating range of a R320 pumper with  $Z/T=0.5$ ,  $D/T=0.5$ ,  $W/D=0.2$ .

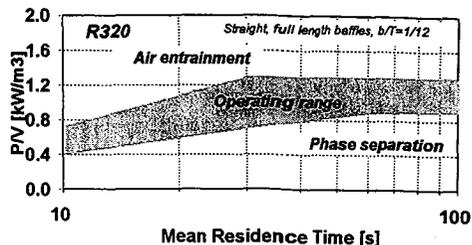


Figure 9: Optimum operating range for a R320-pumper:  $Z/T=1.0$ ,  $D/T=0.5$ ,  $W/D=0.2$ .

The optimum power range for the auxiliary impellers looks much different. They are of course dependent on the impeller type, but they are very dependent on placement as Figure 10 shows. Notice that the A310 in an up-pumping mode requires an order of magnitude less power than the optimized pumper. This lower specific power will allow for some coalescence, without phase disengagement, while still achieving up to 13 turnovers per residence time. Because of the narrow optimum operating range, which is flow and geometry dependent, we highly recommend variable frequency controllers for these low powered auxiliaries, too. This fine tuning capability will enable a SX-plant to exceed expectations. Overpowering the auxiliaries is too easy.

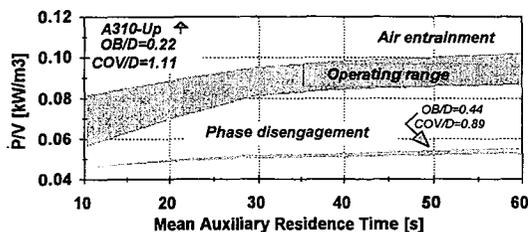


Figure 10: Optimum operating range for an up-pumping A310 auxiliary,  $D/T=0.375$ ,  $Z/T=0.75$ . By placing the A310 closer to the surface, the required power drops a factor of 2.

## CONCLUSIONS

This study resulted in a better understanding of the mixing requirements of the SX-process. As a result, a family of optimized curved-bladed impellers has been designed to improve the solvent extraction process by reducing entrainment losses through higher hydraulic efficiencies. This study has also shown that the optimized pumper design is not only a function of hydraulic efficiency, but it must satisfy head and flow requirements, within upper and lower power ranges. All conventional SX-plants can benefit from these optimized pumps and auxiliaries. There is no need to acquire *new* SX-technologies.

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## PRACTICE IN SMALL-SCALE SOLVENT EXTRACTION PLANTS OF COPPER

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### ABSTRACT

In recent years, several small-scale solvent extraction copper plants have been built in China. The copper resources copper comprise sandstone oxidized copper ores, earthy oxidized copper ores and copper sulphide ores. This paper describes the practice of leaching, solvent extraction and electrowinning in three plants which treat the foregoing copper ores. By analyzing the production and management in these plants it is shown that small-scale solvent extraction plant of copper is economic and flexible, and that it is suitable for countries with limited copper resources.

### INTRODUCTION

Owing to the soaring copper price and other well-known reasons the L-SX-EW technology for copper is becoming increasingly popular and new plants are constantly being established. It has been reported some new L-SX-EW plants with a total capacity of 1.8 mt/a of cathode copper will be built and put into production in Latin America area within the remaining years of this century. The capacity of existing and proposed L-SX-EW plants total over 5 kt/a. The world largest plant, Phelps Dodge's Morenci, AZ, USA, even reached 150 kt/a cathode copper. The production cost of these plants is, without doubt, much lower than that of the conventional smelting-refining plants the with the same capacity. Great process has been achieved in the establishment of L-SX-EW plants in China recent years. There are over 40 L-SX-EW plants in operation and under construction with total capacity of 13 kt/a of cathode copper. This capacity will reach 40 kt/a by the year of 2000. However the capacities of the individual plants are very low. Most of them are in the range of 200 ~ 300 t/a. Even the largest one is only 3 kt/a. It is obviously uneconomical to employ conventional smelting-refining process at such a low production capacity. Some R-L-EW plants, which were in vogue in time in 1960s in China, had to be shutdown for economic reasons. Then, why have the L-SX-EW plants with small capacity developed so prosperously? It is attributed to the advantages that the L-SX-EW process has, such as fewer operation units, fewer kinds of auxiliary materials, low operation cost, low capital cost and short construction period. This process is particularly suitable for exploiting copper deposits

that are scattered, small in quantity and of poor communication conditions, just like in China. There has long been a serious short supply in China's copper market. And, what is more, the copper price was skyrocketing recently. These, of course, enhance the development of this process in China. The cathode copper produced with L-SX-EW technology is about 2 per cent of China's total primary copper production. That is expected to be 10 per cent by 2000.

### **PRACTICE OF L-SX-EW PLANTS**

The plants mentioned below were built according to the characteristics of copper resources. So they employ different leaching methods. Besides, they are all larger ones in China.

#### **Guangtong L-SX-EW plant**

Located in Guangtong town, Lufeng County, Yunnan Province, the Guangtong L-SX-EW Plant commenced production in 1993. It is the first plant of its kind in China that produce more than 1000t cathode copper per year. The ore treated in the plant is a type of sandstone. This type of ore is widely distributed in central Yunnan and are highly scattered. The main copper mineral in the oxide ores is malachite, while in the sulphide ores it is chalcocite. The principal gangue mineral is quartz. The ore can be easily leached with low acid consumption. The typical chemical analysis of the ore are as follows:

1 ~ 1.5% Cu, 1.08% Fe, 0.57% MgO, 0.92% CaO, 86.96% SiO<sub>2</sub> and 4.70% Al<sub>2</sub>O<sub>3</sub>.

The run-of-mine ores are crushed to minus 20 mm in a two stage open circuit with jaw crusher, then transported by tractors to the pad for heap construction. The total area of the pad is 50,000 m<sup>2</sup>. The ores are stockpiled at different zones. Each layer of the heap is 3m high. The 3-spray system consists of soft PVC pipes and wobblers. The spray rate is adjusted at 10 l/m<sup>2</sup>.h. The PLS assays 2 g/l Cu at the pH 1.6. The SX circuit consists of two stages of extraction and one stage of strip. The flow rate of PLS is 100 m<sup>3</sup>/h. The phase ratio O/A for the extraction and strip is 1:1 and 5:1, respectively. To maintain the 1:1 O/A ratio in the mixers, recycling of the phase is required. The mixer-settlers with shallow settlers and double mixers are designed by myself. The residence time for mixing is 2.5 min. The specific flow for settlers is 4.0 m<sup>3</sup>/m<sup>2</sup>/h. The stage efficiency for the extraction is 90%. The extraction reagent is Acorga M5640, a product of ZENECA Specialties. The diluent is lamp kerosene. The content of M5640 in the organic phase is 7 v%. The copper recovery in extraction is 95%. The loaded organic is stripped by spent electrolyte containing 35 g/l Cu and 180 g/l H<sub>2</sub>SO<sub>4</sub>, yielding pregnant solution containing 45 g/l Cu and 168 g/l H<sub>2</sub>SO<sub>4</sub>. After removal of entrained organic by passing through a settling pond and a sand filter the pregnant electrolyte is send to a holding tank and pumped to the tank house cells. There are 54 cells with Pb-Ca-Sn anodes. Direct current is supplied by a silicon controlled rectifier. The current density is 160 A/m<sup>2</sup> and the cell voltage is 2 V. The current efficiency is 95%. To improve surface quality of the cathodes and to protect the anodes Guar gum and sulphate of cobalt (at a Co<sup>2+</sup> concentration of 60ppm) are added to the electrolyte. The purity of cathode copper is 99.98%, which is superior to China's standard of 99.95% for grade A copper. The maximum daily production is 4.5t cathode copper.

#### **Bailongchang L-SX-EW plant**

The raw material treated at Bailongchang Plant is earthy oxide copper ore. The principal mineral-containing layer in the copper belt is silicate dolomite. After the long period of weathering, and the Ca, Mg ions being washed away, it becomes a loose brown earthy matter. The main copper-containing mineral is malachite, associated with small amount of bornite, chalcopyrite and tenorite. As the main gangue mineral, quartz, occurs as the form of irregular grains. Malachite is dispersed as clastics. Part of it is in the form of intergrowth around the

