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International Committee for Solvent Extraction
Chemistry and Technology

ISEC '88

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**Moscow, USSR
July 18-24, 1988**

**Conference Papers
Volume III**

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**LIQUID
MEMBRANES**

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In the Zinc-producing industry there often exist waste waters containing high concentrations of zinc and impurities, such as Cadmium and Lead. We investigated the applicability of Emulsion Liquid Membranes for the simultaneous removal of these and other metals. The principles, mechanism and applications of the Emulsion Liquid Membrane Process is described elsewhere (1), therefore we will only report on the removal of these metals.

A number of extractants are known for the extraction of zinc, but few for Cadmium and Lead. Therefore the investigations were first centered on the choice of a suitable extractant, which will extract simultaneously Zn, Cd and Pb, under the given conditions. In sulfate solutions, organophosphorous extractants seemed to be the most promising, but at a pH of less than 2, which is either given in the feed solution or is achieved by the ion exchange, only sulfur-containing organophosphorus extractants will extract Cd and Pb to a sufficient amount. At first we chose Di-(2-ethylhexyl)dithiophosphoric acid, which is already used in a liquid membrane process for the recovery of Zinc (2). The results of a typical batch scale experiment are shown in table 1.

Table 1

Extraction of Zn, Cd, Pb in a batch experiment

<u>time(min)</u>	<u>0</u>	<u>2</u>	<u>5</u>	<u>10</u>
Zn (mg/l)	820	147	13	1,2
Cd (mg/l)	14	0,1	0,02	0,02
Pb (mg/l)	2,1	0,09	0,03	0,01

As can be seen from this table all three metals could be removed sufficiently within ten minutes. 250 g/l sulfuric acid was used as stripping acid and zinc was concentrated to 41 g/l. So far the results were very promising, but the problem now was, that Cd and Pb were not concentrated in the stripping phase. Only 1,1 mg/l Cd and 0,4 mg/l Pb were measured in the stripping

phase, which means, that these metals are concentrated in the organic phase and would accumulate there in a continuous process and inhibit the zinc-transport. It is true that Cd and Pb are stripped at high concentrations in the organic phase, but the zinc-transport is stopped long before this stripping will take place.

Because of these results an improvement could only be made on the stripping side, and table 2 shows the results of some stripping experiments where various acids and acid concentrations were used.

Table 2

Stripping of Cd and Pb from an organic phase containing 4000 mg/l Cd and 2000 mg/l Pb (phase ratio 1:1)

	Cd (mg/l)	Pb (mg/l)
H ₂ SO ₄ , 5n	2	
H ₂ SO ₄ , 10n	5	2
H ₂ SO ₄ , 15n	37	3
H ₂ SO ₄ , 20n	2400	precipitation of PbSO ₄
H ₂ SO ₄ , 25n	3800	precipitation of PbSO ₄
HCl, 5n	2170	860
HCl, 10n	3950	1900
HBr, 5n	3000	2000

This table shows, that only sulfuric acid with a concentration higher than 20n (980g/l) and hydrochloric- or hydrobromic acid can be used for a sufficient stripping of Cd and Pb. But, unfortunately, neither of these acids can be used directly in the liquid membrane process. The highly concentrated sulfuric acid not only shows a very high osmotic pressure gradient, but also decomposes the extractant very quickly, and a stripping phase containing chloride or bromide ions can't be reused in the Zinc-winning process.

The only possibility to solve this problem seemed to be a combination of a liquid membrane and a solvent-extraction process. Zinc, Cadmium and Lead were removed from the waste water by the liquid membrane process as described above, but before reusing the organic phase for the preparation of the next emulsion, a part of this organic phase was stripped in a mixer-settler by hydrochloric acid. By this procedure a constant low level of Cd and Pb in the organic phase could be achieved, which

only slightly affected the zinc-transport. Table 3 shows the results of a continuous process in a pilot-plant (60 l/h), where a third of the organic phase was continuously stripped by a 5N hydrochloric acid.

These results were very satisfying, but nevertheless we didn't use Di-(2-ethylhexyl)dithiophosphoric acid in the next pilot

Table 3

Results of pilot-plant experiments

column height(m)	0	0,75	1,50	2,25	2,80
Zinc (mg/l)	810	103	33	13	2,3
Cadmium (mg/l)	8	2,1	0,6	0,1	0,04
Lead (mg/l)	2,0	0,5	0,1	0,04	0,02

plant tests, which were done in another zinc-producing industry. We used Di-(2-ethylhexyl)monothiophosphoric acid and expected an easier stripping and a better stability of this extractant. This waste water contained less Pb, but a lot of other metals. The experiments were made in a counter-current extraction column with an active height of 6m and a throughput of the waste water of 200 l/h. The results of the first day are shown in table 4. The initial pH was 3,7 and the final pH was 2,0. The throughput of the organic phase was 20 l/h and 2 l/h of the stripping phase, which consisted of 250 g/l sulfuric acid. Because of the used phase ratios an enrichment factor of 100 could be expected, if the metals are completely transported.

Table 4

Average results of the first day (mg/l).

	Zn	Cd	Fe ⁺⁺	Fe ⁺⁺⁺	Pb	Cu	Co	Ni	Mn
Feed	210	2,3	61	96	0,6	0,5	0,30	0,28	16,7
Raffinate	0,3	0,02	61	86	0,008	0,01	0,30	0,29	16,8
Strip	19600	0,2	46	930	4,5	0,043	0,12	0,16	6,0

As we can see in table 4, Zn, Cd, Fe(III), Pb and Cu are completely removed from the waste water, whereas Fe(II), Co, Ni and Mn are not removed. Beside these metals, Mg, Ca and Na were also not removed. Looking at the stripping phase we see, that only Zn and Fe(III) are completely stripped. Contrary to the experiments with Dithiophosphoric acid also Pb is stripped quantitatively, as we could see later when solid PbSO₄ precipi-

tated. By Preliminary batch scale experiments we expected, that Cd and Cu are also stripped by 250 g/l sulfuric acid. But this was not the case, as we can in table 4. Therefore we didn't change anything and operated the pilot plant several days under the same conditions. During this period only the concentrations of Zn, Cd and Cu changed, whereas the concentrations of all other metals remained constant. These variations are illustrated in figure 1, which shows the Zn-concentration in the raffinate and the Cd- and Cu-concentration in the stripping phase. Zn in the stripping phase and Cd and Cu in the raffinate also remained constant.

The results are very interesting. After two days of operation the Zn-concentration in the raffinate increased, as was expected because of the accumulation of Cd and Cu in the organic phase. For about the same time as the Zinc-concentration remained very low in the raffinate, Cd was not stripped. But suddenly within a few hours Cd was stripped to an extent (700mg/l) much higher than the value expected by the mass balance (200mg/l). Several hours later the Cd-concentration in the stripping phase decreased to about 200 mg/l and remained constant. Together with this decrease of the Cd-concentration in the stripping phase, the Zn-concentration in the raffinate decreased to 5 - 10 mg/l and also remained constant. The Cu-concentration in the stripping phase increased gradually and reached the expected value after four days.

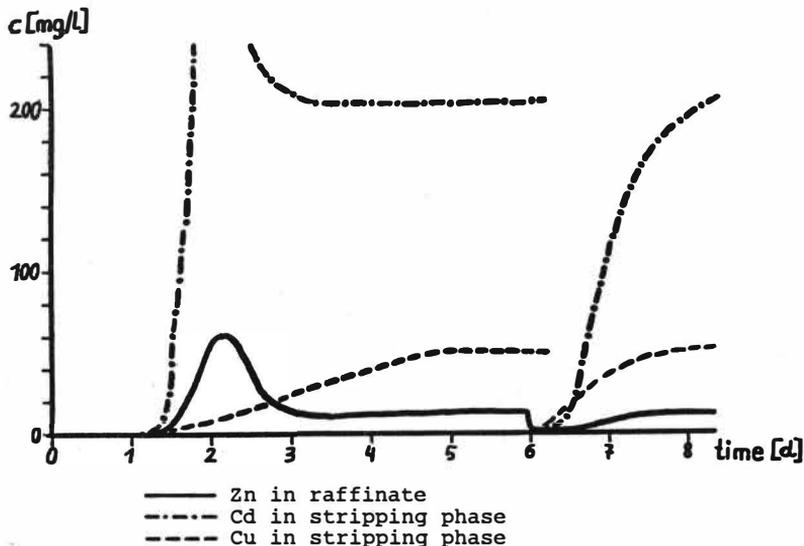


Fig. 1. concentrations of Zn, Cd, Pb during pilot run

After all concentrations remained constant for two days, the extractant concentration was enhanced from 4 to 5% at the beginning of the 6th day.. The purpose was to make more extractant available for the Zn-transport, and improve the Zn-values in the raffinate. The result was, that the Zn-concentration in the raffinate was immediately reduced to 0,3ppm, but that again no Cd and Cu was stripped. Several hours later all concentrations increased again and after one day reached the same values as were before with 4% extractant. The only difference was, that the Cadmium in the stripping phase gradually reached the equilibrium concentration without a maximum. It seems that a higher extractant concentration has no significant influence on the separation of the metals. Other possibilities to reduce the Zn-concentration in the raffinate were not investigated, because it is planned to treat the waste water in two stages, and it is expected that the Zn-concentration can easily be reduced to the required value of 0,5ppm, when no Cd and Cu are present in the second stage. Probably this value can also be reached in one stage, when Cd and Cu are continuously stripped by hydrochloric acid, as described above with Dithiophosphoric acid as extractant.

Conclusion

In two pilot plant tests in the Zinc producing industry it was tried to remove all heavy metals from different waste water streams. In the first test Di-(2-ethylhexyl)dithiophosphoric acid was used as extractant and Zn, Cd and Pb could be removed quantitatively from the waste water, but only Zn was stripped by sulfuric acid. To avoid an accumulation of Cd and Pb in the organic phase, a part was continuously stripped by hydrochloric acid to keep a constant low level of Cd and Pb in the organic phase, which does not affect the Zn-transport.

This stripping by hydrochloric acid has not necessarily be done when Di-(2-ethylhexyl)monothiophosphoric acid is used as extractant, because Pb is stripped easily by sulfuric acid, and Cd and Cu are stripped when having reached a certain level in the organic phase. But in this case the Zn-transport is slightly worsened, so a hydrochloric acid stripping is suggested when very good Zn-separations have to be achieved.

References

1. Marr R., Kopp A. // Int.Chem.Eng. 22(1). 1982. 44-60.
2. Draxler J., Marr R. # Chem.Eng.Process. 20. 1986. 319-329.

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Introduction. Emulsion liquid membranes (ELM) are double emulsions formed by emulsifying two immiscible phases and then dispersing this emulsion in a continuous external phase under moderate agitation as shown schematically in Fig. 1. The emulsion globule consists of a continuous membrane phase with many encapsulated small (0.1 to 5 μm) internal phase droplets. The solute to be extracted from the external feed solution transfers through the thin liquid membrane phase to the internal phase.

For the ELM system of interest here, the solute dissolves in the membrane phase at the external surface of the emulsion globule, diffuses across the membrane, and enters the internal phase by simple phase partition. Removal of solute in the internal phase with a reaction forces extensive solute extraction by enhancing the emulsion capacity for solute. As shown in Fig. 1, a basic internal phase solution promotes extraction of acidic compounds such as phenolics. Similarly, an acidic internal phase will extract basic compounds like amines.

Emulsion liquid membranes are well-suited to toxic chemical removal. One obstacle to the application of this technology is inadequate quantitative predictions of extraction performance in the presence of multiple extractable contaminants. When more than one solute diffuses through the membrane, competition for the available reagent occurs. In their experimental work, Terry et al. have observed that a more reactive solute can force a less reactive solute back into the bulk solution when the supply of internal phase reagent is inadequate [1]. This phenomenon has also been predicted by a multicomponent reversible reaction model described by Baird et al. [2].

While the importance of extraction of multiple solutes from solution is obvious, only a small number of experiments have been reported [1,2]. Baird et al. [2] successfully predicted their measured ELM extraction rates from mixtures of aniline and p-toluidine using the reversible reaction model. Unfortunately, the reactivities and solubilities of these components are too similar to provide a definitive test of the model. In this paper, we present experimental results from ELM batch extraction of binary solutes. We have specifically chosen compounds for which differences in reaction equilibria are large. These results will be compared to the predictions from the reversible reaction model using only independently measured or estimated parameters.

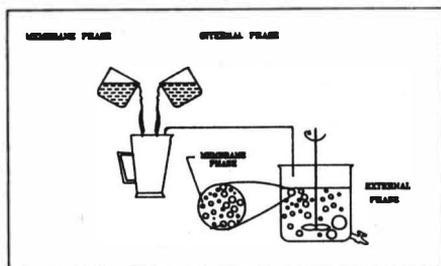


Fig 1. Schematic diagram of ELM preparation

Theoretical Development. It is important that any realistic ELM transport model adequately describe the system's composite nature and the combined effect of reaction kinetics and phase equilibrium. The model should incorporate the fact that the reaction occurs in the internal phase only, while solute diffusion occurs in both phases of emulsion.

Recognizing that the high membrane viscosity probably prevents internal phase droplet circulation, Ho et al. [3] treated the internal droplets as immovable point sinks for the solute. Diffusion through the globule then effectively can be characterized as transport through a continuum with some average of internal and membrane phase properties. Their advancing front model postulates that the diffusing solute instantaneously and irreversibly reacts with the reagent in the internal phase, creating a reaction front which divides the globule into reacted and unreacted regions. Using perturbation techniques, Ho et al. were able to solve their mathematical equations analytically. The advantage of the advancing front model is its analytical form which only requires independently determined parameters. However, by requiring the stripping reaction be irreversible, the advancing front model consistently overpredicts the solute extraction rate. The assumption of reaction irreversibility also inhibits the prediction of multi-solute extraction when the supply of reagent is limited.

The reversible reaction model proposed by Bunge and Noble [4] extended the advancing front model by assuming that the solute-reagent reaction is reversible and that the local reaction equilibrium applies throughout the globule. Reaction reversibility excludes the assumption of an advancing front as well as reacted and unreacted regions inside globule. At any point inside emulsion globule, the solute concentration is determined by the diffusion rate and the reaction and phase equilibria. Because some unconsumed reagent is present throughout the globule, the determination of an effective diffusivity becomes a complicated matter. For single component extraction, Bunge and Noble proposed a procedure to estimate the enhancement of the internal phase diffusivity induced by the reagent reaction. Baird et al. [2] proposed a method for predicting enhanced diffusion in the presence of multiple extractable solutes. These procedures are discussed next.

Effective Diffusivity. In both the advancing front and the reversible reaction models, molar diffusivities for solute in the membrane and the internal phases are estimated using the Wilke-Chang correlation [5] and physical properties of each phase. The composite nature of the emulsion globule is taken account by using the Jefferson-Witzell-Sibbit equation [6]. However, because the product diffusion in the internal phase induces an additional solute flux, the reversible reaction model also includes a factor, γ , which describes the apparent enhancement of the internal phase diffusivity and is given below :

$$\gamma = 1 + \frac{KC_{Bi}^0}{(1 + KC_{Am}/K_{im})^2}$$

where C_{Am} is the solute membrane concentration, C_{Bi}^0 is initial reagent concentration, K is the stripping reaction equilibrium constant, and K_{mi} is phase distribution

coefficient between membrane and internal phases. Since γ is concentration dependent, an integral technique is used to find an average effective diffusivity. Depending on system conditions, the estimated effective diffusivity, D_{eff} , can be 1 to 2 times the effective diffusivity calculated from the advancing front model D_{adv} which does not include any reaction enhancement. The dimensionless time used to compare experimental data and theoretical results from both models, $\theta = Dt/R^2$, is based on the solute molar diffusivity in the membrane phase as estimated by the Wilke-Chang equation. Effective diffusivities in the multicomponent extraction model are estimated by a similar procedure.