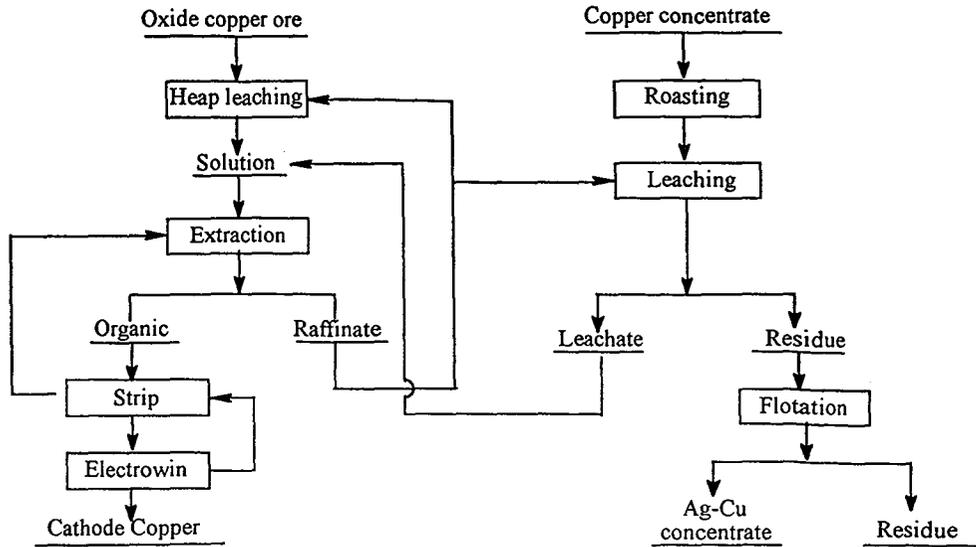
quartz grains and in the limonite as irregular grains. The chemical analysis of the ore are 0.5 ~ 1.4% Cu, 3.79% Fe, 0.006% Co, 0.31% CaO, 0.79% MgO, 5.0% Al<sub>2</sub>O<sub>3</sub> and 81.25% SiO<sub>2</sub>. Since the particle size of the ore is very small (most are minus 5 mm), the ore is thus called "earthy copper ore". This copper belt (region) is of several hundred km long stretching disconnectedly from the northeast to the southwest of Yunnan province. The reserve of several hundred thousand tonnes as copper metal was proved early in the 1960s. However, it was considered unrecoverable, submarginal ore at that time because the recovery of copper by concentrating was only 40%. Only after the first L-SX-EW plant treated such ore was successfully put into operation in 1992, was this once unrecoverable resource get then economic. 4 L-SX-EW plants treating such kind of ores have been put into operation so far. Among them the Bailongchiang Plant is the largest one. It's design capacity is 1000 t/a cathode copper. The ore coming from an open-pit mine is agglomerated with a  $\Phi$  1.6 × 6 m drum agglomerater. The agglomerates are delivered through a belt conveyor to the pad for heap construction. They are cured for 24 hours prior to irrigation leaching. Each layer of the heap is 2.5 m high. When the heap reaches 10 m high, lump ores are buried to increase the percolation of the heap. The PLS containing 2 g/l Cu at pH 1.5 ~ 2.0 is sent to the SX circuit consisting of two stages of extraction and one stage of strip. The organic phase is 7 v% M5640 in kerosene. The flow rate of PLS is 80 m<sup>3</sup>/h. There are 34 cell with Pb-Ca-Sn anodes in the tankhouse. The tankhouse is equipped with a 5000 A/75V silicon controlled rectifier. The daily capacity of the plant is 3t of cathode copper.

#### **Chuxiong R-L-SX-EW plant**

A high-silica, low-sulphur and low-precious metals copper concentrate is treated at Chuxiong Plant. The concentrate assays 25.26% Cu, 4.8% Fe, 43.2% SiO<sub>2</sub>, 3.1% CaO, 0.94% MgO, 3.8% Al<sub>2</sub>O<sub>3</sub>, 0.1% Co, 0.13% Zn and 7.1% S. Large quantities of flux will be needed for treating such a kind of copper concentrate by convention smelting technology. Electric furnace smelting is commonly adopted for this kind of material. Hydrometallurgical processing was chosen by processing Chuxiong Plant. The process is described below and show in Fig.1. The design capacity is 3000 t/a cathode copper-500 t/d from oxide ore, the remainder 2500 t/a from roasted concentrate. The concentrate, grading 25%, is roasted in a rotary kiln at 550 °C. The calcine is leached in tanks for 2 hours. After being washed with raffinate and pressure filtered the leached residue containing 0.6 ~ 1.0% Cu is sent to the flotation circuit for recovering silver. The leachate from agitation leaching is combined with washing solution and the solution from heap leaching of oxide ore, forming the PLS. This PLS containing 6 g/l Cu at pH 1.8 is delivered to the SX circuit which consists of two stages of extraction and one stage of strip. The flow rate of PLS is 100 m<sup>3</sup>/h. The organic phase is a 18 v% solution of M5640 in kerosene. The O/A ratio for the extraction and strip is 1:1 and 2.0:1, respectively. Mixer-settlers with shallow settlers and double mixers, are employed. The loaded organic is stripped with spent electrolyte containing 35 g/l Cu and 180 g/l H<sub>2</sub>SO<sub>4</sub> to produce an electrolyte containing 45 g/l Cu and 168 g/l H<sub>2</sub>SO<sub>4</sub>. This electrolyte is subjected to a gas flotation column and sand filter for removing entrained organic and, then pumped to the EW circuit. There are 74 cells in the tankhouse. Each cell is comprised of 31 Pb-Ca-Sn anodes and 30 cathodes. The current density is 180 A/m<sup>2</sup>. A 6000 A/154V silicon controlled rectifier is installed for providing direct current.

The heap leaching of oxide ore can consume excess sulphuric acid and acidic waste water derived from the calcine leaching circuit. Therefore, there is no spent acid discarded. Besides, the sulphuric acid consumption can be reduced.

Fig.1 Flowsheet of the L-SX-EW Plant



INVESTMENT AND PROFIT

Investment

Generally speaking, the unit investment for conventional smelting-refining plants will be higher than that for the L-SX-EW Plants. The former is commonly USD 3000 /t.a, while the latter is about USD 1500 ~ 2500/t.a. However, the economics will may be questionable if the capacity of the plant is less than 10 kt/a.

China is an undeveloped country, economically. The developer of a number of small L-SX-EW plants within a couple of years is the result of China's peculiar resource and economic circumstances. According to statistics, the unit capital investment of such a small plant is only 8000 ~ 10000 yuan/t.a (RMB). And the investment for the fixed assets accounts only for 70% of the total. Comparisons between investments with different production processes are shown in Table 1. Although the capacity of the L-SX-EW plant is much smaller than that of the smelting-refining plants, the unit investment of the former is still less than that of the latter. Short and direct the reason is that the process, from ore to cathode copper, for the L-SX-EW plant is . Additionally, no special facilities for environment protection. Most of the small L-SX-EW plants are built near mines. Ores are mainly supplied by mine owner. There is no need for constriction large power stations for the small plant as normally the very low power supply requirements can be met locally. The mixer-settlers, electrolytic cells, solution ponds,as well as most of the pipelines and valves are made of or lined with PVC, so considerable costs can be saved. It is more important is that China's economy be considered during the design of the plants. It is also important to make full utilization of the local labour resources. Therefore, a number of small plants, are established and operating with full vitality.

Cost

Unit production costs with different technology are listed in Table 2

It can be seen from Table 2, that the operation cost in China's small L-SX-EW plants is RMB

5.26 yuan/lb (USD 0.63/lb). It is much lower than that in the conventional smelting-refining plants, though it is higher than that in the large commercial scale L-SX-EW plants in USA, Australia etc.

**TABLE 1**  
The comparison of investment for different plants

Process	H-L-SX-EW	Agg-L-SX-EW	R-L-SX-EX	Sm/Ref(blast furnace)
Capacity(t/a cathode copper)	1,000	1,000	3,000	10,000
Investment* (10 <sup>6</sup> yuan,RMB)				
Crushing	0.30		0.30	
Agglomeration		0.35		
Roasting			3.00	
Agitation leaching			1.50	
Heap leaching	0.60	0.80	0.80	
Solvent extraction	0.50	0.50	2.00	
Electrowinning	1.50	1.50	4.50	
Reagents and anodes	2.40	2.40	7.00	
Auxiliary	3.20	3.70	5.30	
Smelting-refining				150.00
Total	8.50	9.25	24.00	150.00
Unit investment(10 <sup>3</sup> yuan)	8.50	9.25	8.13	15.00

\* The data are from real plants. Investment for mining and concentration are not included.

\*\*The data for smelting-refining plants refer to the investment estimation of the related plants.

**TABLE 2**  
Unit Production cost (yuan RMB/t cathode copper)

Process	H-L-SX-EW (1)	Agg-L-SX-EW (2)	R-L-SX-EX (3)	Sm/Ref(blast furnace)
Costs constitute				
Ore***	5,275	4,500	14,083*	16,000
Crushing	200			
Agglomeration		100		
Roasting			200	
Leaching	2,000	3,000	2,000	
SX-EW	2,063	2,063	2,063	
Smelting				6,000**
Management and maintenance	2,000	2,000	2,000	
Total	11,538	11,663	19,483	22,000

\* The price of copper concentrate is 16,000 yuan/t Cu, and for oxide ores is 4,500yuan/tCu.

\*\*Data based on the payment for contracted processing of copper concentrates ordered in China.

\*\*\* The cost for mining, concentration and transportation are included.

### Profit

The economic profit for different plants is listed in Table 3.

**TABLE 3**  
profit for different plants (10<sup>6</sup> yuan RMB)

Plant	H-L-SX-EW (1)	Agg-L-SX-EW (2)	R-L-SX-EX (3)	Sm/Ref(blast furnace)
Capacity of Cathode Copper	1,000	1,000	1,000	10,000
Sales income	24.00	24.00	72.00	240.00
Operation cost	11.54	11.66	58.45	220.00
Gross profit	12.46	12.34	13.55	20.00
Value-added tax	1.88	1.86	2.04	3.02
Income tax	3.39	3.06	3.80	5.61
New profit	7.19	7.02	7.71	11.40
Static payday period(year) (Construction period not included)	1.18	1.32	3.16	13.18

The data from Table 3 indicate that H-L-SX-EW plants can result in the highest profit while the smelting-refining plants, the lowest. The payback period of the capital investment for the former is only 1.18 years, whereas for the latter is about 13 years. That is the real reason why can so many small L-SX-EW plants exist in China.

### CONCLUSION

There was a number of small R-L-EW plants in China in 1960s. Their output of cathode copper once accounted for 0.8% of China's total copper production. Because dilute copper-bearing waste water can not be treated, and the recovery of copper is low, hence the operation cost of these plants is higher than that of the conventional smelting-refining plants. They all had to be shutdown in 1970s. In 1990s some hydrometallurgical copper plants in which solvent extraction technology is predominant were established, based on overcoming the disadvantages the above-mentioned plants. Operating practices in recent years show that with advantages of low capital investment and high profit these L-SX-EW plants, though small in size, can really be competitive with conventional smelting-refining plants. The copper production by these plants accounts for 3% of China's total at present. And it will probably be over 10% by the end of this century.