Experimental Procedure. Five organic acids with significantly different reaction phase equilibria were selected for our multicomponent ELM extraction study. Their reaction equilibrium constants, K_{eq} , and phase distribution coefficients, K_{mb} , at 25 °C are given in Table 1. The K_{mb} for each solute is measured by equilibrating the aqueous solution with S100N (a middle distillate supplied by Exxon, USA) in a wrist-action shaker. The solute concentrations in the initial and equilibrated solutions were determined by a UV-visible spectrophotometer or titration.

Table 1. Phase Distribution and Reaction Equilibrium Constants for Extracted Solutes

	Acetic Acid	Phenol	m-Cresol	Benzoic Acid	Phenylacetic Acid
K_{mb}	0.005	0.6	.7	0.7	0.3
K_{eq}	1.8×10^9	11,000	9,800	6.5×10^9	7.6×10^9

The membrane phase (100 g) was prepared by dissolving 3 grams of Paranox 106 (a nonionic polyamine surfactant, Exxon, USA) into S100N. A LiOH solution (50 g) and the membrane phase were added to a blender and mixed for two minutes at the low setting. The membrane volume fraction of the resulting emulsion was about 0.7. Part of this emulsion (90 g) was added to 0.9 L of deionized water stirred at 500 rpm using a rotary mixer mounted vertically. The volume fraction of emulsion was about 0.9 of the total volume. After the size of emulsion globules stabilized, a small volume (5-10 mL) of concentrated solution (single or multi-solute) was added. Bulk phase samples were taken at different extraction times and analyzed by using a UV-visible spectrophotometer or titration. Sauter mean diameters ($2R$) of the emulsion globules were determined photographically from a sample of at least 500 globules. The detailed experimental procedure can be found elsewhere [7].

Results and Discussion. Single component extractions of all five organic acids shown in Table 1 were performed. Figure 2 shows experimental data for two of these, the extraction of benzoic acid (0.00825 M) and the extraction of m-cresol (0.00825 M) by a 0.25 M LiOH internal phase solution. The reduced concentration of solute relative to the initial value is designated as Y . These data are compared with predictions from both advancing front and reversible reaction models. It is apparent that the advancing front model overpredicts the extraction rates in both cases.

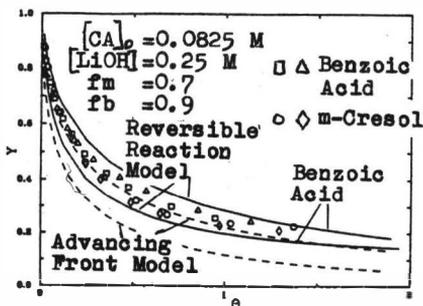


Fig. 2. Single component extraction of benzoic acid and m-cresol

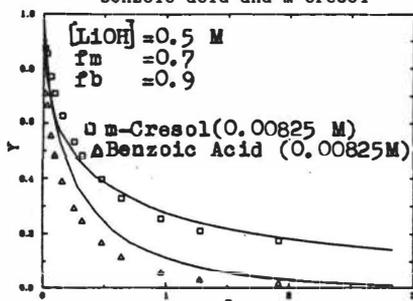


Fig. 3. Binary extraction of benzoic acid and m-cresol by 0.5 M LiOH

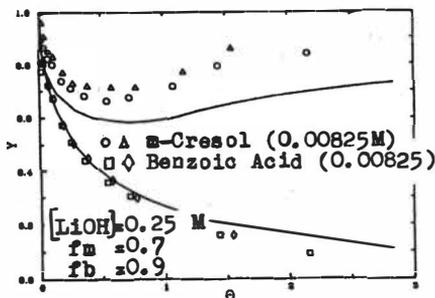


Fig. 4. Binary extraction of benzoic acid and m-cresol by 0.25 M LiOH

More than 20 runs were done for the multicomponent extraction study. The experimental conditions covered different solutes (both binary and ternary mixtures) and initial solute and stripping agent (LiOH) concentrations. Figure 3 shows data and reversible reaction model predictions for the benzoic acid/m-cresol binary pair at 0.5 M LiOH concentration. By comparing Fig. 3 to Fig. 2, we see that the extraction rate of m-cresol is decreased by the presence of benzoic acid even when the reagent concentration is proportionally the same in both cases. The model predicts the same trend.

The influence of benzoic acid presence on the m-cresol extraction rate is more dramatic when the LiOH concentration is reduced to 0.25 M, as shown in Fig. 4. As the extraction proceeds, the already-extracted m-cresol is forced out of the emulsion globules by the more reactive benzoic acid. The reversible reaction model successfully predicts this trend. However, the fit between the model and data is not good. This discrepancy may be caused by the procedure used for estimating effective diffusivities for the multicomponent extraction. A better procedure for determining effective diffusivities for multi-solute extraction is presently under development.

REFERENCES

1. R.E. Terry, N.N. Li, and W.S. Ho//*J. Membrane Sci.* **10**, 305(1982).
2. R.S. Baird, A.L. Bunge, and R.D. Noble//*AIChE J.* Vol.33, No.1, 43(1987).
3. W.S. Ho, T.A. Hatton, E.N. Lightfoot and N.N. Li//*AIChE J.* **28**, 662(1982).
4. A.L. Bunge and R.D. Noble//*J. Membrane Sci.* **21**, 55(1984).
5. R.C. Reid, J.M. Prausnitz, T.K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed. NY; McGraw Hill, 1977.
6. J. Crank, *The Mathematics of Diffusion*, 2nd Ed., Clarendon Press, Oxford, 1975.
7. C.C. Wang//Ph.D. Thesis, Colorado School of Mines, Golden, Colorado (1988).

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Various liquid membranes - of bulk, impregnated, or emulsion type occupy a special place in membrane technology.

An impregnated membrane (di-ethylexylphosphorous acid in n-dodecane) was used in laboratory assembly for extracting copper from galvanic waste. One stage may yield as much as 99.9 p.c. and may be condensed as copper sulphate up to 150-200 g/l.

Extraction and concentration of chromium from sewage water passes through peak value due to functional defects of the impregnated membranes.

In addition to the application of impregnated and bulk-type liquid membranes placed between two porous films we propose a number of original schemes and devices (modules) worked out by us for extraction, transfer and concentration of metals including the use of porous tubes as well as of packages of flat-sheet film chambers.

The principal difference of these schemes and devices consists in thin-layer flow across the outer surface of extraction and reextraction chambers.

The second principal difference of the worked out schemes and devices consists in a possibility of simultaneous extraction and reextraction processes in one and the same assembly. The latter is made in such a way that it permits circulation in the closed system to three liquid volumes : to the feed and the strip solutions, as well as to the organic phase - the liquid membrane.

Replacement of the feed or strip solution by some other specially selected aqueous solutions permits separate extraction and reextraction. In addition to the other characteristic features of the scheme under discussion, and unlike impregnated membranes, no washing out of the liquid membranes from the pores takes place. There is also a possibility of wide-range variation of the interphase contact area of the feed and strip side of the membrane. The scheme solves also the problem of providing continuous flow on joining the block of modules to the technological system. The effectiveness of the device in comparison with impregnated membranes, is demonstrated by the examples of extracting and concentrating chromium from sewage. In the course of one stage 99 p.c. of chromium was acted and concentrated up to 150 g/l.

Application of an electric field to the transport systems opens new functional possibilities for liquid membranes.

A study of platinoid metal reextraction using surface pressure isotherms [1] shows that an increase in tre-amine content in the organic phase (with toluene as diluent) leads to the formation of a mixed layer in which chlorine ions are gradually replaced by palladium anions. Full replacement is achieved at 0.1 Mole content.

It is practically impossible to transfer platinoid metals from the organic solvents on the amine salt base into the diluted mineral acids. This task can be solved by application of an electric field to a liquid membrane containing system based on amine salts in the organic diluent. Carrying out the reextraction processes by passing the current increases significantly extraction degree of platinoid metals, leading to simplification and growth in the yield of the process.

We have elaborated an original scheme of applying an electric field to a membrane system. It is effected by passing a current of varying polarity through the aqueous solutions circulating in the system of extraction and reextraction chambers which act as liquid electrodes.

The polarizing electrodes located in the collector-electrolyzers are shaped in form that allows electrodeposition in the cathode chamber and metal refining in the anode chamber.

Thus electrochemical extraction by means of liquid membranes is combined in one process with hydrometallurgical procedure, which saves a large amount of electric energy.

Of particular interest may prove to be processes based on nonstationary electric regimes, such as, for instance, asymmetric alternating current.

Reference

- I. Serga V.E., Kulikova L.D., Popov A.N. // Izv. AN SSSR. Ser. Khim. 1986. No 2. P. 207-213.

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Liquid membrane extraction is performed by different methods. In general liquid membranes can be classified into three types: bulk, supported and emulsion one. In the latter case the distribution of substances occurs in multiple emulsion. The substance is extracted from an external phase across a liquid membrane into an internal phase of the multiple emulsion.

The addition of surfactants to stabilize this system is necessary. The type and concentration of surfactants affect the processes in the system to a great extent. The liquid membrane thickness of the multiple emulsion is much narrower than that of the other types of the membrane extraction process. This value of thickness ($\delta_m = 0.4 \mu$) can cause great influence of interface phenomena on quasi-equilibrium and kinetics in the multiple emulsion system and on the stability of the emulsion.

The value of specific interface of liquid membrane is equal to $(S/V)_m = 10^6 - 10^7 m^{-1}$ that is considerably greater than that of the common bulk extraction which is $(S/V)_e = 1 - 5 m^{-1}$. The high value of specific interface dispersion of extraction system and the presence of surfactants cause some peculiarities of membrane extraction in multiple emulsion discussed below.

1. Adsorption at the interface of emulsion. Adsorption takes an important place in the processes at the interface of emulsion. In general the total amount of species which is extracted from external phase (Q_Σ) of multiple emulsion consists of three parts: the amount of species which is extracted into the internal phase (Q_i), the one which is in liquid membrane (Q_m) and the one which is adsorbed at the membrane/internal phase interface, the latter being larger than external phase/membrane interface

$$Q_\Sigma = Q_i + Q_m + \Gamma_\infty S, \quad (1)$$

where Γ_∞ - specific adsorption;

S - membrane/internal phase interface square.

The value $\Gamma_\infty S$ can not be neglected. Adsorption can take place not only at initial membrane/internal phase interface but at the interface of microemulsion which is formed in liquid membrane with the aid of mass transfer. This phenomenon occurs in case of extraction of cholesterol from biological liquids which possesses surface-active properties. The value of cholesterol capacity of emulsion calculated from

the cholesterol solubility is 1.2 mg cholesterol/ml emulsion. But emulsion capacity determined experimentally is equal to 2.9 mg cholesterol/ml emulsion, that is 2.5 times as much as mentioned above. This difference is due to adsorption of cholesterol at the interface of emulsion and microemulsion.

2. Formation of microemulsion. The presence of surfactants in liquid membrane can yield the formation of micelles and microemulsion. Mass-transfer in multiple emulsion is a factor promoting these phenomena to a certain extent to take place. Micelleformation in the process of membrane extraction of lizin and cholesterol is proved by the presence of microemulsion in the liquid membrane after separation and by electron microscopy of emulsion with the method of "freezing-spalling" (Fig.1) before and after extraction.

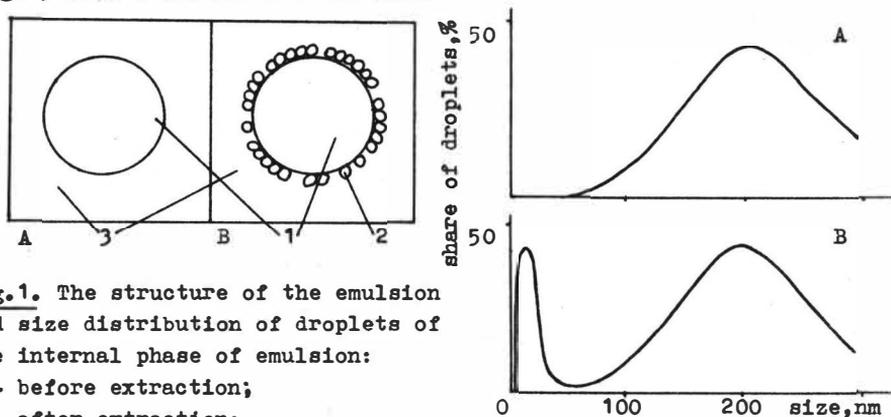


Fig.1. The structure of the emulsion and size distribution of droplets of the internal phase of emulsion:

A - before extraction;

B - after extraction;

1 - droplet of the internal phase of the emulsion ($d=0.2\mu$);

2 - a droplet of the microemulsion ($d=15\text{nm}$);

3 - membrane

The value of interface of emulsion before extraction was $0.9 \cdot 10^7 \text{m}^{-1}$ and after 15 min extraction it increased to 67%. Droplets of microemulsion form a structural-mechanical barrier near the interface. This barrier being the obstacle of coalescence of droplets stabilized the emulsion. Phenomena of increasing stability of emulsion after extraction of lizin was mentioned earlier [1]. Microemulsion which occurs in a liquid membrane stimulate exchange of many components between external and internal phase. Thus water transport into internal phase causes swelling of the emulsion during extraction.

3. Using kinetics factors in separation and concentration of substances. For better separation and concentration of substances it is not advisably to bring process in multiple emulsion to the quasi-equilibrium. It is reasonable to use the extraction rates difference of main solute and other substances presented in the system.

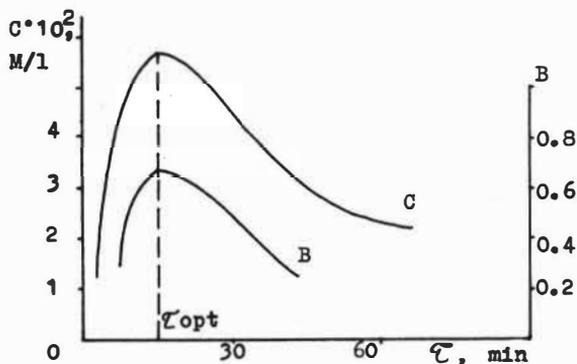
Using selective carrier the transfer of main solute in membrane will be faster than the one of impurities or water transferred by microemulsion.

The nature and concentration of surfactants, properties of liquid membrane (e.g. viscosity), temperature, nature and concentration of carrier, phase ratio in the initial extracting emulsion affect the difference of rates of transfer and consequently the efficiency of usage of kinetics factors.

The comparison of experimental rates of the main solute extraction by carrier and those of micellar water transfer shows that the extraction with carrier is much quicker than the emulsion swelling. That is why the optimization is useful (Fig.2).

Fig.2. Optimization membrane extraction time:

C-concentration of main solute in the internal emulsion phase;
B-generalized function of desirability

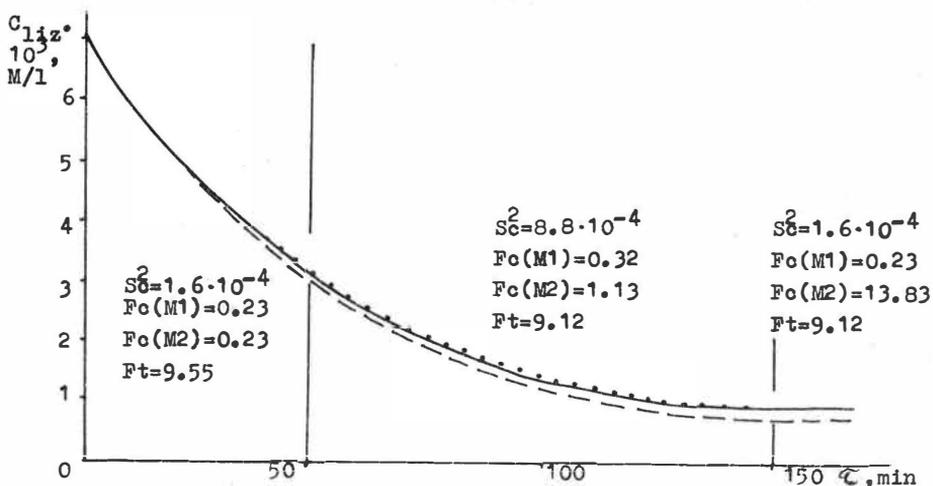


4. Unsteady diffusion in membrane extraction. Model development of membrane extraction is possible on the basis of quasi-steady or unsteady diffusion. The first version is simpler and in the case of the second one the analytical solution is often impossible so that it is necessary to use special methods in each case.

As far as multiple emulsion this matter is concerned with the fact that many diffusion processes are not brought to quasi-equilibrium in experiments owing to emulsion instability. Nevertheless the main difference between unlinear and linear models can be observed far away from points which are used for identification of model parameters. So it is necessary to bring the process to the quasi-equilibrium state.

This can be illustrated by the process of lizin extraction. It was described by the quasi-steady diffusion model and the advancing front model based on the principle of unsteady diffusion. The composition of extracting emulsion was the following:

membrane - di-2-ethylhexyl phosphoric acid (10 %v.),
surfactant (10 %v.),
oil (80 %v.),
internal phase - 1N HCl solution.



..... the advancing front model (M1)
 - - - the stationary diffusionally controlled transport model (M2)
 ——— experiment

Fig.3. Lizin extraction modelling: $S\bar{c}$ -dispersion, Ft -tabular Fisher criterion, Fc -calculated Fisher criterion, C_{11z} -concentration of lizin in the external phase

As shown in Fig.3, the advancing front model (unsteady diffusion) adequately reflects the whole process and the adequacy of the stationary diffusionally controlled transport model can be observed only in points of the kinetics curve which are far from the quasi-steady state of multiple emulsion.

The determination of the relationship of mass transfer coefficient β from the lizin diffusion coefficient D can be presented as

$$\beta \frac{S}{V} = 5.21 D^{0.45}, \quad (2)$$

where V - volume of external phase;

S - membrane/external phase interface.

Such relationship confirmed the point of view concerning unsteady diffusion of lizin in liquid membrane.

Reference

1. Yagodin G.A., Yurtov E.V., Golubkov A.S. // Proceedings of ISEC'86. P.III-677.

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The use of extraction membrane for electro dialysis, together with such evident advantages, like acceleration of substance transport through the layer of extractant, compared with dialysis itself, has the number of serious problems. The possibility of overcoming these problems may be connected with the future development of method itself. Obviously, that the general solution for all types of extractants and extraction systems is a difficult and very unlikely to be quickly solved problem. Therefore, let us consider only definite, but practically very important case of extraction transition metals anion complexes from highly concentrated mineral acids solutions or/and their salts with the help of neutral oxygen-containing extractants. The physico-chemical properties of such systems allow to draw some conclusions, which may simplify the correct description of electro dialysis. We may consider, that in such case the delivery of extracting metal acid-complexes (microcomponent) to the surface of membrane occur by diffusion, and at the same time the concentration profile of mineral acid (macrocomponent) near membrane is practically undisturbed. At high velocity of interphase distribution in systems with neutral extractants the appearance of kinetic limitations is possible in the case of slow formation of extracted complexes of transition metals in aqueous medium. In organic phase the components dissociate with the formation of unit charged anions of mineral acid and acid complex and their antion-solvated cation of hydroxonium. It is clear that, the transport of components through the layer of extractant takes place by means of electromigration. Under these conditions we may evaluate the input equation for flow density j_1 of extracted microcomponent through membrane in stationary conditions:

$$j_1 = \frac{L_1}{2} \left\{ C_1 + \frac{t_1 C_2}{t_2 K_{S1}^0} - \frac{i t_1}{F L_1} - \left[\left(\frac{t_1 C_2}{t_2 K_{S1}^0} - \frac{i t_1}{F L_1} - C_1 \right)^2 + 4 \frac{t_1 C_1 C_2}{t_2 K_{S1}^0} \right]^{1/2} \right\},$$

where i - electric current density; F - Faraday's number; C_1 and C_2 - concentrations of micro- and macrocomponents; K_{S1}^0 - coefficient of electro dialysis selectivity of liquid membrane for the microcomponent when $i \rightarrow 0$; L_1 - effective coefficient of microcomponent's transport from volume of the solution to the organic phase; t_1 and t_2 - electromigration numbers of ion's transport of micro- and macrocomponents.

In the region of small current densities these equation may be simplified:

$$j_1 = - \frac{i}{F} \cdot \frac{t_1 C_1}{t_1 C_2 / t_2 K_{S1}^0 + C_1},$$

where $t_1 = u_1 / (u_1 + u^+)$; $t_2 = u_2 / (u_2 + u^+)$; $K_{S1}^0 = (K_{d1} u_1) / (K_{d2} u_2)$. That

is the selectivity and transport properties of liquid membrane will be defined by equilibrium physico-chemical characteristics: coefficient of distribution K_{di}^0 , degree of dissociation α_i , mobility u_i of component in extragent.

At high electric current density, the transport's velocity of acidocomplex will reach its maximum value:

$$j_1 = L_1 C_1 = \frac{\gamma_1 \varepsilon \beta_1}{\gamma_1 + \varepsilon \beta_1} C_1,$$

where $\gamma_1 = D_1/\delta$; $\beta_1 = \hat{k}_1 (D_1^{\text{extr}}/\hat{k}_1)^{0.5}$; ε - pourousity of the membrane material. It may depend on conditions of delivery of components to the surface of membrane through the diffision layer δ , as well as from constants of the formation (\hat{k}) and decay (\bar{k}) of extracted complexes, if only forms of the element existance in aqueous and organic phase are different.

Calculated on the base of these model depedence $j_1 - i$ in the case of Pt (IV) and Zn (II) chloride complexes transport through impenated by three-butylphosphate (TBP) membrane are in a good agreement with experiment (Fig. 1). The microcomponent transport's velocity is limited

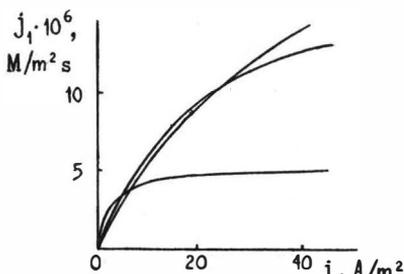


Fig. 1. Acidocomplexes transport from 1M HCl: 1-Pt(IV); 2-Zn(II); 3-Fe(III). $C_{Me} = 10^{-3}M$

by its diffusion through unmoved layer of aqueous phase with the thickness of about 35-40 μm . Just opposite, the transport of Fe(III) tetrachloride complex (Fig. 1) is significantly limited by the stage of its formation in the closest to the membrane layer of aqueous solution [1]. The value of constants of the formation and decay $[FeCl_4]^-$ complex, calculated from experimental dates are in interval, which is characteristic for the values of exchange speed by ligands

of Fe(III) aquachloride complexes [2]. In the region of maximum microcomponent transport density the membrane is losing its selectivity (Fig. 2). The development of rather fine Kinetic effects, connected with slow reconstruction of metall's ion coordinate sphere may be considered as invariability of physico-chemical properties of extracting system in the case of electromembrane process with impregnated membrane. The attempts to prevent the organic phase losing from pourous matrix by way of two cellophane films leads to the sharp decrease of microcomponent extraction (Fig. 3), and may be explained by the increase by order the diffusion's resistivity through these polymer. Electrodialysis transport through membrane impregnated by neutral extra-

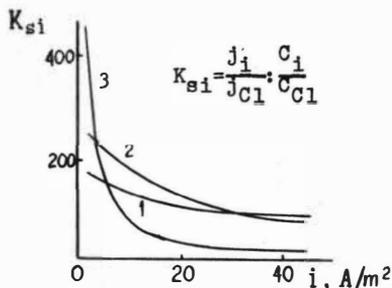


Fig. 2. Selectivity of TBP-membrane for extraction from 1M HCl: 1- Pt(IV); 2- Zn(II); 3- Fe(III). $C_{Me} = 10^{-3}M$

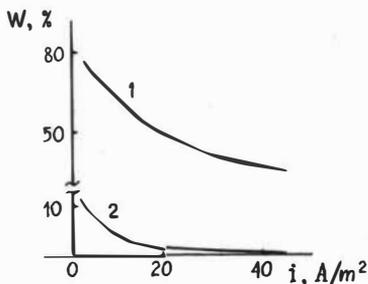


Fig. 3. Output versus current of Zn(II) (1M HCl, TBP-membrane) 1- impregnated; 2- cellophane films. $C_{Zn} = 2 \cdot 10^{-2}M$

gent is often, complicated by oversaturation by water of the organic phase (Fig. 4). The increase of water concentration above the equilibrium value is known for other systems of liquid membranes - it is the layer of organic on the bottom of U-shape tube [3] and between two cellophane films [4]. In the process of selective extraction of transition metals anion complexes the appearance of external quality of water inside of TBP-membrane takes place from the side of anodic chamber. Therefore, the most probable explanation is, that the transport of water molecules occur by means of hydrate-solvate sphere of hydroxonium cation. The change of extragent's surface structure, connected with the formation water microemulsion, roughly decreases its selectivity. Thus, the use of the electric current of opposite polarity leads to sharp decrease of microcomponent transport, because in these case the properties of extragent have been changed

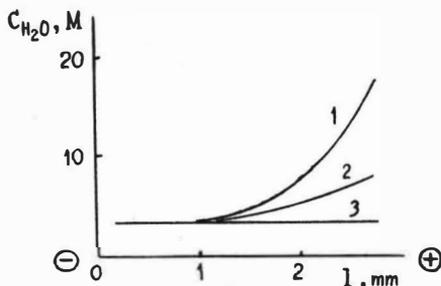


Fig. 4. Contents of water in TBP after electro dialysis in system: 1M HCl - TBP - 1M HCl. $i(A/m^2)$: 1- 11; 2-4.2; 3- 0

(Fig. 5.). Therefore, if oversaturation by water of the organic phase were from the side of initial solution, impregnated by TBP membrane could not be used for extraction of transition metals' acidocomplexes. In fact, the change of extragent's anodic side properties is displayed by slow decrease of microcomponent transport (Fig. 6.). The sharp fall of liquid membrane se-

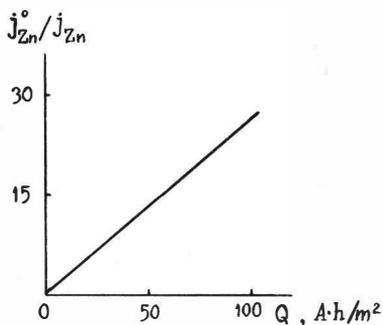


Fig. 5. Relative penetration of Zn(II) for TBP-membrane in system 2M HCl - TBP - 2M HCl. j_{Zn}^0 , j_{Zn} - flow density before and after the use of opposite electric current. $C_{Zn} = 10^{-3}M$

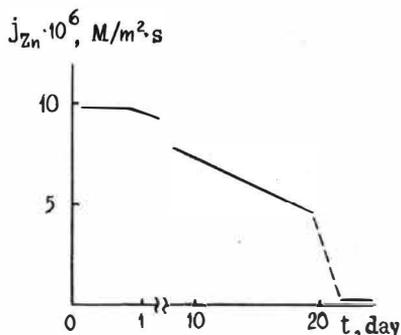


Fig. 6. Transfer of Zn(II) from 2M HCl through TBP-membrane. $i = 6.5 A/m^2$; $C_{Zn} = 10^{-3}M$; membrane thickness 2.6 mm

lectivity, caused by penetration of increased quantity of water up to opposite side of interphase border, takes place after passing of $10^3 - 5 \cdot 10^3 A \cdot h/m^2$ of electricity.

Therefore, in spite of the differences in the construction of liquid membranes on the base of oxygen-containing extractants, the change for the worse selectivity-transport properties in the process of electro dialysis substance separation is connected with the change of physico-chemical properties of organic phase, namely with its oversaturation by water. To find the conditions, excluding this effect, means to determine the conditions of practical application of extraction membrane of a given type.

References

1. Moskvin L.N., Shmatko A.G. Krasnoperov V.M. //Electrochimia. 1987. Vol.23. P.30.
2. Basolo F., Pirson R. Mechanism of inorganic reactions. Moskva: Mir, 1971,
3. Moore J.H., Schechter R.S, //AIChE J. 1973, Vol.19. P.741.
4. Golubev V.N., Kontush A.S. //Electrochimia. 1987. Vol.23. P.249.

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The mass transfer through liquid membranes is a brand new and intensively studied separation process. Liquid membranes or liquid pertraction gave rise to an enormous interest among the specialists in chemical engineering in a world scale, due to the potential possibilities for simultaneous and efficient separation, extraction and concentration of valuable substances from industrial and natural dilute solutions, waste waters, etc.

Recently various perspective techniques were developed for accomplishing of mass transfer processes in three-phase liquid systems. Most studied among them are the double emulsion method (DEM) [1,2] and the solid supported liquid membranes (SSLM) [3,4]. The main problems, hindering now the wide application of these methods are associated with the difficulties in destruction of emulsions, as well as with the insufficient stability of the liquid membranes during the prolonged and continuous operation. In order to overcome these shortcomings of the known methods a new alternative method, called liquid creeping film pertraction (CFP) was developed [5,6] in the Institute of Chemical Engineering in Sofia.

Liquid Creeping Film Pertraction

The principal diagram of the proposed method is shown in Fig.1. The two aqueous phases, the treated one (denoted by "F") and the receiving one (denoted by "R") flow down along the hydrophilic vertical porous planes. These planes are supports of the liquid phases. They are situated at small distances from each other. The whole package of alternatively arranged F- and R-supports is dipped into the organic phase "S". The latter plays the role of a liquid membrane between the phases F and R.

The aim of the present study is to demonstrate the possibilities and advantages of the CFP-method for recovery of useful or toxic substances from very dilute aqueous solutions.