The practices of China's small L-SX-EW plants indicate that production of cathode copper through solvent extraction technology in small plants near mines with low reserves and poor communication condition is not only technically feasible but also economically attractive. It can also be said that solvent extraction technology can be used to exploit and utilize the copper resources of countries with poor resources.

### ACKNOWLEDGEMENT

The author wishes to thank Muding copper mine for providing technical data.

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# MULTIVARIABLE EXTRACTION COLUMN CONTROL THROUGH POPULATION BALANCE EQUATION MODELLING

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## ABSTRACT

In this work, a model predictive control study is conducted on an Oldshue-Rushton extraction column pilot plant. The extraction column is modeled by full-scale Bivariate Population Balance Equations (BPBE). A rapid numerical procedure is developed for solving the equations. Control of the raffinate concentration and dispersed phase volume fraction are performed by a modified dynamic matrix control algorithm integrated with the BPBE model. Computer simulations of the control study are performed. The results of this study can demonstrate the advantages of the use of a full dynamic model in control algorithms and analyses.

## INTRODUCTION

To design and control process equipment in which the dispersed phase is present, appropriate models for the system must be constructed that accurately describe the phenomena occurring within it. Theoretical approaches for the modeling of agitated liquid-liquid dispersions have been pursued over the past several decades. An approach, which is based on population balance equations (Hulburt and Katz, 1964; Randolph and Larson, 1966; Ramkrishna, 1974), has been employed to explain well the non-uniform holdup profiles and drop size distributions along the contactor. However, the extraction control designer and researcher still does not make sufficient use of the fundamentally sound information available for rigorous simulation. Hence, the operating point is usually set at a lower efficiency condition because a large safety margin of operation is required for control using classical control theories or empirically derived process models.

Two of the reasons that restrict the application of the Population Balance Equation model are the computational intensity and hardware requirement. Solving the full equations for highly interactive systems will not meet the time requirement demands by real time control algorithms. However, solutions of the full population balance equation would yield, for the general case, more information than what is frequently needed. Hence, it is desirable to abstract only the necessary information from the full population balance equation models. One of the approaches, i.e. method of moments (Hulburt and Katz, 1964), had been used extensively.

This study integrates the advantages of dynamic modelling (Bivariate Population Balance Equation) and advanced control algorithms (Nonlinear Dynamic Matrix Control) to improve the efficiency of extraction columns by using the Oldshue-Rushton column as an example. We have also employed the method of moments and several other numerical solution techniques to reduce the computational intensity and hardware requirements.

## MODELING OF THE EXTRACTION COLUMN

We have modeled the extraction of butyric acid from the continuous phase (water) to the dispersed phase (toluene). The multistage extraction column is considered to be a series of interconnected stirred tanks. By assuming (1) spatial homogeneous drop distribution for each stage, (2) mass transfer coefficients are independent of the age of drops, and (3) drop volume,  $v$ , and solute mass of a drop,  $m$ , are the only internal coordinates, a population balance equation can be written for each cell. These equations account for drop coalescence, breakage, flows between cells and mass transfer between phases and take the form:

$$\frac{\partial}{\partial t} n^n(v, m, t) + \frac{\partial}{\partial m} \left[ \frac{dm}{dt} n^n(v, m, t) \right] = F^n(v, m, t) - E^n(v, m, t) + B_+^n(v, m, t) - B_-^n(v, m, t) + C_+^n(v, m, t) - C_-^n(v, m, t)$$

where  $n(v, m, t)$  is the bivariate number density function, the superscription  $n$  represents the stage number,  $F(v, m, t)$  is the number frequency of the net flow of drops into the cell,  $E(v, m, t)$  is the number frequency of the drop leaving the cell,  $B_+(v, m, t)$  and  $B_-(v, m, t)$  represent the source and sink due to breakage events, and  $C_+(v, m, t)$  and  $C_-(v, m, t)$  are the source and sink due to coalescence events, respectively. The expressions given by Tsouris and Tavlarides (1994) and Tsouris et al. (1994) for the coalescence, breakage and exit frequencies are adopted here.

The second term on the left hand side represents the flux of drops into the control volume due to mass transfer. The two film theory for the interphase mass transfer modeling is applied. The overall mass transfer coefficient  $Kd$  can be calculated from the individual mass transfer coefficient for dispersed phase,  $kd$  (Handlos and Baron, 1957), and continuous phase,  $kc$  (Skelland and Moeti, 1990).

For the continuous phase modeling, we assume the mass transfer does not affect the total volume and density of the continuous phase. Thus, the conservation equation for the continuous phase can be written as

$$V_{cell}^n \frac{d(1-\phi^n)}{dt} = Q_c^{n+1} - Q_c^n$$

and the conservation equation for the solute mass in the continuous phase is

$$V_{cell}^n \frac{d(1-\phi^n)C_c^n}{dt} = Q_c^{n+1}C_c^{n+1} - Q_c^nC_c^n - \int_0^{\infty} \int_0^{\infty} m \frac{\partial}{\partial m} \left[ \frac{dm}{dt} n^n(v, m, t) \right] dm dv$$

The last term in the right hand side accounts the interphase mass transfer for a given cell. To solve the above model equation in a fashion that provides the necessary information for control purposes, we introduce a mass conditional density function  $f(m, t|v)$  and its marginal function as  $n(v, m, t) \equiv f(m, t|v)N(v, t)$ . Then, the method of moments (Hulburt and Katz, 1964) is applied, which transfers the above model equations to a set of moment equations. For this problem, we are only interested in the values of the dispersed phase volume fraction and the raffinate concentration for the column. These values can be easily calculated from the zero and first moment. A bracket operator,  $\langle \rangle$ , is employed so that the  $j$ 'th mass moment is simply represented as  $\mu_j(v, t) = N(v, t) \langle m^j \rangle_v$ . Also, these equations are discretized along the drop volume with a equal grid spacing. As a result, the first moment equation for the  $i$ 'th class droplets in stage  $n$ , can be formulated as

$$\begin{aligned} \frac{d}{dt} \mu_{i,i}^n(t) = & N_i^n(t) \left\langle \frac{dm}{dt} \right\rangle_i + N_i^{n-1}(t) z_{q,i}^{n-1}(t) \langle m \rangle_i^{n-1} + N_i^{n+1}(t) z_{eb,i}^{n+1}(t) \langle m \rangle_i^{n+1} \\ & - N_i^n(t) [z_{q,i}^n(t) \langle m \rangle_i^n + z_{eb,i}^n(t) \langle m \rangle_i^n] + \sum_{l=i+1}^L 2g_l(t) \beta(l;i) N_i^n(t) \left\langle \frac{v_l}{v_i} \right\rangle \langle m \rangle_i^n \\ & - g_i(t) N_i^n(t) \langle m \rangle_i^n + \sum_{l=1}^{i-1} \frac{1}{2} h(i-l, l) \lambda(i-l, l) N_i^n(t) N_{i-l}^n(t) [\langle m \rangle_{i-l}^n + \langle m \rangle_i^n] \\ & - \sum_{l=1}^L h(i, l) \lambda(i, l) N_i^n(t) N_l^n(t) \langle m \rangle_i^n \end{aligned}$$

Similarly, the zero and higher moment equations can be derived. The zero and first order moment equations can be used to solve the continuous phase conservation equations.

### DYNAMIC MATRIX CONTROL

A multivariable control algorithm based on the Dynamic Matrix Control (DMC, Garcia 1984) has been developed. The block diagram of the control algorithm is shown in Figure 1. The BPBE model is mainly used to predict the future process output trajectory. However, the BPBE model can also be used to update the element values of the dynamic matrix which results in a nonlinear DMC algorithm. Both linear and nonlinear control algorithms are considered in this study. As shown in the block diagram, the algorithm is considered to be nonlinear when the highlighted block exist. The control variables are the average holdup and the raffinate concentration. A process interaction analysis has been implemented to determine the proper manipulated variables. As a result, the agitation speed and dispersed phase inlet solute concentration were selected as the manipulated variables.

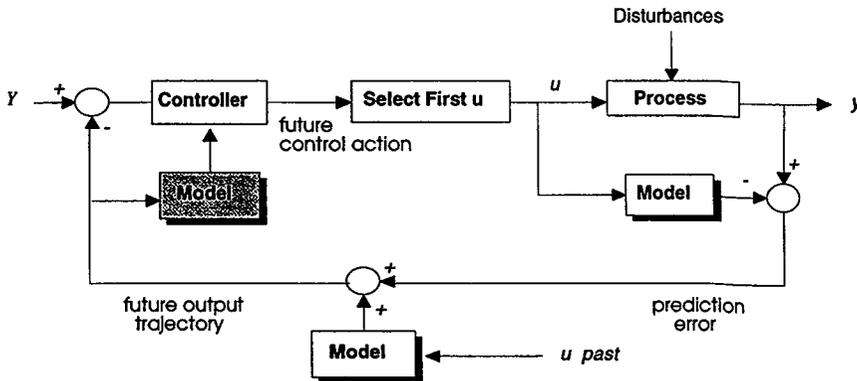


Figure 1 Block Diagram of Control Algorithm

## RESULTS

In Figure 2, the calculated concentration and holdup profiles of the dispersed phase are compared to the experimental data obtained by Tsouris (1992). The upper profiles are the dispersed phase solute concentration in different stages, whereas, the lower profiles show the comparison of average holdup. As indicated, good agreement between the experimental data and the calculated results has been achieved without adding any adjustable parameters to the calculations. Furthermore, the solution method used in this study has reduced the computing time such that the BPBE model can be used directly in the real time control algorithm. For a typical run, such as the calculation shown in Figure 2, calculated results can be obtained within 80 sec on a P5-66 PC, which is far less than the transient times for the actual process (~1500 sec).