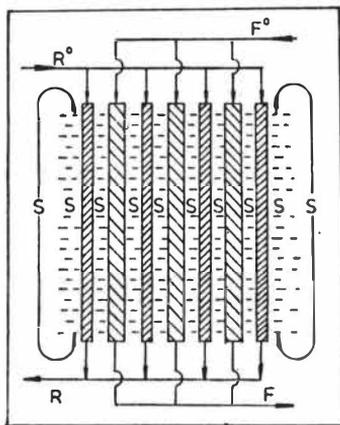


Fig.1

Experimental

Model Systems

For the study of the creeping film pertraction the following liquid systems were used: (I) - phase "F" - aqueous solution of phenol with an initial concentration $X_F^0 = 115 \text{ g/m}^3$ and $\text{pH}_F^0 = 5.0$, phase "S" - a mixture of normal paraffines (a C_{11} - C_{13} - fraction), phase "R" - 0.1 N aqueous solution of NaOH; (II) - phase "F" - aqueous solution of ZnSO_4 with concentration of zinc ions $X_F^0 = 3.97 \text{ mol/m}^3$, $\text{pH}_F^0 = 4.0$, phase "S" - 2% (vol.) solution of D2EHPA in normal paraffines, phase "R" - 2N H_2SO_4 aqueous solution; (III) - phase "F" - aqueous solution of CuSO_4 with initial concentration of Cu^{2+} $X_F^0 = 1.6-4.5 \text{ mol/m}^3$, $\text{pH}_F^0 = 4.0$, phase "S" - 1% (vol.) solution of ACORGA P-5100 in normal paraffines, phase "R" - 3N H_2SO_4 aqueous solution.

Experiments on Mass Transfer and Results

The experiments were carried out on 3 different pertractors with main geometric characteristics given in Table 1.

Table 1

	Apparatus 1	Apparatus 2	Apparatus 3
width of the supports (cm)	6.0	6.0	10.0
height of the supports (cm)	18.0	42.0	42.0
thickness of the "F"-supports (cm)	0.1	0.4	0.4
thickness of the "R"-supports (cm)	0.05	0.05	0.4
porosity of the "F"-supports (%)	70	85	85
porosity of the "R"-supports (%)	55	55	85
number of the "F"-supports (-)	3	3	3
number of the "R"-supports (-)	4	4	4
distances between the supports (cm)	0.3	0.3	0.6

It was established, that at a constant initial concentration X_F^0 of the transferred solute in the phase F and at a certain linear velocity of this phase U_F , the degree of extraction E (given as $E = 1 - X_F / X_F^0$) is essentially influenced by the circulation velocity U_S of the organic membrane S. The results for the phenol pertraction show that the efficiency E increases with about 50%, when the organic phase S

circulates, independently on the linear velocity U_F of the water film F (cf. Fig. 2). Moreover, the increase of U_S leads to a more complete extraction of zinc and copper ions from the solution F (cf. Fig. 3 and Fig. 4). Obviously the diffusion resistance of the membrane phase S is eliminated by the intensive circulation of the latter. Computations were carried out by means of a developed mathematical model for the creeping film pertraction [7]. They show, that at the pertraction of cupric ions in apparatus No3 at circulation velocity $U_S = 2.8 \cdot 10^{-3} \text{ m/s}$ the mass transfer resistance in the membrane phase S (i.e. $2/m_F k_S$) becomes less than that in the phase F (i.e. $1/k_F$), whereas the resistance in the receiving phase R (i.e. $m_R/m_F k_R$) is about five orders of magnitude less than $1/k_F$. These results are summarized in Table 2. The maximum necessary circulation velocity for the considered model systems is $3.5 \cdot 10^{-3} \text{ m/s}$, independently of the system and the membrane thickness.

The results evaluated from the pertraction of copper ions in the three apparatuses by means of the mathematical modelling are given in Table 3. It is evident, that the overall coefficient of pertraction $K_P = 1 / (1/k_F + 2/m_F k_S + m_R/m_F k_R)$ is in the range of $(1.2 - 6.0) \cdot 10^{-6} \text{ m/s}$ and $K_{P_{A_{F/S}}}$ varies within $0.75 \cdot 10^{-3} \text{ s}^{-1}$ and $17.4 \cdot 10^{-3} \text{ s}^{-1}$. A comparative experiment with the same model system, but by DEM-method showed, that at phase ratio $V_F/V_R = 20$ $K_{P_{A_{F/S}}}$ was $2.4 \cdot 10^{-3} \text{ s}^{-1}$, and for $V_F/V_R = 50$, $K_{P_{A_{F/S}}} = 8 \cdot 10^{-4} \text{ s}^{-1}$ [6]. It is obvious, that at higher phase ratio the CFP-method is more efficient than the double emulsion method.

Moreover, in contrast to the DEM- and SSIM-methods, the CFP-method gives stable and reproducible results during 2000 hours continuous operation.

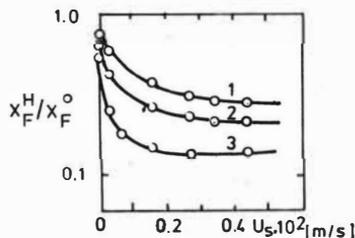


Fig. 2. 1- $U_F = 0.15 \cdot 10^{-3} \text{ m/s}$;
2- $U_F = 0.11 \cdot 10^{-3} \text{ m/s}$; 3- $U_F = 5 \cdot 10^{-5} \text{ m/s}$

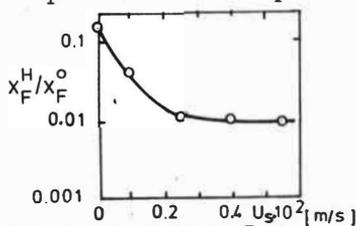


Fig. 3. $U_F = 0.24 \cdot 10^{-3} \text{ m/s}$

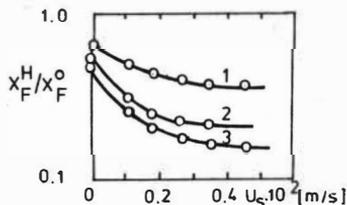


Fig. 4. 1- $X_F^0 = 4.2 \text{ mol/m}^3$;
2- $X_F^0 = 3.2 \text{ mol/m}^3$; 3- $X_F^0 = 2.4 \text{ mol/m}^3$

Table 2

$X_F^0 = 1.82 \text{ mol/m}^3$, $u_F = 1.5 \cdot 10^{-4} \text{ m/s}$
 $U_R = 7 \cdot 10^{-6} \text{ m/s}$, $1/k_F = 2.55 \cdot 10^5 \text{ s/m}$

U_S	$m_R/m_F k_R$	$2/m_F k_S$
$1.7 \cdot 10^{-3}$	37	$5.49 \cdot 10^5$
$2.8 \cdot 10^{-3}$	14	$1.44 \cdot 10^5$
$3.9 \cdot 10^{-3}$	8	$7.18 \cdot 10^4$
$5.0 \cdot 10^{-3}$	7	$5.03 \cdot 10^4$

Table 3

	K_p	a_F/S	$K_p a_F/S$
Pertractor No1	$(1.2-6.0).10^{-6}$	2857	$(3.42-17.4).10^{-3}$
Pertractor No2	$(1.2-5.4).10^{-6}$	625	$(0.75-3.37).10^{-3}$
Pertractor No3	$(2.7-6.0).10^{-6}$	625	$(1.68-3.75).10^{-3}$

Conclusions

The experimental study on the pertraction of phenol, zinc and copper from diluted aqueous solutions shows, that creeping film pertraction is an effective liquid membrane method, notable for the higher stability of the mass transfer process at continuous operation.

It is established, that CFP is a liquid membrane method, more suitable for production of high-concentrated solutions R, since it enables higher volumetric mass transfer coefficients $K_p a_F/S$ at higher phase ratios of aqueous solutions F and R than those attained by the DEM-method.

It is proved, that at no circulation of the membrane phase the mass transfer resistance is in the latter one. The intensive circulation of this phase leads to a shift of the mass transfer resistance to the treated aqueous solution F.

Notation

- X - solute concentration, g/m^3 or mol/m^3 ;
k - mass transfer coefficient, m/s;
 K_p - overall mass transfer coefficient, m/s;
m - distribution coefficient, -;
a - specific interfacial area, s^{-1} ;
U - linear flow velocity, m/s;
V - phase volume, m^3 .

References

1. Li N.N. // AICHE J. 1971. Vol.17, No2. P.459.
2. Lorbach D., Barth H.J., Marr R. // Ger.Chem.Eng. 1986. No9. P.321;
3. Cussler E.L. // AICHE J. 1971. Vol.17. No6. P.1300.
4. Babcock W.C., Friesen D.T., Lachapelle E.D. // J.Membr.Sci. 1986. No26. P. 303.
5. Boyadzhiev L., Bezenshek E., Lazarova Z. // J.Membr.Sci. 1984. No21. P.137.
6. Boyadzhiev L., Lazarova Z., Bezenshek E. // Proc.Int.Conf.ISEC'83. 1983. P.391.
7. Boyadzhiev L., Lazarova Z. // Chem.Eng.Sci. 1987. Vol.42. No5. P.1131;

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Supported Liquid Membranes (SLM) represent a new methodology for metal ion separation and/or concentration which is particularly suitable for radionuclides present at high dilutions in aqueous solutions. Some major advantages associated with the use of SLM are listed in Table 1. The transport properties, theories and applications of SLM's have been extensively described [1 - 3].

Table 1. Advantages of SLM separations

-
- High selectivities
 - Ions can be pumped "uphill"
 - Fluxes are higher than with solid membranes
 - Lower capital and operating cost
 - Expensive extractants can be utilized
 - High separation factors are achieved in a single stage
 - High feed/strip volume ratios
-

The design of a practical SLM requires the detailed knowledge of the solvent extraction chemistry of the system involved. Distribution ratios of the various metal species between the aqueous feed and strip solutions separated by the membrane and the organic phase utilized as liquid membrane, have to be known. Moreover their exact dependence on the various concentration parameters and diluent nature, as well as the kinetics of the reactions, must be available. This information, although necessary, is not however sufficient to design a practically usable SLM. In addition the system must be chemically inert with the respect to the microporous polymeric material used as support for the organic phase. This means that organic solvents such as chlorinated hydrocarbons, nitrobenzene or low molecular weight aromatic hydrocarbons are in general unsuitable. The single-stage nature of ordinary SLM processes also requires the use of more selective extractants than in most solvent extraction processes. Some other chemical and physical characteristics required by the carriers (extractants) and diluents of SLM's are listed in Table 2. The diffusional behaviour of the system must be also well characterized. The diffusivities of the carrier and carrier-metal complex in the membrane phase must be sufficiently high to ensure sufficiently fast processes as there is a practical limit to the minimum thickness of usable supports. Polymerization reactions in the organic

Table 2. Characteristics of Carriers and Organic Diluents for Coupled-Transport through SLM

<u>Carrier</u>	<u>Diluent</u>
◦ High selectivity	◦ Low polarity
◦ Negligible water solubility	◦ Low viscosity
◦ High solubility in the organic diluent in the free and complexed form	◦ Low volatility
◦ Weak surfactant	◦ Chemically compatible with porous support material
	◦ High organic/water interfacial tension

phase must be controlled in order to avoid too viscous organic media and the formation of too large diffusing species which would slow down the transport rate. The geometry and hydrodynamics of the system represent other factors of primary importance. Diffusion layers have to be minimized without negatively affecting the mechanical strength of the SLM and reducing the contact time of the fluids with the membrane. The theoretical aspects of the mass transfer properties and their coupling with the relevant chemical reactions, must be well understood. In addition, to ensure long life-times of the SLM the used porous supports must have high hydrophobicity and small pore radii. Small pore radii are necessary to maximize the capillary forces responsible for the entrapment of the organic phase into the support. (Fig. 1A). High hydrophobicity of the support and high interfacial tensions are also beneficial for the stability of the SLM as they prevent the dislodgement of the organic phase from the support when the membrane is subjected to large osmotic gradients (Fig. 1B). The solubility of water into the liquid membrane

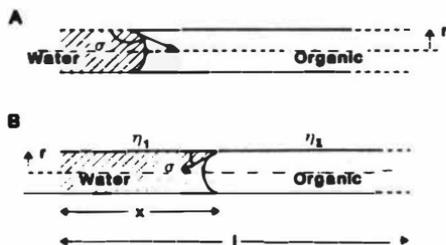
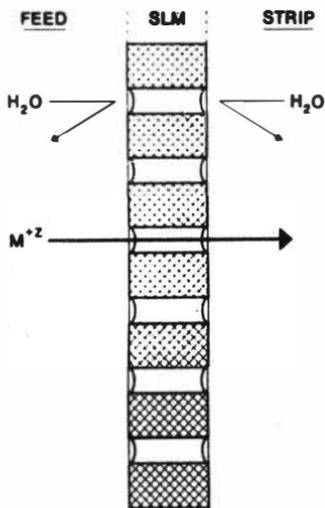


Fig. 1

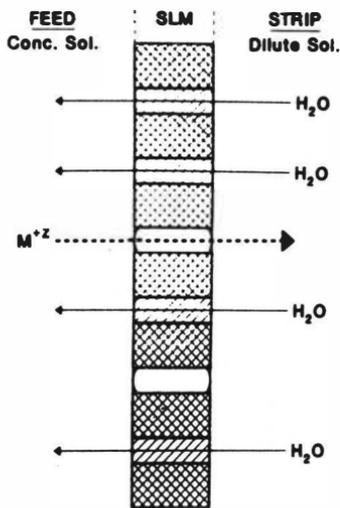
must be much lower than with traditional solvent extraction systems as water transport has been shown to negatively affect SLM life-times. A schematic description of SLM's having different interfacial tensions and abilities of solubilizing water, in the presence and absence of an osmotic pressure gradient, and the correlation of these factors with the SLM stability is presented in Figure 2.

$\Delta \Pi = 0$
 Solubility of water into the SLM = LOW
 γ (Liquid Membrane/aqueous phase) = HIGH



STABLE SLM
 No Water-transport

$\Delta \Pi$ Very Large
 Solubility of water into the SLM = HIGH
 γ (Liquid Membrane/aqueous phase) = LOW



UNSTABLE SLM
 Large Water-transport

Fig. 2

The work highlights in a qualitative and quantitative way, utilizing available physico-chemical correlations, the similarities and differences existing between SLM's and solvent extraction systems and gives guidelines for the practical selection of solvent extraction systems most suitable for supported liquid membrane applications.

References

1. P.R. Danesi, Sep. Science and Techn. 1984-85, Vol. 19, P. 857
2. R.D. Noble and J.D. Way, ACS Symposium Series, 347, 1987, P. 110
3. D. Pearson, Progress Report No. 1 LR 474 (ME) M, Warren Spring Laboratory, U.K. 1984

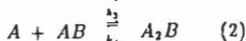
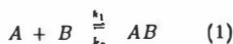
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Introduction: Facilitated, or carrier-mediated transport is an accelerated separation process due to carriers used in a liquid membrane layer. Carrier molecules chemically bind with solute molecules, transport them through the liquid membrane layer and release them on the other side. Some applications of facilitated transport through liquid membranes are: transporting O_2 through hemoglobin solutions and removing CO_2 from life-support equipment. Removal of acid gases (CO_2 and H_2S) from natural gas and recovery of CO and H_2 are additional applications of facilitated transport [1 and 2].

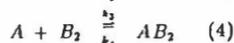
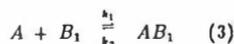
Kemena et al. [3] used $A + B \rightleftharpoons AB$ (A:solute, B:carrier) reaction mechanism in their model to determine the optimum dimensionless equilibrium constant to obtain the maximum facilitation factor for a given inverse Dankohler number (ϵ) and mobility ratio (α). Their analysis covered the entire range between diffusion-limited and reaction-limited mass transport. The existence of the maximum was demonstrated. They also showed that the facilitation factor would increase with increasing α , decreasing ϵ and has a maximum with increasing dimensionless equilibrium constant.

In this study, two different models, explaining facilitation through liquid membranes, were studied for the entire range between diffusion-limited and reaction-limited mass transport.

Model 1 — Site Access is Sequential



Model 2 — Site Access is Independent



The objective of this study is to determine the range of the dimensionless equilibrium constants which will produce the maximum facilitation factor, F for both of the models. The uses of the results include screening of possible carriers, selection of solute concentration and comparing actual to optimal performance.

Theory: The model formulation yielded four second order differential equations for both of the models. After considering some simplifying assumptions, these governing mass transport equations for the two models were solved numerically. The dimensionless variables in the equations were then optimized to yield the highest facilitation factor. The boundary conditions on the non-volatile species represent the fact that they are constrained to stay within the membrane. The boundary conditions on A indicate the maximum concentration gradient across the membrane. The dimensionless variables are: α is mobility ratio of carrier to solute, K is dimensionless equilibrium constant, C_A^* is dimensionless solute concentration and X is dimensionless membrane thickness. ϵ_1 and ϵ_2 are the inverse Dankohler numbers and give a measure of the relationship between diffusion and the reverse reaction rate. Small values of ϵ_1 and ϵ_2 indicate a diffusion limited process and large values indicate a reaction limited process.

Results and Discussion: Before presenting the results, it is worthwhile to give a mathematical definition of the facilitation factor, F .

$$F = \frac{-\frac{dc_A}{dX}\big|_{X=1} \text{ (for a given } \alpha\text{)}}{-\frac{dc_A}{dX}\big|_{X=1} \text{ (for } \alpha = 0\text{)}} \quad (5)$$

Model 1: The forward rate of the 2nd step should be higher than reverse rate in order to obtain as much A_2B complex as possible. It is the A_2B transport which will make this process more efficient than a single step process. The results of F calculations for given K_1 , K_2 , ϵ_1 , ϵ_2 and α values demonstrated the same approach. Increasing K_2 at constant K_1 has a larger effect on F than increasing K_1 at constant K_2 . F also increases with increasing α , since α is proportional to the total carrier concentration. Figure 1 demonstrates the existence of a maximum in F for $\alpha=100$. Both ϵ 's and K 's were set equal to allow this result to be plotted graphically. As expected the maximum F is larger and more pronounced as ϵ_1 and ϵ_2 decrease (move toward reaction equilibrium) at constant K_1 and K_2 values. The same result was also shown by [3]. Because, as k_2 and k_4 increased, k_1 and k_3 also increased to keep K_1 and K_2 constant and the whole process becomes more efficient. As a result of these interpretations and numerical results, it can be concluded that 2nd step is a more important step (but not desirable as a rate limiting step) than 1st step. F depends on the 2nd step more than 1st step, since the product of the 2nd step is carrier molecules transporting 2 solute molecules instead of 1 as in 1st step. 1st step is necessary and important since it is the initial step for the 2nd step and it has to be efficient.

Model 2: Since both active sites react independently and they both have the same chemical structure, ϵ_1 and K_1 should have the same effect as ϵ_2 and K_2 does on F . α should have again an increasing effect on F . F calculations for model 2 showed the same result (Figure 2). Kemena et al. [3] pointed out the same result for their single step model.

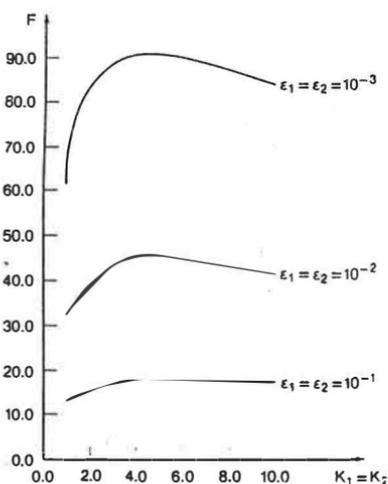


Fig. 1. F vs. $(K_1 \text{ and } K_2)$ for different ϵ 's (Model 1).

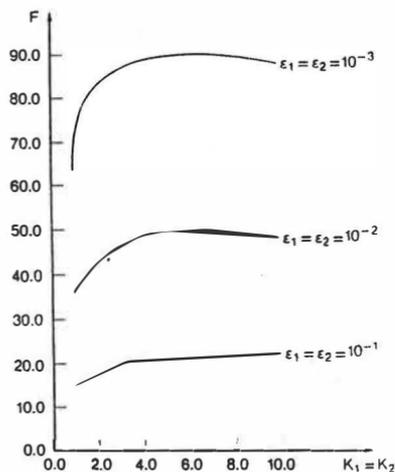


Fig. 2. F vs. $(K_1 \text{ and } K_2)$ for different ϵ 's (Model 2).

For model 1; as $\epsilon_1 = \epsilon_2$ decreased, optimum K_1 decreased and optimum K_2 had a minimum value at certain $\epsilon_1 = \epsilon_2$ value. These minimum values were also observed for different α values. The same trend was also found in [3]. Optimum F values of model 1 are higher than the results of [3] for the same ϵ and α values. Figure 3 is a four part map which shows optimum K_1 , optimum K_2 and corresponding optimum F values for different α and $\epsilon_1 = \epsilon_2$ values.

For model 2; optimum K_1 (= optimum K_2) had minimum value for decreasing $\epsilon_1 = \epsilon_2$ at different α values (Figure 4). Figure 5 shows the corresponding optimum F values for different α values. Optimum K_1 (=optimum K_2) and optimum F values are higher than the results of [3] for the same ϵ and α values.

where

$$\epsilon_1 = [\text{Diffusivity coefficient of carrier-solute complex}] / [k_2(\text{ membrane thickness})]$$

$$\epsilon_2 = [\text{Diffusivity coefficient of carrier-solute complex}] / [k_4(\text{ membrane thickness})]$$

$$K_1 = [k_1 (\text{ initial solute concentration})] / k_2$$

$$K_2 = [k_3(\text{initial solute concentration})] / k_4$$

$$\alpha = [(\text{Diffusivity coefficient of carrier-solute complex}) (\text{Initial carrier concentration})] / [(\text{Diffusivity coefficient of solute}) (\text{Initial solute concentration})]$$

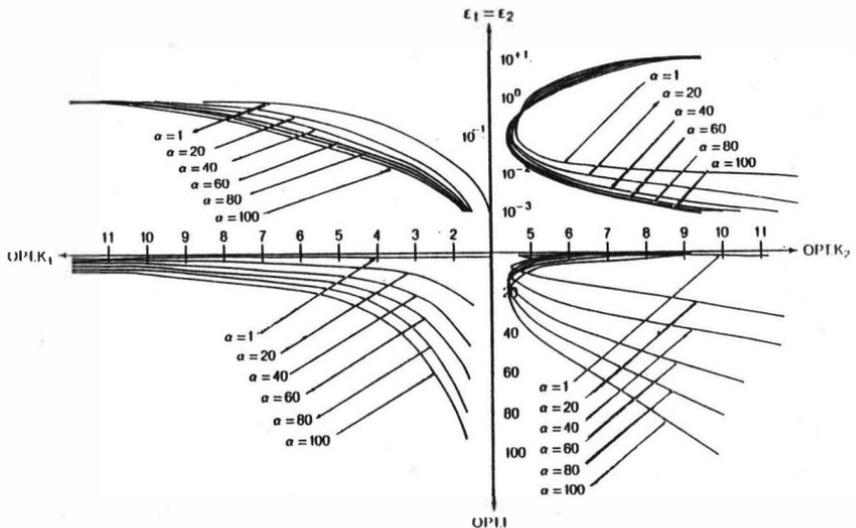


Fig.3. (α and ϵ 's) vs. (Optimum K_1 , optimum K_2 and optimum F) (Model 1).

Both of the models gave optimum K_1 and optimum K_2 between 1 and 10 for $10^{-3} \leq \epsilon_1, \epsilon_2 \leq 1$ and $1 \leq \alpha \leq 100$. Optimum K_1 and optimum K_2 are very important parameters in choosing the types of carrier. 1 to 10 is a good range to choose carrier type.

It should be noted that similar results were obtained for both models when ϵ_1 is different than ϵ_2 . So, the conclusions are also valid for this situation.

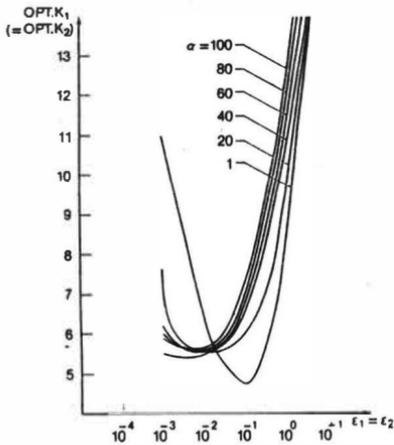


Fig.4. Optimum K 's vs. ϵ 's (Model 2).

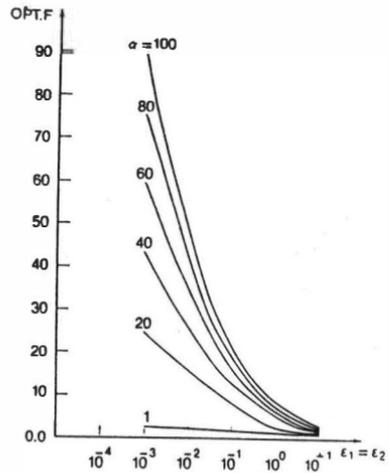


Fig.5. Optimum F 's vs. ϵ 's (Model 2).

Conclusions: The optimization of two different models have been performed to find the maximum facilitation factor and corresponding dimensionless equilibrium constants K_1 and K_2 , for given inverse Damkohler numbers ϵ_1 and ϵ_2 , and mobility ratio α . Optimum K_1 and optimum K_2 values varied from 1 to 10. Results of both models are important in terms of arranging the experimental conditions and comparing the experimental results with the optimum conditions and optimum results.

References

1. J.D. Way, R.D. Noble, T.M. Flynn and E.D. Sloan, Liquid membrane transport: A survey, *J. Mem. Sci.*, 12(1982)239.
2. S.G. Kimura, S.L. Matson and W.J. Ward, III, Industrial applications of facilitated transport, *Rec. Dev. Sep. Sci.*, 5(1979)11. near equilibrium, *Chem.Eng.Sci.*, 20(1965)121-129.
3. L.L. Kemena, R.D. Noble and N.J. Kemp, Optimal regimes of facilitated transport, *J. Mem. Sci.*, 15(1983)259-274.

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Emulsion Liquid Membrane Permeation is a relatively new technology and first industrial applications are realised at present. Most of them are in the field of hydrometallurgy especially in the field of zinc removal from aqueous solutions [1]. The interest in emulsion liquid membrane technology has been caused because of the capability to remove aqueous pollutants to very small concentrations with a reasonable pay back time of investment costs. For easier design of pilot plant experiments and for easier scale up a simulation model was developed for the recovery of copper from aqueous solutions which is shortly described in this paper.

A mass transfer model has been developed for carrier transport in emulsion liquid membranes earlier [2,3,4] which uses the instationary diffusion equation for the description of mass transfer in the emulsion globules. This model is now used for the simulation of experimental results of copper removal from aqueous solutions in a counter-current contactor with emulsion liquid membranes.

Mass transfer in an emulsion globule is comparable to the diffusion and reaction problem in a solid catalyst with complex kinetics. The mass transfer model which has been already proposed [3,4] to describe carrier facilitated transport into an emulsion globule uses the following assumptions:

- Emulsion globules are stabilized by an effective surfactant and thus coalescence and redispersion is suppressed in any emulsion liquid membrane permeation apparatus. Once an emulsion globule is formed it has a life time in the apparatus according to the residence time of the emulsion.

- The diffusion of the metal-ions to the external interface of an emulsion globule is described by the two film theory while the diffusional resistance of the protons from the interface into the continuous phase III is neglected.

- The reaction between the metall-ions and the organic carrier (Acorga PT5050) is assumed to take place at the interface between phase III and the organic phase II (the continuous phase of the emulsion). Thus this reaction can be described by interfacial reaction kinetics.

- The reaction stoichiometry is as follows:



- The kinetic equation of the extraction reaction is of the following form.

$$r_{\text{ex}} = k_f \cdot \left(\frac{[\text{Cu}]^* \cdot [\overline{\text{RH}}]^*}{([\text{H}]^*)^{0.25}} - \frac{1}{K_{\text{ex}}} \cdot \frac{[\overline{\text{CuR}_2}]^* \cdot ([\text{H}]^*)^{1.75}}{[\overline{\text{RH}}]^*} \right) \quad (2)$$

The concentrations in equation (2) are interfacial concentrations at interface III-II:

- The diffusion of the metall-carrier complex into the emulsion globules can be described by the general diffusion equation which has to contain an additional reaction term to describe the stripping reaction. This stripping reaction is supposed to be a pseudo-homogeneous reaction in the emulsion globules and no additional diffusional resistances are anticipated at the interface III-II. In addition the stripping reaction is very fast for the copper system so that chemical equilibrium is assumed between phase II and phase I.

The above outlined mass transfer model can be applied to counter-current phase contact if the following three phenomena can be calculated: 1. the copper concentration in the continuous aqueous phase III, 2. the pH (free proton concentration) of the continuous phase III, 3. the lifetime of an individual emulsion globule at any stage in the column. The first two problems can be solved by relatively simple mass balances for a thin slice of the column which allow the calculation of the concentration profiles for the copper ions and the protons in phase III. If the dispersion model is used to describe axial mixing effects of the continuous phase the resulting equation which is describing the Cu^{2+} -concentration reads

$$\begin{aligned} v_c \cdot \frac{d([\text{Cu}]_c)}{dz} + D_{\text{ax}} \cdot \frac{d([\text{Cu}]_c)^2}{dz^2} = \\ = N \cdot 4 \cdot \int_0^{\infty} R^2 \cdot \beta_{\text{Cu}} \cdot ([\text{Cu}]_c - [\text{Cu}]_c^*) \cdot f_1(R) \cdot dR \end{aligned} \quad (3)$$

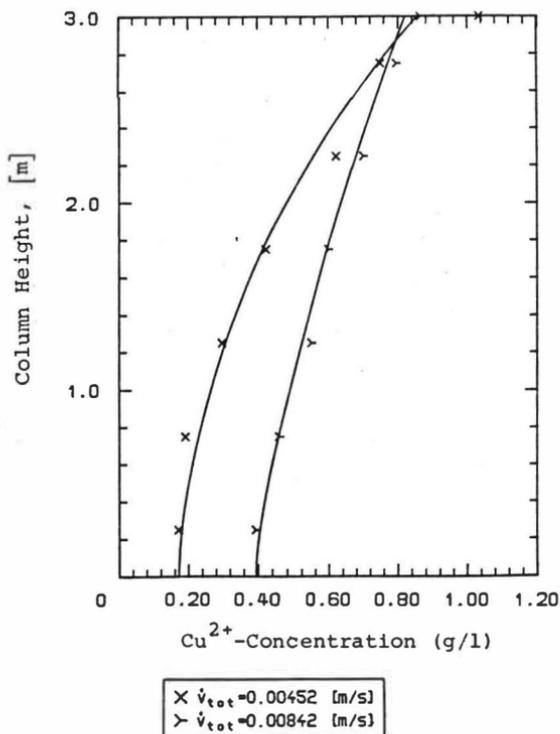
and the proton concentration can be calculated as a function of the metal-ion concentration.