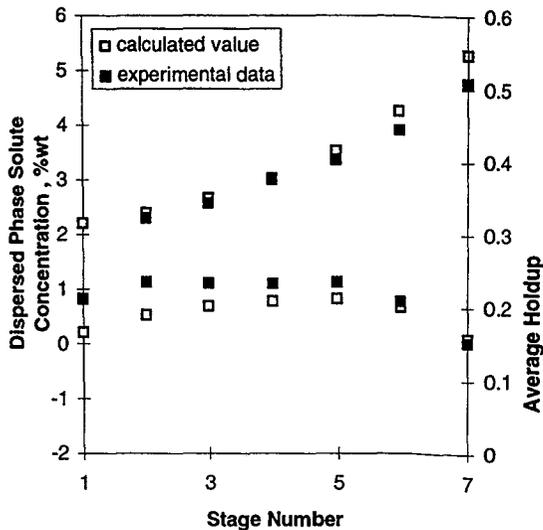


Figure 2, Comparison of calculated and Experimental Results ( $Q_d/Q_c=0.36/0.54$  L/min ; rpm=160 ;  $C_{c,i}/C_{d,i} = 4/2$  %)

Figure 3.a and Figure 3.b show the results of a computer servo control simulation. The system was allowed to reach the steady state of 15% holdup by volume and 3% raffinate concentration by weight. Then, step setpoint changes were introduced to the system at time zero. The setpoint of the average holdup was increased to 30%, whereas, the raffinate concentration was reduced to 1% by weight. Figure 3.a shows the response of the control variables and Figure 3.b shows the control actions of the manipulated variables in order to achieve the required setpoint changes. The solid line shows the results of the nonlinear algorithm whereas the dotted line shows the linear algorithm. As shown in the figures, the nonlinear controller successfully brought the system to the new setpoints, while an oscillatory control action of the dispersed phase inlet concentration was observed for the linear controller. This observation also indicates the nonlinearity of the process.

## CONCLUSION

The hydrodynamics and mass transfer behavior of the extraction process in the multistage column are modeled in this study. A rapid solution method is also developed. Comparison of the steady state calculated values and experimental data show good agreement. The fast solution plus its ability to provide necessary information make the solution method valuable to many practical applications. One of the applications, i.e. process control, is also shown. Computer servo control simulations have indicated that the studied system is strongly nonlinear. Thus, a nonlinear control algorithm, such as the nonlinear dynamic matrix control algorithm developed in this study, has potential to improve the efficiency of the extraction column.

### Manipulated Variables

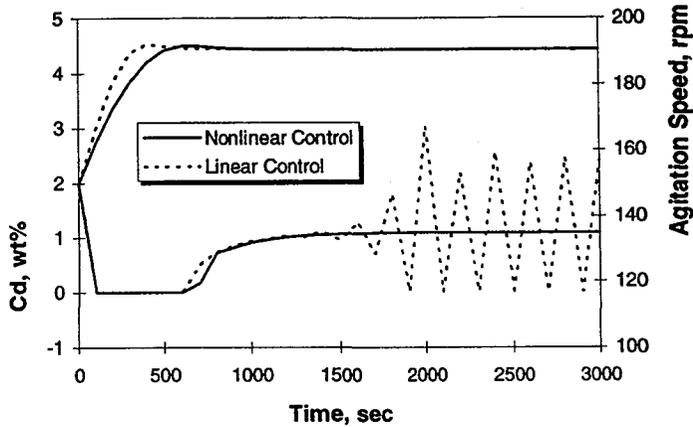


Figure 3.a Control Actions of Step Setpoint Change  
( $Q_d/Q_c=0.54/0.54$  L/min ;  $C_{c,i} = 4\%$  wt)

### Control Variables

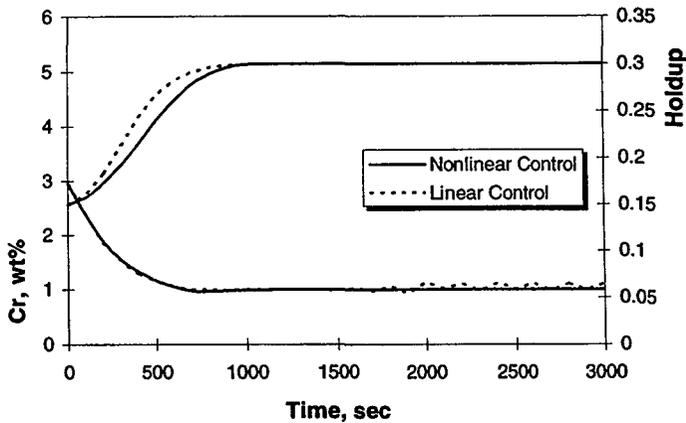


Figure 3.b Response of the Control Variables of Setpoint Changes

### ACKNOWLEDGMENTS

The authors gratefully acknowledge the National Science Foundation through Grant CTS-9017138 and the New York State Center for Advanced Technology in Computer Applications and Software Engineering (CASE Center) at Syracuse University for the support of this work.

## NOMENCLATURE

### Letters

$f$	mass conditional density function
$g$	breakage frequency
$h$	collision frequency
$K, k$	mass transfer coefficient
$m$	solute mass
$N$	number of drops per unit volume
$n$	number of drops per unit volume and solute mass
$Q$	flow rate
$V, v$	tank, drop volume
$z$	exit frequency

### Greek Symbols

$\beta$	daughter drop probability density function
$\lambda$	coalescence efficiency
$\mu$	mass moments
$\phi$	holdup

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## EXPERIENCE WITH COLUMN FLOTATION IN ELECTROLYTE CLEAN-UP DURING PROCESS UPSET CONDITIONS

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### ABSTRACT

In 1993 two new Leach SX-EW Plants were commissioned in Australia; Girilambone (GCC) and Nifty (NCO). Both plants utilised Jameson Cell column flotation devices (1) as the principle means of removing entrained organic from electrolyte, prior to the electrolyte being pumped to electrowinning. During the commissioning of both plants the performance of the Jameson Cell was monitored. Results indicated that the cells were recovering in excess of the 85% organic entrainment recovery upon which they were designed.

Subsequent operations at Girilambone and Nifty encountered process upset conditions. During the periods of process upset, severe degradation in the performance of the cells were noted with highly variable organic recoveries of 0 to 70%. Subsequently downstream processes were significantly affected by the increase in organic exiting the Jameson Cell.

Investigation of the process upset conditions indicated that the major cause, at both sites, was related to degradation of the solvent extraction organic. The degradation resulted in the generation of surfactants within the organic which dramatically affected the physical characteristics of the organic, leading to a significant reduction in surface tension and increase in phase disengagement times. These effects were further amplified by the presence of colloidal silica within the organic.

The recovery of entrained organic from electrolyte, using the Jameson Cell, is primarily a function of the surface characteristics of the organic. As a consequence the reduction in surface tension of the organic will reduce the ability of the cell to recover organic.

Upon removal of the surfactant and silica from plant organic it was found that the original physical characteristics of the Jameson Cells improved and design recoveries of organic were again achieved.

## **JAMESON CELL PRINCIPLES**

The Jameson cell is a device designed to provide an ultrafine dispersion of air bubbles in an aqueous media by utilising an orifice and downcomer arrangement. For solvent extraction applications the recovery of entrained organic from electrolyte is a function of the differences in surface tension between the two liquids and the hydrophobic nature of the organic as the dispersion of air bubbles is mixed with the electrolyte. When there is contact between bubble and organic the organic will coat the air bubble as a thin film. The coated air bubbles rise to the cell surface and then break. On breaking the released organic will coalesce and remain at the cell surface until purging.

In order to improve recovery of organic the downcomer operating pressure can be increased. This results in an increase in orifice jet velocity. As a consequence air volume increases along with mixing within the downcomer. Conversely decreasing downcomer pressure will reduce organic recovery.

## **JAMESON CELL OPERATIONS**

Previously published data, Readett and Steemson (1993) and Readett and Clayton (1993) indicates that two parameter which can adversely effect performance of the Jameson cell are the presence of crud in feed material and the presence of surfactant.

At Mount Isa Mines, Miller and Readett (1992) and Readett (1992), during a period of high crud in feed (and a low operating pressure of 60 kPa) the Jameson cell recovery was variable between 30 and 60%. The nature of the crud material recovered showed minimal free organic association and very poor compaction properties (ie a 'stable' crud). After a campaign of crud removal and an increase in downcomer operating pressure to 170 kPa, recoveries were improved to 70 - 90%.

During the commissioning of the Morenci Jameson Cell there was considerable crud in the feed. Both organic and crud recoveries were within design specifications of > 75 % recovery at feed organic entrainment levels > 40 ppm. However two major differences in the operation (compared to MIM) were noted. Firstly the cell was operating at significantly higher operating pressures of 180 - 220 kPa and secondly the nature of the recovered crud. This crud exhibited a very unstable nature, i.e. it compacted very readily and within minutes the recovered crud had compacted to about 1/10th of its original volume.

Whilst conducting laboratory trials of the Jameson Cell a surfactant was added to the electrolyte to reduce the effective liquid surface tension. Results from the tests indicated that the presence of the surfactant had a dramatic negative effect on organic recovery.

## **GIRILAMBONE COPPER COMPANY (GCC) - OPERATIONS**

Whilst commissioning was in progress at the Girilambone SX-EW plant the performance of the Jameson Cell was monitored. Early data collected indicated that the Jameson Cell was recovering in excess of 85% of the entrained organic. The feed entrainment levels recorded at this time were between 20 and 50 ppm.

Soon after commissioning the SX organic suffered some degradation due to the presence of manganese in electrolyte Miller (1995). As a consequence of the degradation, surfactants were generated which acted to decrease the surface tension characteristics of the organic from ~ 26 dyne/cm down to 20 dyne/cm. The symptoms detected in the SX plant as a consequence were extended phase disengagement times (from 60 seconds to a range of 240 - 300 seconds), excessive entrainment (50 - 100 ppm) and poor Jameson Cell performance (variable organic recovery of 0 - 70%). As previously discussed the Jameson Cell performance characteristics are a function of the surface tension characteristics. Hence any reduction in surface tension had the effect of reducing the cells capacity to recover organic.

It was anticipated that once the surfactant was removed from the organic, using clay treatment Mattison, Kordosky and Champion (1983), then the general performance of SX and specifically the Jameson Cell performance would improve. Unfortunately this was not the case. Further investigation of Jameson Cell operations at GCC showed organic recovery behaviour was still below design specifications of > 75% at feed entrainments of > 40 ppm.

The survey of Jameson Cell performance (November - December 1993) at GCC indicated the cell recovery of organic and crud was variable within the range of 20 - 75% with performance reducing as the crud/solids loading in S-I increased (toward the end of the test period). Two samples of recovered organic/crud were taken from the surface of the Jameson cell. This crud exhibited very poor compaction properties and minimal association with 'free' organic. The natural compaction of the crud material was such that even after 24 hours the crud had only compacted to 60% of its original volume.

Inspection of samples showed that much of the entrainment entering the cell was in the form of crud. Crud is a generic term used to describe a stable combination of organic, aqueous and particulates. This material tends to be specific for each operation. By definition crud is deleterious to SX as it, 1) retains a significant proportion of organic rendering its useless in an SX context and 2) results in transfer of impurities between stages.

The Jameson Cell relies on the fact that in an aerated, aqueous media entrained organic has a preference to air (hydrophobic). When organic contacts an air bubble it then forms a thin film around the bubble. When the bubble breaks at the solution surface the organic coalesces and can be recovered in a bulk form.

The actual feed to the cell contained significant quantities of crud. If this crud is stable, ie has a high affinity for organic, then upon contact with an air bubble in an aqueous environment the crud will behave as a discrete particle. That is the organic will not be released from the crud and then coat the air bubble. The fundamental mechanism for recovery by the Jameson Cell then changes to the recovery of discrete particles (ie synonymous with mineral flotation). For this recovery mechanism the surface characteristics of the crud must be hydrophobic. By its very nature the hydrophobicity of the crud will be less than the organic, hence recoveries will suffer accordingly. Secondly the Jameson Cell operational regime must be changed to that for particulate recovery,

ie air flow may have to be reduced to reduce turbulence in the cell which could dislodge weakly attached particles from the rising air bubbles, or re-entrain discrete crud particles at the surface of the cell.

Analysis of collected crud indicated the major component (>50%) was amorphous silica. If the crud exhibits surface characteristics like silica then crud removal will be difficult due to the silica's hydrophilic characteristics (for silica to float a solution pH 7 is required). A separate paper has been published detailing the presence and effect of silica on the GCC operation Miller , Readett and Hutchinson (1996).

The performance data for the GCC cell is shown in Figure 1. During this entire test period however the Jameson Cell had been operating at 90 - 140 kPa, below the recommended operational pressure range of 140 - 180 kPa. It was also noted on several occasions that the cell operating level was well below that recommended for optimum cell residence time.

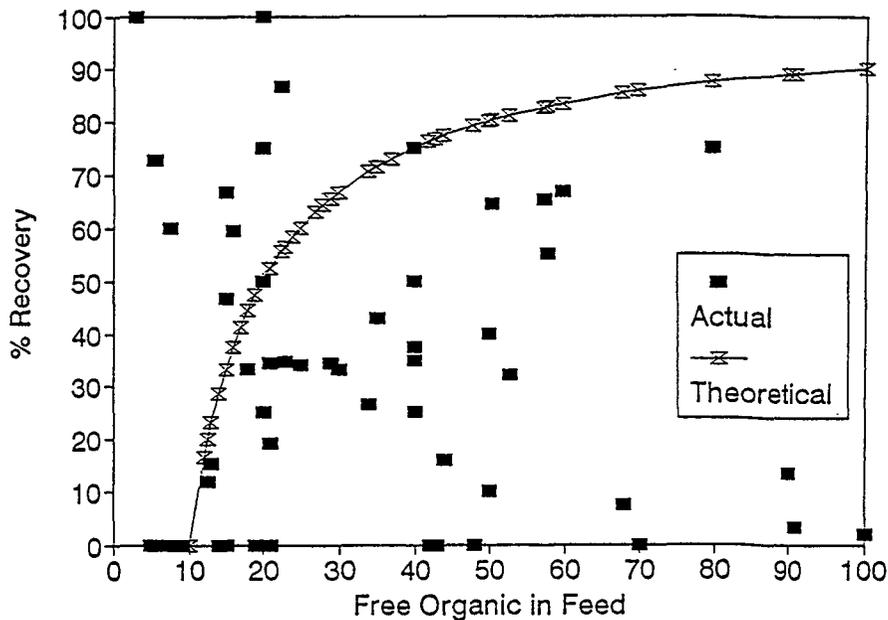


Figure 1. Jameson Cell performance data - November/December 1993

In view of the findings it was anticipated that if 1) optimum cell operating parameters (pressure and level) were maintained, 2) the high stable crud loadings were reduced significantly and 3) the colloidal silica in electrolyte was also reduced significantly then organic recoveries of 75% or more should be achieved.

As reported by Miller, Readett and Hutchinson (1996), and Readett and Miller (1995), changes were made in the operation of the GCC SX circuit. Briefly the loaded organic system was modified to allow E-1 to be run organic continuous. By doing this silica levels in organic were reduced significantly (from 450 ppm to an undetectable level), as was the crud generation in S-1. The reduced silica and crud loading in S-1 reduced both organic and crud entrainment levels in electrolyte entering the Jameson Cell. Soon after this the Jameson Cell orifice plates were replaced to give feed pressures of ~ 180 kPa. Monitoring of the cells performance, following operational changes, was undertaken. The results are given in Figure 2. This highlights the dramatic improvement in Jameson Cell performance following resolution of the silica problem.

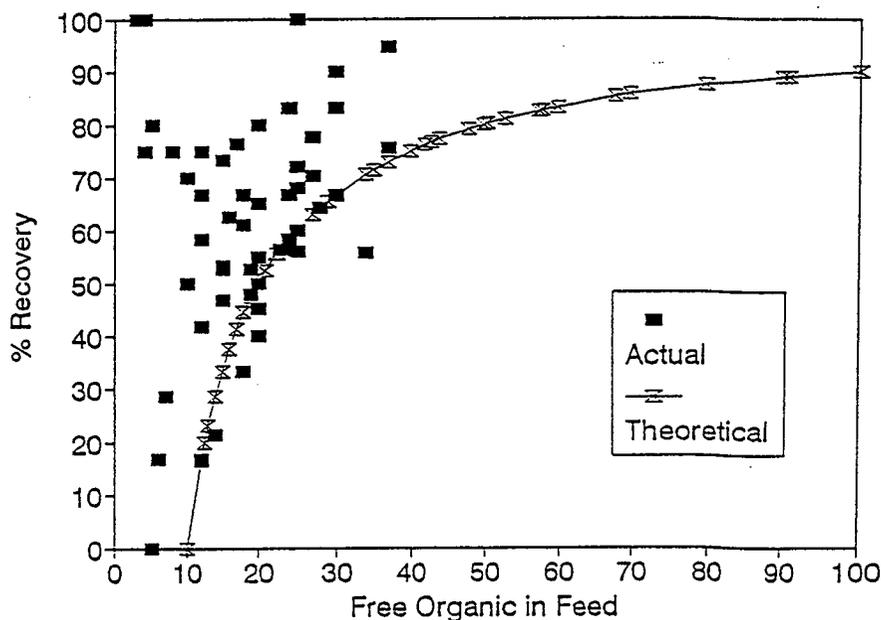


Figure 2. Jameson Cell performance data - post circuit modification

#### NIFTY COPPER OPERATIONS (NCO)

As with the GCC operations Nifty Copper Operations also encountered similar process upset conditions. In December 1993 a significant quantity of manganese entered the electrolyte and resulted in some organic degradation leading to extended phase break times (of 2 to 5 minutes), excessive entrainments (of 50 -150 ppm) and poor Jameson cell performance with variable recoveries of 20 - 60 %. With clay treatment of organic, effective recovery of organic entrainment was achieved by the Jameson Cell, when operating organic continuous in E-1.

Under conditions of running E-1 aqueous continuous it was noted that symptoms of silica contamination were encountered. These symptoms included increased entrainments, increased crud make and reduced Jameson Cell performance. Upon flipping E-1 back to organic continuous, these symptoms no longer prevailed and Jameson Cell performance returned to normal.

### CONCLUSION

Under normal operating conditions within an SX plant Jameson Cell performance is acceptable. Minor manipulation of mechanical aspects of the cell, such as downcomer pressure, air inlet volume and cell operating depth can be used to optimise operations. However under some process upset conditions (such as high crud, degraded organic or presence of silica) the performance can deteriorate. In order to recover from this type of upset, where the physio-chemical properties of the electrolyte/organic are altered, it is necessary to treat the original cause of the problem in SX. It is not practical to alter the Jameson Cell operation to significantly improve organic recovery, during an upset condition.