The most difficult problem to solve is the calculation of the residence time of an emulsion globule in a column which is necessary to calculate the time derivative of the instationary diffusion equation. To solve this problem a convective dispersion model [5] was used for the dispersed phase (emulsion) and the time derivative in the instationary diffusion equation could then be replaced by the following expression:

$$\frac{\partial}{\partial t} = v_r \cdot \frac{\partial}{\partial z} \quad (4)$$

In the above expression V_r is the rise velocity of an emulsion globule relative to the column. V_r is dependant on the emulsion globule diameter. With a convective dispersion model axial mixing of the dispersed phase can only be accounted for if a globule size distribution is used.

The instationary diffusion equation combined with the mass balances of the continuous phase can be solved very effectively with the method of lines [6]. This method reduces the instationary diffusion equation for mass transfer in the emulsion globules (parabolic PDE) to a system of ODE's. The mass balance equation for the copper concentration in the continuous phase (2nd order ODE) can be reduced to two 1st order ODE's. The resulting system of ODE's describing emulsion liquid membrane per-



formance in a counter current stirred column can be solved by standard methods. If axial mixing effects of the dispersed phase are included in the simulation procedure the calculation time increases with the number of globule size classes. An effective integration routine (e.g. Gauss-Legendre Quadrature) for the integration of the integral in equation (3) can cut the calculation time substantially.

Calculated results of the above presented simulation model for emulsion liquid membrane permeation are shown in Figure 1 for the permeation of copper from aqueous solutions. The calculated results are represented by the lines and single points represent

experimentally measured results. The agreement is quite good if one takes into account that all parameters of the mass transfer model are not fitted to these results but were independantly determined in a constant interface stirred cell and in a single drop apparatus [3].

Conclusions from the present work are that indeed emulsion liquid membrane performance can be described by the instationary diffusion model. The assumption of non coalescing emulsion globules holds also for emulsion liquid membrane operation in counter current stirred columns.

Nomenclature

- β_{Cu} transport coefficient of copper - cont. phase, m/s.
[Cu]... concentration of copper, kmol/m³.
[CuR₂]... concentration of the copper-carrier complex, kmol/m³.
 D_{ax} axial dispersion coefficient, m/s.
 $f_1(R)$.. globule size distribution.
H concentration of the proton concentration, kmol/m³.
 k_f reaction rate coefficient, m^{3.25}/kmol^{0.75}/s.
 K_{ex} equilibrium constant, extraction reaction.
 N number of emulsion globules/unit volume.
 r_{ex} reaction kinetics-stripping reaction, kmol/m²/s.
 R radius of emulsion globule, m.
[RH]... concentration of the organic carrier, kmol/m³.
 t time, s.
 \dot{V}_c superficial velocity - continuous phase, m/s.
 V_r rise velocity of an emulsion globule relative to the column, m/s.
 z axial coordinate, m.

Literature

1. Draxler J., Marr R.// Chem. Eng. Process., 20 (1986). 319-239.
2. Teramoto M., Takihana H., Shibutani M., Yuasa T., Hara N.// Sep. Sci. Technol. 18 (1983). 397-419.
3. Lorbach D., Bart H., Marr R.// Ger. Chem. Eng., 9 (1986). 321-327.
4. Lorbach D., Marr R.// Chem. Eng. Process., 21 (1987). 83-93.
5. Lo et al. Handbook of Solvent Extraction, John Wiley & Sons, New York, 1983
6. Finlayson B.A. Nonlinear Analysis in Chemical Engineering, McGraw Hill, Inc., New York, 1980

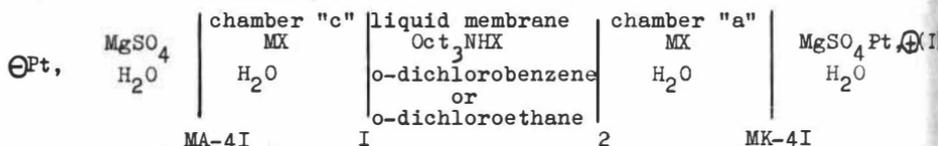
ION EXCHANGE BETWEEN AQUEOUS AND ORGANIC PHASES IN
ELECTRODIALYSIS OF LIQUID MEMBRANES - SOLUTIONS OF
TRIOCTYLAMINE SALTS IN HALOCARBONS

6-10

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When transfer of anions through the liquid membranes - solutions of salts of tertiary amines in polar halocarbons - takes place, and electric current passed through it, a number of peculiarities is observed distinguishing this process from that of membrane extraction. The extractable ions are transferred by electric field from the source aqueous phase through a liquid membrane to the receiving aqueous phase in the traditional scheme [1]. Moreover, an organic phase, into which the extractable ions have been extracted, preliminarily, may be used as a liquid membrane. Electrodialysis of such membranes is a reextraction method of ions from nonaqueous phase [2], it is formally similar to the process of demineralization using solid ion-exchange membranes.

Comparison of the efficiency of the two system of electrodialysis in the present study is made on the example of extraction of ClO_4^- ions by liquid membranes - salt solution of n-trioctylamine (Oct_3NHX , where $\text{X} = \text{Cl}^-$ or ClO_4^-) in o-dichlorobenzene and 1,2-dichloroethane. The measure cell schematically is shown bellow.



where $\text{M} = \text{K}^+, \text{Na}^+, \text{H}^+$, MA-4I, MK-4I are solid ion-exchange membranes.

A liquid membrane with the thickness of $2 \cdot 10^{-3} \text{m}$, the area of $7,5 \cdot 10^{-2} \text{m}^2$ was inserted between two vertical hydrocellulose films. A liquid membrane with open vertical interfaces supported by adhesion forces in teflon, was applied in some experiments. The electrolyte cell, electronic circuit, and the experimental procedure employed for the voltammetry of the liquid membrane were described previously [2].

The overpotential of ion transfer through the interfaces does not exceed some volts [3], which is negligible in comparison with the ohmic drop of potential on the membrane, which amounts to hundreds of volts. The ohmic resistance of nonaqueous phase completely determines the value of current passing through the membrane. During the electrodialysis process, the concentration of ions in the membrane and, actually, its ohmic resistance may change considerably due to the limited volume. It leads to non-linearity of the dependance of the current and the potential. Ion concentration in the organic phase is determined by the ratio of anion flux through the interface and electric conductance of the membrane. The voltammogram is linear when the current corresponds to the conductance of organic phase volume.

For example, the dependance of the current and the potential in transfer of Cl^- ions through the membrane - solution of Oct_3NHCl in o-dichlorobenzene - is linear, the initial lengths of voltammograms for other systems are linear, as well (Fig.1-3). It is interesting to note, that in all cases replacement of the neutral salt of the aqueous solution for the corresponding acid in chamber "a" does not alter the type of voltammograms. It leads to a suggestion that the proton does not participate in electricity transfer through a membrane, containing a salt of trioctylamine.

The electric conductance of $\text{Oct}_3\text{NHClO}_4$ is approximately 5 times larger than the electric conductance of solution Oct_3NHCl in o-dichlorobenzene. The type of voltammograms for the membrane, containing $\text{Oct}_3\text{NHClO}_4$, considerably depends on the concentration of ClO_4^- ions in the source phase. However, the initial linear lengths of the dependances coincide and have a slope typical for the system containing 1,0 M of HClO_4 solution in chamber "c" (Fig.1). Such a coincidence points to the fact that electricity through the membrane in these cases is transferred only by anions, and electric conductance of the membrane entirely determines the value of the current. Due to lessening of the concentration of ClO_4^- ions in the source solution fact the ion flux from the aqueous phase into the organic one becomes smaller than the current passing through the membrane volume. Moreover, protons start to participate in the current transfer through the interface I. These protons are created by deprotonization of trioctylamine cations. A large current rise follows after this process, when the current has passed through its maximum, the concentration of the ion-exchanger in the membrane diminishes to the value corresponding to the ion flux from the aqueous phase (Fig.1-3). Presence of the excess of a background electrolyte in chamber "c" leads to

the suppression of migration current of ClO_4^- ions into the membrane. The total current of univalent anions through the interface I diminishes twice [4], due to which a peak on voltammograms corresponds to approximately twice lesser potential on the membrane. At low concentration of the electrolyte in the aqueous phase, a peak of current is not observed on the curves, but hysteresis is typical for the voltammograms (Fig.1).

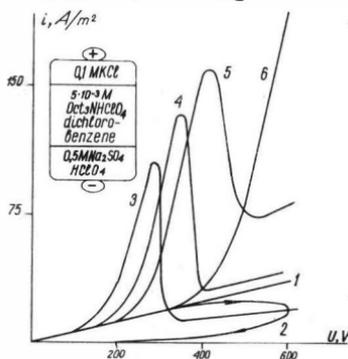


Fig.1. Voltammograms of the liquid membrane. HClO_4 concentration (M): 1-1.0; 2-0.01; 3-0.01; 4-0.033; 5-0.066; 6-0.1. Curves (1,2) were registered in background electrolyte absence. Rate of potential sweep on the membrane 6 V/s

Evidently in the given case an ejection of Oct_3NH^+ cations from the organic phase into the aqueous phase occurs. This transfer is followed by the appearance of emulsion.

The change of pH in chamber "c" begins only with a steep current rise (curve 1, Fig.2.). Electric charge (shown by the shaded area in

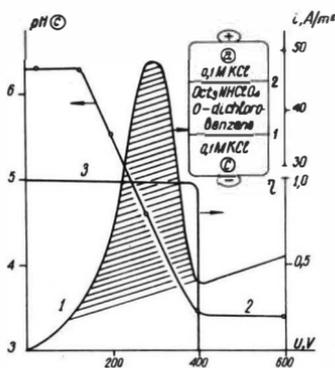


Fig.2. 1-voltammogram of the liquid membrane; 2-change of pH in chamber "c"; 3-current efficiency for ClO_4^- ions re-extraction. Rate of potential sweep - 6V/s

Fig.2) having passed through the membrane, corresponds to the change of H^+ ion concentration in chamber "c". The end of pH change coincides with the end of reextraction process of ClO_4^- ions from the organic phase. Further current through the membrane is transported only by Cl^- ions. A large increase of the current passing through the membrane, corresponding to the appearance of the peak, is followed by acceleration of the reextraction rate of ClO_4^- ions from the organic phase

volume. Substitution in chamber "c" of neutral solution for a corresponding acid practically does not influence the type of voltammograms, as well as the nature of current transfer through the membrane. Interaction of trioctylamine in the neutral form and the acid in the region of interface I is negligible, which apparently is connected with the

low proton concentration in this layer caused by passing of electric current.

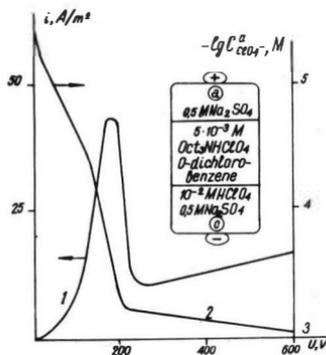


Fig.3. 1-voltammogram of the liquid membrane; 2-change of ClO_4^- concentration in receiving solution. Rate of potential sweep - 1.2V/s

The constant of reextraction rate (length II of curve 2, Fig.3) is higher than the constants of transfer rates of ClO_4^- ions through the membrane (lengths I and III of the same curve). Thus, the impact of electric current is the most effective in reextraction of ClO_4^- ions from the organic phase. The presence of ClO_4^- ions in the receiving solution (chamber "a") does not influence the reextraction rate of these

anions. In fact, it allows to apply electro dialysis of such membranes for concentration of perchlorate ions.

Qualitatively extreme dependance of the current and the potential, apparently may be described from the view point of percolation theory.

Reextraction of ClO_4^- ions from the organic phase with a current efficiency near 100% is performed according to the scheme given in Fig.4.

In this case current through the interface aqueous solution of an alkali/membrane is transferred exclusively due to the neutralization reaction of Oct_3NH^+ cations. Current through the opposite interface is transferred by reextractable anions. In contrast to liquid reextraction by an alkali, these processes turn out to be spatially divided by the liquid membrane. The dependance of the current and the potential is described by the equation:

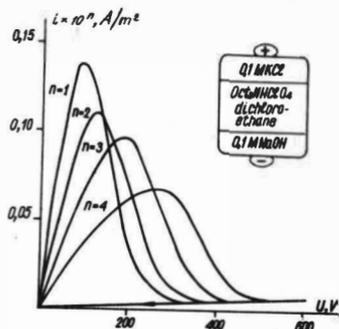


Fig.4. Voltammograms of the liquid membranes. Concentration of alkylammonium salt in the membrane (M): 1- $5 \cdot 10^{-6}$; 2- $5 \cdot 10^{-5}$; 3- $5 \cdot 10^{-4}$; 4- $5 \cdot 10^{-3}$. Rate of potential sweep - 12 V/s

$$i = gWl^{-1}C_0 t \exp(-0,5 gWF^{-1}l^{-2}t^2), \quad (2)$$

where i - the current density, g - the rate of potential sweep, l - the thickness of the membrane, W - the equivalent conductance of the electrolyte in the organic phase, F - Faraday's number, C_0 - the initial concentration of alkylammonium salts.

Curve (2) passes through a peak

$$i_{\max} = C_0 (gWF)^{1/2} \exp(-0,5) \quad (3)$$

and the peak current of which is proportional to the concentration of alkylammonium salt. Linear dependance (3) can be used for quantitative determination of the amine salt in the organic phase.

References

1. Purin B.A.// Izv.AN LatvSSR, 1971, N^o 5, p.31-36.
2. Popov A.N., Timofeyeva S.K.// Izv.AN LatvSSR, ser.him., 1983, N^o 4, p.406-413.
3. Koryta I.// Ion-Selective Electrode Rev., 1983, Vol.5, p.131-164.
4. Vetter K. Elektrochemische Kinetik. Berlin: Springer-Verlag, 1961.

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A growing interest to membrane extraction is due to high intensity of extraction and separation of substances in this process [1]. From existing ways of practical realization of certain interest is the pertractor with flowing down liquid films [2].