With the likelihood of some process upsets during the life of a SX plant, thought must be given to alternative short term options to cope with excess organic entrainment in electrolyte. A temporary siphon system was installed at GCC and a pumping system installed at NCO, both for removal of organic from the EW scavenger cells. These have allowed for continued production of LME Grade 'A' Copper during the periods discussed.

Most commonly SX plants now have both a Jameson Cell (or alternative flotation devices) followed by a dual media filter system. This ensures consistent clean electrolyte feed at all times to electrowinning.

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## DEVELOPMENTS IN COST EFFECTIVE SOLVENT EXTRACTION PLANT DESIGN

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### GROWTH PERIOD

Over the past thirty years, solvent extraction has played an increasingly important role in the separation and recovery of metals. Its use in hydrometallurgy began in the nineteen forties and fifties in specialised processes in the nuclear industry including the purification of uranium, reprocessing of fuels and separation of fission products. In the sixties and seventies, it spread to the large scale processing of copper and uranium ores. By the early nineties, the applications list had lengthened to include zinc, nickel, cobalt, vanadium, tungsten, rare earths and was growing steadily.

Because of the rapid increase in solvent extraction plant size and the development of higher cost synthetic extractants there has been increased focus on the reduction of both capital and operating costs. The most widely used contacting device, the mixer-settler, has been subject to intense scrutiny along two fronts, first to develop improvements to the conventional design, and second to invent new concepts. Along with this there have been major efforts in the areas of plant arrangement, materials of construction, ancillary equipment, piping, instrumentation and controls.

### CONVENTIONAL MIXER-SETTLERS (FIG. 1)

Mixer-settlers were utilized in the nuclear program because of their low head room which minimized the amount of shielding required. Other attractive features included simplicity and low maintenance. Typically, the nuclear mixer-settlers consisted of partitioned "boxes" to avoid interstage piping, and relied on density differences to provide driving force for liquid flows. Since then, mixer-settlers have continued to enjoy favour in the mining and metallurgical industry due to their simplicity, ease of operation, stability under a wide range of flows, and accessibility for clean-out. Throughout this time, there has been a consistent effort to develop improvements, mainly aimed at reducing costs.

The first major improvement in mixer-settler design was the introduction of pump-mix impellers to provide head for interstage solution flows. This allowed the use of the shallower settlers and

thinner organic layers, which reduced capital cost and initial organic inventory. Pump-mixers rapidly became standard features in uranium and copper solvent extraction plants.

Other developments included:

- minimization of thickness of the organic layer in the settlers
- provision of adjustable aqueous weirs to allow for optimization of organic layer thickness during plant operation
- development of settler inlet distribution systems and picket fences to maximize phase separation efficiency
- use of full width organic and aqueous weirs to minimize settler discharge velocities
- introduction of baffles or packing in the settlers to accelerate coalescence
- use of two or more mixing stages to maximize stage efficiency and reduce construction cost
- development of low shear agitators to minimize organic entrainment losses
- minimization of settler sidewall height

### **ALTERNATIVE COMMERCIAL MIXER-SETTLERS DESIGNS**

The main disadvantages of conventional mixer-settlers are large space requirement, long piping runs and large organic inventory. The sheer size of the settlers is also reflected in the cost of earthwork, concrete, structural steel, piping and service distribution systems. From the operating point of view, despite the introduction of separate pump-mixers and auxiliary agitators, the entrainment of organic in aqueous and vice versa remains an unresolved problem. These issues have provided incentive for the development of alternative mixer-settler designs.

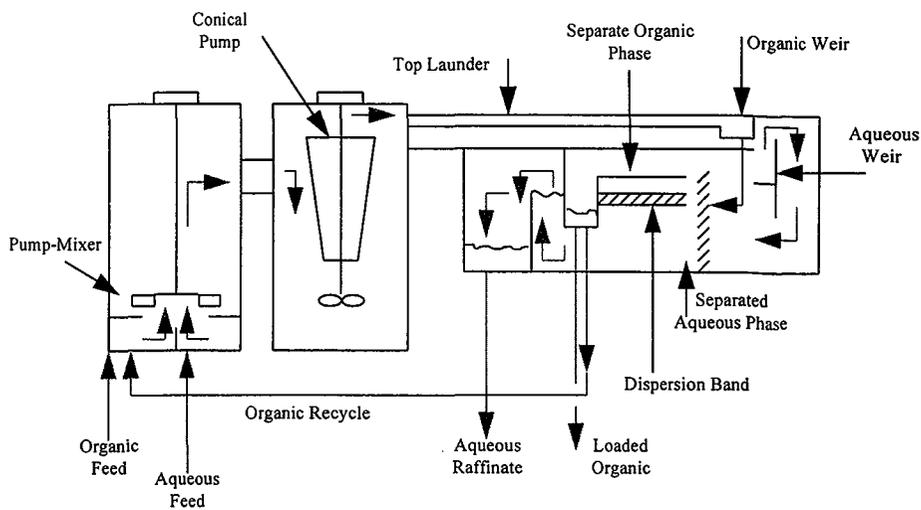
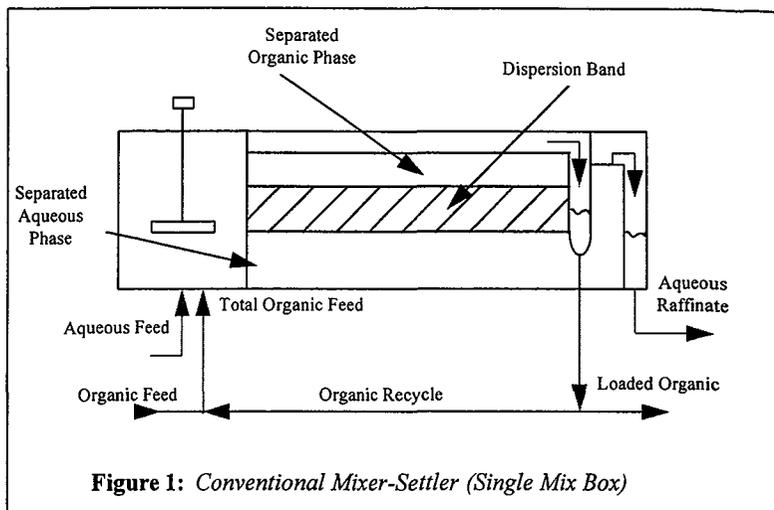
#### **Krebs Mixer-Settler (Fig. 2)**

The Krebs design has been the most widely used alternative mixer-settler design. By using a double-deck settler, with a shallow upper deck, Krebs achieved significant reductions in both foot-print area and organic inventory. Also, because the direction of flow is reversed in the lower deck, all the piping is located at the feed end of the settler which results in cost savings and operational convenience. In order to provide the additional head to lift solution to the upper deck, the mix box feeding the settler is equipped with a conical pump arrangement mounted on the same shaft as the agitator.

#### **Davy Combined Mixer-Settler (CMS)**

As the title suggests, this unit combines the mixing and settling steps into a single vessel. The mixing zone is in the middle of the vessel and is equivalent to the mix box in a conventional mixer-settler. Above and below this are zones where phase separation takes place assisted by dampening baffles. A pump-mix impeller is located in the mixing zone to provide head for interstage solution transfer.

Advantages include elimination of recycle piping, tolerance to high solids in the aqueous feed, increased operating stability, lower organic inventory, reduced capital costs and lower foot-print area. The CMS design appears to be most suitable for systems with fast kinetics. It has found commercial application for the extraction mixer-settlers in uranium solvent extraction plants.



## **Outokumpu VSF Design**

In their vertical smooth flow (VSF) design, Outokumpu have replaced conventional agitators with a SPIROK stirrer, assembled out of helical rods to produce vertical flow through the mixer. This type of stirrer is said to avoid high shearing rate and produce a narrower droplet size range than conventional units. Interstage transfer of liquids is achieved with a large slow moving turbine, again to minimise shear. Reduced organic entrainment losses, and therefore lower operating costs, are claimed for the design. Other benefits include low air entrainment and reduced crud formation. Outokumpu have commercial operating units in their nickel and cobalt recovery operations in Finland. The first units for copper solvent extraction have been installed at the Zaldivar plant in Chile.

## **Proposed Designs**

Over the years, many other innovative mixer-settler designs have been proposed and some have been developed up to pilot plant scale. Typical examples include:

- a) The C.E. Natco SX Process System which utilized controlled electrostatic coalescence.
- b) The Kenics Mixer-Settler consisted of a static mixer to produce a narrow droplet size range followed by a horizontal tubular settler.
- c) The Davy Segmented Circular Settler (SCS) consisted of a conventional mix box situated at the centre of a relatively small cylindrical settler. The mixed phase entered the settler through pads of knitted metal and plastic which promoted rapid coalescence.

## **OTHER TYPES OF CONTACTORS**

A number of other contactors have been used for particular applications. These include centrifugal contactors, mechanically agitated columns and pulsed columns.

## **DEVELOPMENT OF ANCILLARY EQUIPMENT**

Much attention has also been focused on the development of key ancillary equipment which effect capital and operating costs and impact on associated processes such as electrowinning.

## **SX Feed Clarification**

Ideally, the SX feed solution should contain very low levels of solids, typically less than 10 - 20 ppm. The presence of significant solids can lead to crud formation and adversely affect the operability of the extraction contactors. In the case of heap leaching operations, the solids contents are usually low and provision of large feed ponds are sufficient to provide a suitable SX feed. However, with agitated leaching operations, a more positive clarification procedure is usually necessary. For small plants, a clarifier followed by a pressure precoat filter operation can be used. For larger scale operations, a common approach has been to adopt dual media filters which accommodate higher unit flows. Although successful at first, many dual media filter installations have run into difficulty due to the precipitation of gypsum, silica and other salts in the media. One plant overcame this by using two clarifiers in series and by-passing the filters.

## **Organic Clean-Up**

Organic clean-up from aqueous effluent streams has become a major issue in copper solvent extraction and other plants utilizing expensive extractants and coupled with electrowinning. In the early days of copper solvent extraction, a wide array of clean-up methods were tested for electrolyte clean-up, with varying success. These included coalescers and various types of flotation cells. The breakthrough came as a typical operators' innovation. The dual media filters at the Anamax plant in Arizona had been abandoned from SX feed solution duty due to plugging, and the operating staff hit upon the idea of trying them for electrolyte clean-up. It worked, and dual media filters became the standard of the industry to this day. Recently, various column flotation designs have been used for preclean-up ahead of filters, but so far have not totally replaced filters. Flotation has also been used for partial organic recovery from raffinate, where the cost of filters can be excessive due to the large flow rate.

## **Crud Treatment**

The two earliest methods for recovering valuable organic from crud were filtration and centrifuging. However, both of these can be expensive and do not work on all types of crud. More recently, Chuquicamata in Chile found that washing the crud in an agitated tank under organic continuous is an effective inexpensive method.

## **Clay Treatment**

Many copper solvent extraction plants have begun to use clay treatment as a way to rejuvenate partially degraded organic recovered from ponds and to "spruce up" their organic inventory for winter operation. Clay treatment has also proven to be an effective way to clean-up organic after degradation by contact with permanganate formed in the electrowinning circuit from manganese entrainment. Savings in operating costs and improved capacity in winter conditions are generally obtained.

## **MATERIALS OF CONSTRUCTION**

As plants became larger there was incentive to utilize less expensive materials of construction.

### **Mixer-Settlers**

As the largest items, mixer-settlers naturally came under close scrutiny. Early uranium plants used epoxy-sand mixers or even wood. However, these gave way to FRP units which could either be completely shop fabricated or made in sections and assembled on site. The size of the mixer-settlers for copper eventually grew beyond FRP capability and 316 stainless steel became the industry workhorse. One of the challenges faced by designers has been to minimize the plate thickness to save material cost without jeopardizing the integrity of the units. The first really large copper SX plant built at Nchanga in Zambia was originally designed for lead lined concrete construction. However, at the last minute, severe corrosion was discovered in the pilot plant settlers at the aqueous-organic interface. Lead was quickly abandoned and thin gauge stainless steel was adopted. A significant advance for large settlers was made at Chuquicamata Chile in the mid-eighties, when HDPE lined concrete was used for the first time. Because of the chloride

in solution, 316 stainless steel could not be used. Once proven successful, this type of construction proved to be cheaper than stainless steel, a classic example of necessity being the mother of invention.

### **Piping**

Many of the uranium SX plants utilized FRP piping while stainless was adopted for the often very large diameter piping needed for copper installations. Another fruit of necessity, this time in the late seventies, led to the introduction of HDPE piping for organic duty, which has been standard ever since. During the commissioning of Anaconda's Bluewater uranium expansion, the project faced a delay (at Christmas time of course!) while a specialist was flown out to repair an FRP pipe on organic service. During the night shift, an enterprising foreman hit upon the idea of using a home-made HDPE bend, which proved to be a great success. Based on this, HDPE was used for all the piping, including organic duty, for the large scale copper SX plant at Inspiration, Arizona (now Cyprus Miami). It has been industry standard ever since.

### **PLANT ARRANGEMENT**

One of the major development areas for cost effective SX plants has been plant arrangement. For large scale plants, the cost of earthworks and settler supports can be significant, and optimisation during the design stage is essential. Factors entering the equation include the materials selection, site topography, and the relative positioning of other plant sections such as electrowinning. Low level settlers with two or more mix boxes have become a common feature because of this.

### **THE FUTURE**

The way is still open for the ideal contactor to be invented. Until this happens, mixer-settlers will continue to dominate, and modified mixer-settlers such as the Krebs and Outokumpu designs are likely to gain further ground.

The search is also still on for an efficient inexpensive clean-up device to replace dual media filters. For the time being, the use of flotation columns will continue to spread in an ancillary capacity. The installation of coalescing medium in surge tanks and even in the settlers themselves will also receive more attention.

Centrifuges are likely to fall out of favour as the prime tool for crud processing, while more plants will adopt the organic washing process.

The use of plastics will continue to develop for ancillary tanks, for example, HDPE lined concrete common wall tanks are becoming more popular.

Of course the established suppliers and would-be suppliers will continue with their efforts to produce new and improved extractants. These in their own right may open the door for more cost effective plants.



## Application of NEURAL NETS TO SOLVENT EXTRACTION SYSTEMS

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### ABSTRACT

Frequently the equilibrium behaviour and hydrodynamics of complex solvent extraction systems are poorly understood, so that it is not always feasible to use a phenomenological approach to modelling and design. In such instances the alternative is usually an empirical modelling approach, which requires the specification of the functional forms used in a regression analysis on experimental data. Due to their non-parametric nature, artificial neural networks offer an attractive alternative to such parametric empirical modelling, and have been used successfully in a variety of process engineering applications. The principles of these nets are demonstrated in two case studies, i.e. (a) the efficiency of extraction of rare-earths from the HEH (EHP)-kerosene-HCl system, and (b) the correlation of variables in a study on drop coalescence in liquid/liquid dispersions by flow through glass fibre beds. It is shown that feature extraction from data can be used to cluster the behaviour of different solvents, and that the well known self-organising map (SOM) is not always the most efficient tool for this purpose.

### INTRODUCTION

Both the equilibrium and hydrodynamics of mass transfer processes are notoriously difficult to model from first principles, or even empirically, owing to a wide range of possible interactions between the chemical species. This is especially true of rare earth solvent extraction systems, where the similarities of the lanthanides as well as their propensity for interaction make it difficult to predict their equilibrium behaviour. The science of molecular simulation has by no means progressed to the stage where the phase distribution in solvent extraction could be predicted from site-site potentials and rotational energies. Currently most non-ideal solvent extraction problems where the interaction between species is poorly understood or where the hydrodynamics is ill-defined, are simulated by empirical methods. In this paper it will be demonstrated how neural nets as a non-parametric technique could be used to model such ill-defined systems without prescribing a functional form which is normally required in parametric empirical methods.

For example, Alstad et al. (1974) used a rudimentary regression model to predict the effect of nitrate and sulphate complexes on the distribution of the rare earth elements during extraction. Hoh and Bautista (1979a) developed a thermodynamic model for the separation of  $\text{La}(\text{NO}_3)_3\text{-Nd}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O-D2EHPA-AMSCO}$  and  $\text{La}(\text{NO}_3)_3\text{-Nd}(\text{NO}_3)_3\text{-Sm}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O-D2EHPA-AMSCO}$ . Their model was based on the degrees of formation of the species, but unfortunately, data for all the variables concerned are not readily available, thus limiting the general applicability of the model. Hoh and Bautista (1979b) later found that their model was only valid for equimolar lanthanide concentrations in the feed. Han and Tozawa (1988) developed a model for a single component lanthanide-chloride-D2EHPA-kerosene system, based on the lanthanide and hydrogen

activity coefficients, concentrations for the main reactive species and terms denoting the complexation of the aqueous lanthanide species, but did not account for the polarity of the diluent. The model required the thermodynamic stability constants of the rare earth complexes which vary according to the nature and concentration of the species, and which show no clear correlation with atomic number (Marcus, 1966). Consequently, such semi-empirical models are of limited value.

### ARTIFICIAL NEURAL NETS

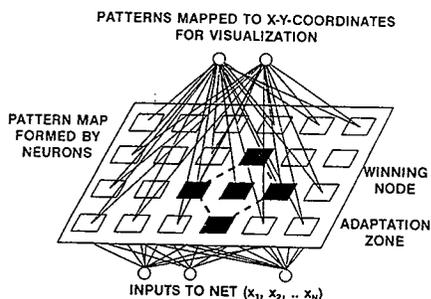
Artificial neural networks (ANN's) consist of large numbers of computational units connected in a massively parallel structure. ANN's learn from exemplars, and have been shown to be universal approximators that can represent any functional relationship to some degree of accuracy. In process engineering, ANN's have been used mainly to generate non-linear models for the design of model-predictive control systems, for fault diagnosis, error detection, data reconciliation, process analysis, kinetic models, and in the analysis of videographic process data (Bulsari, 1995). Back propagation ANN's are wide-spread in engineering research due to their simplicity, compact design and flexibility. Since the theory of ANN's has been discussed extensively in the literature (Lippmann, 1987; Hornik et al., 1989; Bulsari, 1995), only a brief review of the technique is given below.

In back propagation ANN's, processing elements or units are typically divided into distinct layers. The processing units from each layer are linked to the processing units in successive layers by weighted connections. Collectively these connections, as well as the transfer functions of the processing units, can form distributed representations of relationships between input and output data. Back propagation net training, which involves the adjustment of the weight matrix of the net in order to represent a desired relationship, is accomplished by repeatedly presenting the network with sets of exemplars of the process being modelled. During the training process, the weights of the network are adjusted continuously based on the error signal generated by the discrepancy between the output of the network and the actual output of the training exemplars. This is accomplished by means of learning algorithms designed to minimize the mean square output error.

### SELF-ORGANISING NEURAL NETS

ANN techniques aimed at the projection and visualisation of data characterise the structure or distribution of the data, and project these data to a lower (typically two or three) dimensional space in order to facilitate analysis and interpretation. Of these the Kohonen self-organising neural net is the most popular. These nets create two-dimensional feature maps of input data in such a way that order is preserved. This characteristic makes them useful for cluster analysis and the visualisation of topologies and hierarchical structures of higher-dimensional input spaces.