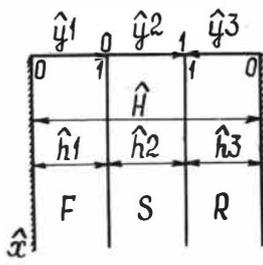
The process goes as follows: the substance is transported from the phase F to the phase R. These two phases are separated by the third phase S that does not mix with the former ones which are usually of a similar nature. Thus, the process of extraction takes place between the phases F and S, and the process of reextraction is between phases S and R. In these conditions one gets the possibility to shift an equilibrium in a desired way with the minimum volume of intermediate phase S. In contract to supported liquid membranes, where at least one phase is motionless, in pertractor with flowing down films are three liquid phases are in motion. It guarantees high rate of mass transfer for all stages of substance transport from the phase F. In the pertractor liquids F and R under the influence of gravity are flowing down over the hydrophile surfaces of vertical plates forming a packet. The transport liquid S is not soluble in liquids F and R, it also flows down under the influence of gravity. In spite of the fact that in the pertractor with flowing down films the mass transfer intensity is 1 to 2 orders greater than for supported liquid membranes, a detailed investigation of three-phase extraction with flowing down films is not done yet. A theoretical analyses was made without taking into account the real hydrodynamic features or the distributed component concentration profile for each phase [3].

This report is based upon a numerical solution of Navier-Stocks equations for hydrodynamically stabilized region. A distribution of velocities and thickness of films flowing down under the influence of gravity as a function of liquid flow rate and a distance between the plates of pertractor packet is obtained. From a numerical solution of convective diffusion equations for each phase in a conjugate treatment concentration profiles in longitudinal and transverse directions of the pertractor are found. In the process of numerical solution a "implicit triangle" scheme was proved to be stable for conjugate problem and real profile of velocities.

We shall consider a stationary flow of three liquid films along the coordinate x which coincides with the direction of gravity acceleration \hat{g} when the first and the third films are flowing down along the plates while the second one is filling the space between them.

The value of each quantity we shall denote by a letter and a number following it so that the number will mark the phase. The number can be replaced by letter I (index) which value will be indicated. If the value is not indicated or the index is omitted it takes the value 1,2,3. The absence of the summation index value also means its variations from 1 to 3. Dimensional values we shall mark by accent circonflex. For example, $\hat{\rho}^1$ is the density of the first phase, $\sum \hat{q}^I = \hat{q}^1 + \hat{q}^2 + \hat{q}^3$ is the total hydrodynamic flow rate, etc.. We shall consider as fixed values the distance between plates (so that $\sum \hat{h}^I = \hat{H}$), the irrigation density, physical and chemical properties of liquids and equilibrium constants at interphase surface. These properties of liquids are supposed to be the same at all extent of pertractor.

In a coordinate frame (fig.1) the equation system for variation of momentum and mass transfer, with the remarks made above, takes the form



$$\begin{aligned}
 & -\frac{\partial \hat{\rho}^I}{\partial \hat{x}} + \hat{\mu}^I \frac{\partial^2 \hat{u}^I}{\partial \hat{y}^I{}^2} + \hat{\rho}^I \hat{q} = 0; \quad (1) \\
 & -\frac{\partial \hat{\rho}^I}{\partial \hat{y}^I} = 0; \\
 & \hat{u}^I(\hat{y}^I) \frac{\partial \hat{c}^I}{\partial \hat{x}} = \hat{D}^I \left(\frac{\partial^2 \hat{c}^I}{\partial \hat{y}^I{}^2} + \frac{\partial^2 \hat{c}^I}{\partial \hat{x}^2} \right). \quad (2)
 \end{aligned}$$

Fig.1. The coordinate frame

The boundary conditions for (1)-(2) are the following ones:

$$\text{if } \hat{x} = 0 \text{ then } \hat{c}^1 = \hat{c}_0, \hat{c}^2 = 0, \hat{c}^3 = 0. \quad (3)$$

At plates surface at $\hat{y}^1 = 0$ and $\hat{y}^3 = 0$ we have

$$\text{when } \hat{y}^1 = 0 \text{ we have } \hat{u}^1 = 0, \frac{\partial \hat{c}^1}{\partial \hat{y}^1} = 0; \quad (4)$$

$$\text{when } \hat{y}^3 = 0 \text{ we have } \hat{u}^3 = 0, \frac{\partial \hat{c}^3}{\partial \hat{y}^3} = 0. \quad (5)$$

At liquids F and S interface we have

$$\text{when } \hat{y}^1 = \hat{h}^1 (\hat{y}^2 = 0) \text{ we have } \hat{u}^1 = \hat{u}^2, \hat{\mu}^1 \frac{\partial \hat{u}^1}{\partial \hat{y}^1} = \hat{\mu}^2 \frac{\partial \hat{u}^2}{\partial \hat{y}^2}, \quad (6)$$

$$\hat{c}^1 = M^1 \hat{c}^2, \hat{D}^1 \frac{\partial \hat{c}^1}{\partial \hat{y}^1} = \hat{D}^2 \frac{\partial \hat{c}^2}{\partial \hat{y}^2}; \quad (7)$$

and between phases S and R we have

$$\text{when } \hat{y}_2 = \hat{h}_2(\hat{y}_3 = \hat{h}_3) \text{ we have } \hat{u}_2 = \hat{u}_3, \hat{\mu}_2 \frac{\partial \hat{u}_2}{\partial \hat{y}_2} = -\hat{\mu}_3 \frac{\partial \hat{u}_3}{\partial \hat{y}_3}, \quad (8)$$

$$\hat{c}_2 = M_2 \hat{c}_3, \quad \hat{D}_2 \frac{\partial \hat{c}_2}{\partial \hat{y}_2} = -\hat{D}_3 \frac{\partial \hat{c}_3}{\partial \hat{y}_3}. \quad (9)$$

Initial and boundary conditions (3)-(9) should be completed by the demand of flow rate conservation in each phase:

$$\int_0^{\hat{h}_I} \hat{u}_I(\hat{y}_I) d\hat{y}_I = \hat{q}_I, \quad I = 1, 2, 3. \quad (10)$$

Eqs.(1)-(2) with initial and boundary conditions (3)-(9) and flow rate continuity condition (10) form a mathematically closed problem which makes it possible to calculate hydrodynamic characteristics and mass transfer for three-phase liquid extraction as well as the effective length of pertractor with flowing down films.

To solve the hydrodynamic problem we used the following dimensionless variables

$$\begin{aligned} \hat{q}_I &= q_I \Sigma \hat{q}_I; & m_I &= \hat{\mu}_I / \Sigma \hat{\mu}_I; \\ \Gamma_I &= \hat{\rho}_I \hat{q}_I \hat{h}_I^3 / \Sigma \hat{\mu}_I \Sigma \hat{q}_I; & \hat{h}_I &= h_I \hat{H}; & \hat{y}_I &= y_I \hat{H}; \\ \hat{\rho} &= \rho \Sigma \hat{\mu}_I \Sigma \hat{q}_I / \hat{H}^2; & \hat{u}_I &= u_I \Sigma \hat{q}_I / \hat{H}. \end{aligned} \quad (11)$$

It follows from eqs.(1) that $\partial^3 u_I / \partial y_I^3 = 0$, which brings to the conclusion that the velocity profile in each phase forms a parabola

$$u_I(y_I) = A_I y_I^2 + B_I y_I + \Gamma_I. \quad (12)$$

Parabola coefficients for each phase can be obtained from the solution of nonlinear equations system

$$\begin{aligned} \Gamma_1 = \Gamma_3 = 0; & \quad m_1(2A_1 h_1 + B_1) = m_2 B_2; \\ m_2(2A_2 h_2 + B_2) + m_3(2A_3 h_3 + B_3) &= 0; \\ A_1 h_1^2 + B_1 h_1 + \Gamma_1 = \Gamma_2; & \\ A_2 h_2^2 + B_2 h_2 + \Gamma_2 = A_3 h_3^2 + B_3 h_3 + \Gamma_3; & \end{aligned} \quad (13)$$

$$(1/3)A|hI|^3 + (1/2)B|hI|^2 + \Gamma|hI| = qI;$$

$$h1 + h2 + h3 = 1; \quad T1 + 2m1A1 = T2 + 2m2A2;$$

$$T2 + 2m2A2 = T3 + 2A3m3.$$

For the solution of the diffusion problem we used the following dimensionless variables:

$$\begin{aligned} \hat{y}I &= \hat{h}I yI; & \hat{x} &= x \hat{H} \Sigma \hat{q}I / \Sigma \hat{D}I; & \hat{c}I &= \hat{c}_0 cI; \\ \hat{\omega}I(\hat{y}I) &= \omega I(yI) \hat{H} \hat{D}I \cdot \Sigma \hat{q}I / \hat{h}I^2 \Sigma \hat{D}I; \\ \varepsilon 1 &= \hat{D}1 \hat{h}2 / \hat{D}2 \hat{h}1; & \varepsilon 2 &= \hat{D}3 \hat{h}2 / \hat{D}2 \hat{h}3. \end{aligned} \quad (14)$$

With these variables eqs.(3), initial and boundary conditions take the form

$$\omega I(yI) \frac{\partial cI}{\partial x} = \frac{\partial^2 cI}{\partial yI^2} + \left(\frac{\Sigma D I}{\Sigma q I} h I \right)^2 \frac{\partial^2 cI}{\partial x^2}; \quad (15)$$

when $x=0$ we have $c1 = 1, \quad c2 = c3 = 0;$

when $y1=0$ we have $\partial c1 / \partial y1 = 0,$ when $y3=0$ we have $\partial c3 / \partial y3 = 0,$

when $y1=1(y2=0)$ we have $c1 = M1c2; \quad \varepsilon 1(\partial c1 / \partial y1) = \partial c2 / \partial y2,$

when $y2=1(y3=1)$ we have $c2 = M2c3, \quad \varepsilon 2(\partial c3 / \partial y3) = -\partial c2 / \partial y2.$

A system of differential equations (15) with boundary conditions (16) and velocities profile (12) has been solved numerically with implicit differential scheme with use of trial run method.

A complete information about the films flow in pertractor has been obtained in the process of solution. The same information about mass transfer can be obtained for three-phase film extraction.

References

1. Yagodin G.A., Ivahno S.Yu. // Teor.osn.khim.tekhn. 1986. Vol.20. No 3. P.291.
2. Malyusov V.A. // Teor.osn.khim.tekhn. 1987. Vol.21. No 1. P.26.
3. Boyadjiev L. // Teor.osn.khim, tekhn. 1987. Vol.18. No 16. P.735.

DEVELOPMENT AND TESTING OF A PILOT ELECTRODIALYSIS PLANT INVOLVING THE USE OF A CATION-EXCHANGE MEMBRANE, ON THE BASIS OF MATHEMATICAL SIMULATION OF MASS TRANSFER THROUGH A MEMBRANE

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The ion-exchange membranes used in electrodialysis are known to be less selective to like-charge ionic impurities [1]. The selectivity can be increased by carrying out electrodialysis with liquid membranes containing extractants, complexing agents, and macrocyclic compounds which are selective to certain ions [2].

The study of processes that take place in electrodialysis through liquid membranes are yet in the initial stage. For practical use of this promising method it is necessary that profound studies be made in to problems like theoretical description of mass transfer through liquid membranes when electric current is passed through them, selection of an electrodialysis scheme involving the use of a liquid membrane (LM), and development of reliable production equipment for the realization of the given method.

This report contains the results of our studies aimed at developing a pilot electrodialysis plant involving the use of a LM. Aqueous solutions of Na and Sr nitrates were used as test systems for studying the processes of mass transfer and ion separation through a LM.

In choosing the LM composition, we were guided by the following: (a) the distribution coefficient of Sr^{2+} ions between the organic and aqueous phases $D_{Sr} = C_{Sr}^o / C_{Sr}^{aq}$ is high enough ($D_{Sr} > 10$); (b) the LM is selective to Sr^{2+} ions; (c) the LM diluent is least fire and explosion hazardous and is not very toxic; (d) the LM diluent badly dissolves water and has density very different from that of water so as to ensure fast separation of the aqueous and organic phases.

The literature data and the results of our preliminary studies reveal that perchloroethylene (PCE) is the most suitable diluent. The solubility of water in PCE equals 0.04% at 25°C [3].

The extractant was chosen by studying the characteristics of extraction of Sr and Na from 0.01 M aqueous solution of their salts at 25°C (pH 6.0) by PCE-based liquid membranes using the following reagents: HEDEHP, V-acid, DB18C6, DC18C6, PEG, picric acid and others, and also their mixtures.

The selectivity of LM for Sr in preference to Na was estimated by the Sr and Na ions separation factor $K_{Na}^{Sr} = D_{Sr} / D_{Na}$. The experiments have revealed that Sr is best extracted with HEDEHP, and the addition of DC18C6 to a PCE solution of HEDEHP causes D_{Sr} and K_{Na}^{Sr} to increase abruptly (synergistic effect).

In further experiments the LM had the following composition: 0.05 M HEDEHP + 0.05 M DC18C6 solution in PCE. Here, $D_{Sr} = 460$ and $K_{Na}^{Sr} = 1200$.

Table 1. Stripping of Sr and Na from a liquid membrane at 25°C

No	Solution	\bar{D}_{Sr}	\bar{K}_{Na}^{Sr}	No	Solution	\bar{D}_{Sr}	\bar{K}_{Na}^{Sr}
1	0.1 M HNO ₃	0.04	0.04	8	1.0 M Ca(NO ₃) ₂	0.57	0.67
2	1.0 M HNO ₃	0.67	0.91	9	0.01 M Ca(NO ₃) ₂ + 0.1 M HNO ₃	0.28	0.30
3	5.0 M HNO ₃	0.80	2.11	10	0.01 M BaCl ₂	0.02	0.014
4	0.1 M HCl	0.04	0.04	11	1.0 M BaCl ₂	0.57	0.51
5	1.0 M HCl	0.52	0.74	12	0.01 M BaCl ₂ + 0.1 M HNO ₃	0.23	0.20
6	5.0 M HCl	0.66	0.89				
7	0.01 M Ca(NO ₃) ₂	0.02	0.016				

This liquid membrane was used to strip Sr and Na ions from an organic phase by aqueous solutions of different composition. In this case, $\bar{D}_{Sr} = C_{Sr}^{aq}/C_{Sr}^o$ and $\bar{K}_{Na}^{Sr} = \bar{D}_{Sr}/\bar{D}_{Na}$.

From the results listed in Table 1 it is concluded that even concentrated solutions of acids and salts do not enable sufficiently complete stripping to be effected.

For mathematical simulation of mass transfer through a liquid membrane, we considered the system shown in Fig. 1. A model was constructed for the simplest case - when one aqueous solution of salts of singly charged cations M⁺ and N⁺ (source solution, s) is separated from the other (receiving solution, r) by a liquid membrane, l, layer. The M⁺ ions were assumed to be formed in the LM phase of a complex of type MLR, and the N⁺ ions, in a complex of type NR (here, L is a neutral carrier and R is a cation-exchange carrier). It is generally agreed that the carrier L is present in excess in LM and its content equals C_L, and the diffusion coefficients of complexes and the carrier R are equal (D_{MLR} = D_{NR} = D_R).