The main distinguishing feature of Kohonen networks is that no output data are required to train the net. Such a net typically consists of an input layer, which is fully connected to a two-dimensional Kohonen layer as shown in Figure 1. Each process element in the Kohonen layer measures the (Euclidean) distance of its weights to the input values (exemplars) fed to the layer. For example, if the input data consist of M-dimensional vectors of the form  $\mathbf{x} = \{x_1, x_2, \dots, x_M\}$ , then each Kohonen element will have M weight values, which can be denoted by  $\mathbf{w}_i = \{w_{i1}, w_{i2}, \dots, w_{iM}\}$ . The Euclidean distance  $D_i = \|\mathbf{x} - \mathbf{w}_i\|$  between the input vectors and the weights of the net are then computed for each of the Kohonen elements and the winner is determined by the minimum Euclidean distance.



**Figure 1: Generic structure of a self-organising neural net**

The weights of the winning element, as well as its neighbouring elements which constitute the adaptation zone associated with the winning element, are subsequently adjusted in order to move the weights closer to the input vector, i.e.  $w_{ij,new} = w_{ij,old} + \alpha(x_j - w_{ij,old})$ , where  $\alpha$  is an appropriate learning coefficient which decreases with time (typically starting at 0.4 and decreasing to 0.1 or lower). The adjustment of the weights of the elements in the immediate vicinity of the winning element is instrumental in the preservation of the order of the input space and amounts to an order preserving projection of the input space onto the two-dimensional Kohonen layer.

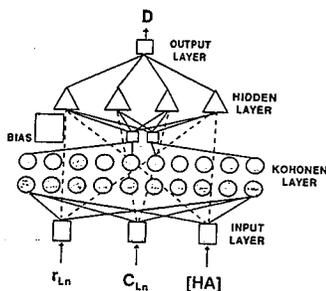
## CASE STUDIES IN SOLVENT EXTRACTION

### Equilibrium Rare-Earth Extraction

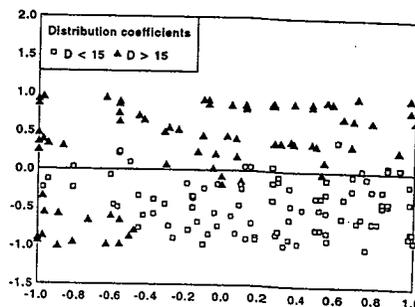
Han (1983) studied the solvent extraction of individual rare earth elements, including yttrium, from a HEH(EHP) (1.0 M)-kerosene-HCl system at varying lanthanide and extractant concentrations, phase ratios and solution acidities. He proposed a series of linear correlations to represent the relationship between the inverse distribution ratios and the equilibrium aqueous rare earth concentrations. Giles (1994) proposed a regression equation for this system incorporating the lanthanide crystal radius ( $R_{Ln}$ ), the initial aqueous rare earth concentration ( $C_{Ln}$ ) and the acidity of the solution ( $[HA]$ ) to give the distribution ( $D$ ) of a given lanthanide between the two phases. It was found that it is essential to incorporate the crystal radius in order to extrapolate to other lanthanides.

In view of the complexity of interaction between species, it was found that an ordinary back propagation neural net consisting of a three-node input layer, two sigmoidal hidden layers with four and two processing elements respectively, as well as a sigmoidal output layer with one processing element, was unable to simulate the data set accurately. For this purpose a data set of 200 exemplars was randomised, and 100 were used for training while the rest were used for testing. All variables were scaled logarithmically, without which even less satisfactory predictions were obtained. Consequently, a hybrid net shown in Figure 2 was used. This net consisted of a three-node input layer as before, and a two dimensional Kohonen layer, as well as the sigmoidal hidden layer of the back propagation neural network. The Kohonen layer was trained first, after which its weights were fixed and the training of the back propagation neural network was commenced.

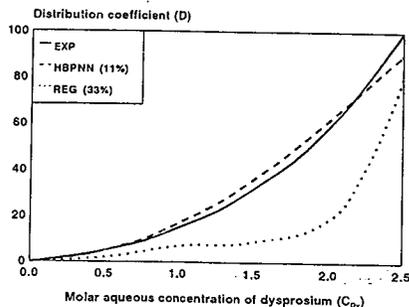
The output of the Kohonen layer is shown in Figure 3, in terms of a topological mapping of the input vectors of the training data. Clearly, inputs associated with comparatively high distribution ratio



**Figure 2: Structure of a hybrid neural net with a self-organising Kohonen layer for rare-earth extraction**



**Figure 3: Clustered mapping of distribution coefficients of Han's (1983) system by means of a Kohonen layer**



**Figure 4: Modelling of the distribution coefficient of dysprosium with the hybrid neural net (HBPNN), as well as the regression (REG) model of Giles (1994)**

values are distinguished from inputs associated with low distribution ratios. This system (HBPNN) predicted the test data with an absolute average error of 11%, while the regression model of Giles (1994) yielded 33% and the ordinary back propagation net yielded 15%, as shown for dysprosium in Figure 4. The reason for this improvement is that the outputs of the Kohonen layer facilitate segmentation of the input space, which enables the back propagation neural network to be trained more effectively.

### Drop Coalescence in Liquid/Liquid Dispersions

Grilc et al (1986) presented experimental data for the separation of fine dispersions of organic solvent in water by passage through glass fibre beds. They measured the interfacial tension ( $T$ ), the viscosity ( $v_d$ ) and density ( $s_d$ ) of the organic phase, the fibre diameter ( $d_f$ ), the mean droplet diameter ( $d_{ps}$ ), the bed depth ( $L$ ) and the critical separation velocity ( $u_{cr}$ ). Three separate empirical expressions were used to correlate the data in terms of dimensionless groups for the aliphatics (ALIPH), aromatics (AROM) and Shell Sol K (SHELL). It was found that the density of the

organic phase could be neglected in any type of correlation. A simple back propagation neural net could be used successfully to correlate these variables, but in that case it is still a problem to distinguish between the different solvents.

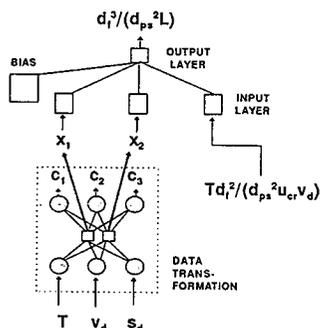


Figure 5: Hybrid neural net structure for correlating drop coalescence in liquid/liquid dispersions

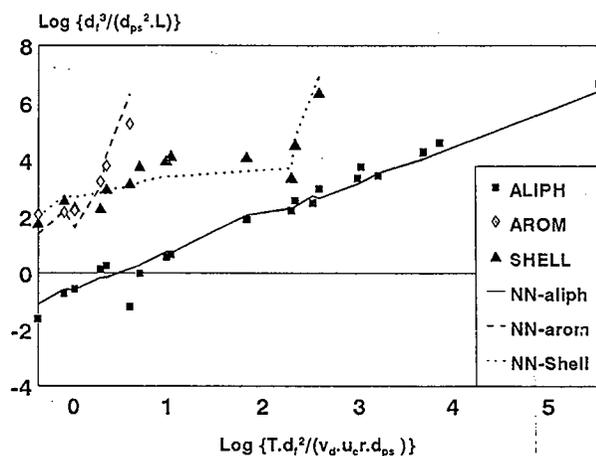


Figure 6: Dimensionless correlation of the experimental results by Grilc et al. (1986) using the neural net in Figure 5

However, Figure 5 shows that the physical characteristics ( $T$ ,  $v_d$ ,  $s_d$ ) of the organic phase could be related to the type of solvent via a back propagation two dimensional layer, which extracts artificial characteristics ( $x_1$ ,  $x_2$ ) from the input data. These co-ordinates ( $x_1$ ,  $x_2$ ) in a back propagation map have been extracted to distinguish between the different solvents, and could serve as additional input to a net with the hidden layer removed, as shown in Figure 5. This single hybrid net successfully simulates the behaviour of the different solvents, as shown in Figure 6. As expected, the back propagation net mapping shown in Figure 7 provides a distinct clustering of the different solvents. In general, such a simulation approach could be used to distinguish and compare different solvents, or in a mixing problem, compare different agitators or column packings.

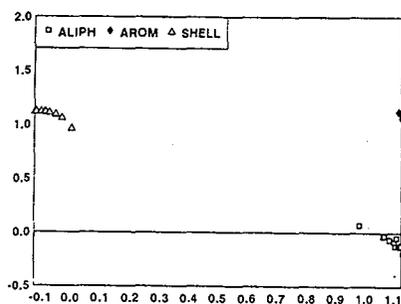


Figure 7: Back propagation mapping of the effect of different solvents used by Grilc et al. (1986).

### CONCLUSIONS

It has been shown that neural nets can be used to simulate ill-defined solvent extraction systems such as the recovery of lanthanide elements from acidic solution. The crystal radius of the lanthanide elements could be used to generalise the behaviour in single and multi-component systems. Sigmoidal back propagation neural nets were more able to capture the equilibrium behaviour of these systems than most regression models. Pre-processing of data can have a significant effect on the accuracy of neural net models.

In some cases a hybrid type of net, which for example combines the sigmoidal hidden layer of a back propagation net with a two dimensional Kohonen layer is preferred. This was demonstrated for the case of rare-earth extraction. It is also possible to relate the physical characteristics of a system to a set of classes via a layer of co-ordination points using a back propagation net. In this way the effects of different solvents could be distinguished and clustered on a two dimensional map. These co-ordination characteristics could serve as input to a further net, yielding most satisfactory results, such as in the case where drop coalescence in liquid/liquid dispersions was studied. In summary, substantial scope still exists for the application of neural nets to solvent extraction problems.

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