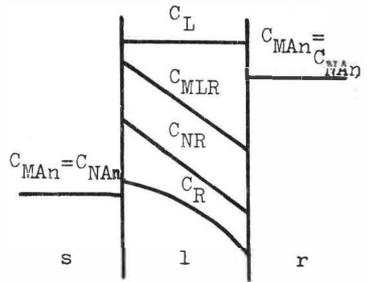


Fig. 1. Model of a liquid membrane system

The following expressions were obtained for M⁺ and N⁺ ions currents passing through a membrane:

$$j_{MLR} = \frac{D_R}{h} \left(\frac{C_R + \frac{ih}{2FD_R}}{1 + \frac{1}{K_N^M C_L} \frac{C_N^S}{C_M^S}} - \frac{C_R - \frac{ih}{2FD_R}}{1 + \frac{1}{K_N^M C_L} \frac{C_N^R}{C_M^R}} \right), \quad (1)$$

$$j_{NR} = \frac{D_R}{h} \left(\frac{C_R + \frac{ih}{2FD_R}}{1 + \frac{1}{K_N^M C_L} \frac{C_M^S}{C_N^S}} - \frac{C_R - \frac{ih}{2FD_R}}{1 + \frac{1}{K_N^M C_L} \frac{C_M^R}{C_N^R}} \right), \quad (2)$$

where j_{MLR} and j_{NR} are the currents of MLR and NR complexes passing

through the liquid membrane; h is the thickness of LM; C_R is the total concentration of the carrier R^- in LM; i is the electric current density; F is the Faraday constant; C^S and C^R are the concentrations of ions in the source and receiving phases, respectively, and K_N^M is the M^+ and N^+ ions separation factor.

The proposed model makes it possible to estimate the effect of external factors (electric current density, concentration of carriers in LM, membrane thickness, etc.) and the membrane extraction process implementation conditions on the separation ability of a concrete device. In particular, it has been ascertained that the passage of electric current through LM increases the rate of mass transfer process, but at the same time impairs the equilibrium and separation characteristics of the process.

The used laboratory-scale electro dialysis cell consists of two caprolon pressure plates with platinated titanium electrodes. The plates have collectors for the incoming and outgoing solutions. Between the plates are arranged cation-(MK-40) and anion-exchange (MA-40) membranes and 1.2 mm thick polyethylene frames. The latter form the working chambers. The bulk LM is separated from the aqueous chambers by MK-40 membranes. Each chamber has a polyethylene net - vortex generator. The effective area of the membrane equals 70 cm². Each solution is circulated through a closed circuit consisting of a reservoir for solution, pump, rotameter, cooler, and respective chambers in the electro dialysis cell.

In different experiments the near electrode chambers were washed with s or r solution and also with HCl. The mass transfer processes have been studied in electro dialysis cells of different designs. Best results were obtained when the anode chamber was washed with the source solution and the cathode chamber, with HCl solution. Figure 2 shows the

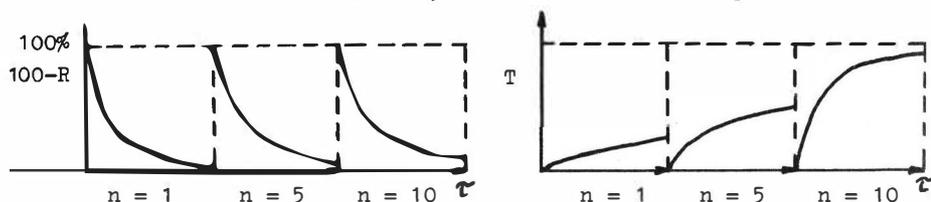


Fig.2. R and T curves of Sr for different n. Duration of experiments - 30 minutes

dependences of recovery $R = (C^S/C_0^S) \times 100\%$ and transfer $T = (C^R - C_0^R)/C_0^S \times 100\%$ ratios on time and the number of purification cycles, n. It is evident that with the increase in n, as LM saturates, the recovery ratio decreases insignificantly and the transfer ratio increases and attains a value R in this experiment.

The separation of Sr^{2+} and Na^+ ions was also studied. It was found that in all regimes under which electro dialysis was carried out the

separation of ions was practically not observed. According to the data of different experiments, K_{Na}^{Sr} varies between 1 and 2. Theoretical analysis as well as the analysis of experimental data on extraction, stripping and electrodialysis have revealed that integration of extraction and stripping processes is the main cause of lack of selectivity in the considered systems. Affinity of LM to a definite type of ions, which plays positive role at the extraction stage, adversely affects the stripping stage and impairs the conditions of mass transfer of the preferable ion from the organic phase into the receiving phase.

A two-stage scheme has been suggested for selective separation of Sr from solutions. First, extraction is carried out in a conventional manner. Then the saturated LM is pumped into the electrodialysis cell where stripping takes place. The separation coefficients for Sr^{2+} and Na^+ ions, obtained by this method, were between 20 and 40 for \bar{D}_{Sr} varying from 10 to 20, which is much more than the values of \bar{D}_{Sr} attained in conventional stripping (Table 1).

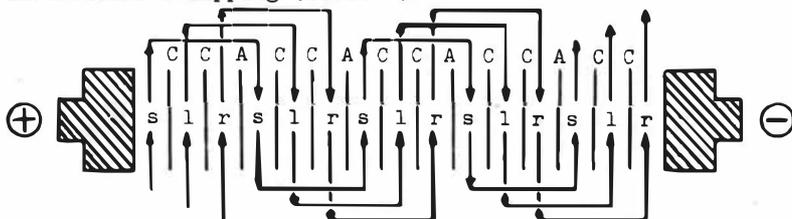


Fig.3. Schematic diagram of electrochemical plant (A - MA-40;C-MK-40)

Figure 3 shows the pilot electrochemical plant with LM. Here, the labyrinth-parallel flow of currents with minimum electrical current losses ensures favourable hydraulic conditions for the process, i.e. pressure differences between the neighbouring chambers are minimum.

Tests have shown that the plant performs well when 0.1 M test solutions of Na and Sr nitrates are purified in 20 cycles ($K_{Na}^{Sr} = 12.7$).

Plant's performance data

Electrode material	Platinated titanium
Pressure plates material	Caprolon
Flow capacity of each circuit, l/h	100
Source solution chambers	5
Liquid membrane chambers	5
Receiving solution chambers	5
Anion-exchange membranes MA-40	4
Cation-exchange membranes MK-40	10
Effective area of membrane, mm	200x400
Membrane distance, mm	1.2
Output in terms of final component, mole/h	1.0

References

1. Grebenyuk V.D. Electrodializ. Kiev: Tekhnika, 1976, P. 160.
2. Igawa M., Saitou K. et al.//Chem. lett. 1985, P. 861-864.
3. Laskorin B.N. et al.//Papers at All-Union Conf. on Extraction. Abstracts. Riga: Zinatne, 1982, Vol. 1, P. 99-100 (Russian).

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The preparation and extraction use of liquid membranes as well as their desintegration for the purpose of an enriched inner solution acquisition and the valuable membrane material recovery rather complicate the extraction processes in both laboratory and industrial scales. It seems necessary to control and supervise main physical experimental conditions at least, to reach their reproducibility.

A conventional turbine-type impeller/emulsifier has been constructed for the emulsions preparation [1]. The diameter $\varnothing 21$ mm of its rotor with 3 blades and the number of 30 grooves on the working part of its stator give a shear velocity 6.6 m/s and frequency 9 kHz under revolution speed of 100 r.p.s. (6000 r.p.m.) usually used. The speed of revolution is measured by means of a photoelectric sensor and stabilized by a feedback controller.

The extraction itself in laboratory conditions is often performed in ordinary beakers in which emulsions are gently stirred by means of a magnetic or mechanical stirrer. It is suitable if the stirrer revolutions can be checked and set occasionally at least. Especially for laboratory magnetic stirrers, a contactless tachometer with range up to 10 r.p.s. based on an inductive sensor has been constructed. The meter can be used for mechanical stirrers too if a small permanent magnet is fixed on the shaft.

Bringing in contact of small amounts of emulsions with large volumes of water solutions by extraction preconcentration processes is performed with advantage in a flow-through arrangement [2]. The equipment is very versatile in rearrangement and enables easily to change number of stirred compartments and their volumes. The stirrer revolutions are rather important experimental parameters ensuring the dispersion of emulsions in a solution and preventing them from settling in undisturbed regions. In spite of it, some types of emulsions manifest a tendency to flock and stick to immovable parts of the equipment. The simplest way how to prevent it seems to remove any immovable parts, such as baffles and separators, from a vertical cylindrical extractor. Two types of stirrers were developed to stir its volume: one with four spindle-shaped rotors driven by a 25 W asynchronous motor with a mechanical variator (type MR 25 produced by VEB MLW Freital, GDR) and another one, an axial inertial stirrer driven by a step-motor which velocity, acceleration, direction and amplitude of motion was controlled by a microprocessor.

Physical methods of the emulsions desintegration are preferred even in a laboratory scale because they do not influence the composition of the final product - inner solution. In our laboratory a desintegra-

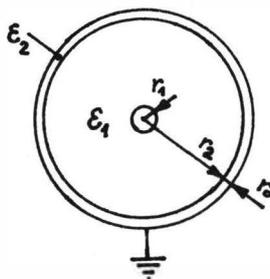
tion method using a h.f.-h.v. Tesla transformer has proved. The device with power consumption of 15 W affects the emulsions directly through glass walls of laboratory beakers and test tubes. The device produces on its output electrical impulses with damped oscillating courses of appr. these parameters: number of pulses ca. 400 per second, pulse energy 8 mJ, peak voltage 10 kV, basic frequency 250 kHz, damping depending on a load. Its equivalent circuit can be imagined as a serial resonance circuit with following parameters: $L = 4$ mH, $C = 100$ pF, $R = 1$ k Ω . Its successful exploitation initiated an investigation of its working conditions which could be eventually transferred in an industrial scale. There were established three main characteristic features of such a device:

- i. There is a critical value of the electric field intensity E_k which is necessary for the coalescence appearance,
- ii. The conditions for a local overcoming of the critical field intensity are favourable in an inhomogeneous electric field even at lower overall voltage comparable with a homogeneous field,
- iii. After overcoming of the critical value it is necessary to prevent an uncontrolled electric breakdown spread between electrodes: it can be done by a suitable geometric arrangement of the electrodes and, in an AC electric field, using electric insulation too.

These knowledge were known partially from literature [3]. A coaxial electrode arrangement according to the Fig. with an insulated outer electrode has been proposed and analysed. Let us assign an emulsion permittivity ϵ_1 and the permittivity of the insulation material used ϵ_2 . The intensity of the electric field in an emulsion depends on the radius r from the axis of symmetry according to a relationship

$$E = \frac{U}{r \left(\ln \frac{r_2}{r_1} + \frac{\epsilon_1}{\epsilon_2} \ln \frac{r}{r_1} \right)},$$

where $r_1 < r < r_2$ and U is the voltage applied between inner and outer electrodes. As the emulsion contains water, its permittivity ϵ_1 is large and it would seem natural that the insulation material permittivity ϵ_2 should be comparatively large too. However, the critical field intensity is



overcome nearby the inner electrode surface first and the emulsion decomposition is manifested by its local conductivity increasing [4]. From the point of view of backward influence on the electric field configuration, this phenomenon is equivalent to an increasing of the

inner electrode diameter. The electric field intensity close by the inner electrode surface ($r = r_1$) changes with its radius r_1 after the equation

$$\frac{dE}{dr_1} = \frac{(1 - \ln \frac{r_2}{r_1} - \frac{\epsilon_1}{\epsilon_2} \ln \frac{r_0}{r_2}) U}{\left[r_1 \left(\ln \frac{r_2}{r_1} + \frac{\epsilon_1}{\epsilon_2} \ln \frac{r_0}{r_2} \right) \right]^2}$$

This equation points out that for

$$r_1 < r_2 \cdot \exp\left(\frac{\epsilon_1}{\epsilon_2} \ln \frac{r_0}{r_2} - 1\right)$$

the field intensity decreases with increasing of the radius r_1 and vice versa. For

$$r_2 \rightarrow r_0 \text{ and/or } \epsilon_2 \gg \epsilon_1,$$

the exponential term reaches a value $1/e$, i.e. the value valid for bare coaxial electrodes [5]. A fair utilization of the space between the inner electrode and the insulation is reached fulfilling a condition $\epsilon_1/\epsilon_2 \cdot \ln(r_0/r_2) = 1$, when all the space is at disposal for the emulsion destruction. The voltage applied between electrodes influences the working space if kept in a range

$$E_k r_1 \left(\ln \frac{r_2}{r_1} + \frac{\epsilon_1}{\epsilon_2} \ln \frac{r_0}{r_2} \right) < U < E_k r_2 \exp\left(\frac{\epsilon_1}{\epsilon_2} \ln \frac{r_0}{r_2} - 1\right),$$

where E_k is a critical value of the electric field intensity. Under condition given above we obtain $E_k \cdot r_1 \cdot (1 + \ln(r_2/r_1)) < U < E_k \cdot r_2$. These relationships were partly identified experimentally in a system consisting of a central electrode with O.D. 1.2 mm made of a stainless steel injection needle and of a cylindrical glass vessel with I.D. 16 mm made of a thin-wall ($t=0.5$ mm) injection ampoule provided with an aluminium armature. Testing emulsions consisting of 0.1 M HCl inner solution and a 3% SPAN 80 dissolved in toluene were broken down with 80% efficiency and voltage applied not exceeding 250 V / 50 Hz in several minutes. An apparent power consumption was only 5 mW per 10 ml of emulsion. The influence of other physical and chemical parameters is studied now.

References

1. Švec A., Rajec P.// Chemical Papers. 1983. Vol.77. P.206.
2. Mikulaj V., Rajec P., Švec A.// Ibid. 1986. Vol.80. P.545.
3. Hsu E.C., Li N.N.// Separation Sci. Technol.1985. Vol.20. P.115.
4. Stepanenko A.N., Panko V.V.// Kolloidnyj Zhurn. 1982. Vol.44.P.801.
5. Weiss S., Siebeneicher H.// Paper No.D5.19 (1282) at 9th Internat. Congress of Chem. Equip. Design and Autom.Prague, 1987.

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The emulsion swelling is one of the significant problems in the application of liquid surfactant membrane process to commercial scale separations. The swelling not only dilutes the internal phase and makes the recycle of the emulsion difficult, but also changes the properties of the emulsion (e.g. viscosity, density, phase ratio, etc.) so that the design and the operation of an equipment become difficult. The swelling is caused by two factors: one is water permeation due to the osmotic pressure gradient between two sides of the membrane, the other is the entrainment during mixing. In this paper, a model for water permeation was developed and the factors affecting the swelling were experimentally studied.

Permeation Swelling Model. Up to now, Colinart et al [1] has proposed a model based on the assumption of water-surfactant associations, while Fujinawa et al [2] proposed a model according to the osmotic pressure gradient, but the changes of the interfacial area for water permeation was neglected. In fact, the emulsion volume changes a lot with time due to the swelling. Therefore, the changes of the interfacial area must be considered. In this paper, the assumptions applied for establishing the model are given as follows:

1. The swelling is only caused by the water permeation.
2. The static pressure difference can be ignored compared to the osmotic pressure difference between two sides of the membranes.
3. The breakage of the emulsion are neglected.

The water permeation rate through the membranes can be described by the following equation:

$$\frac{1}{A\bar{V}_1} \frac{dV_i}{dt} = \frac{D_1 C_1 \bar{V}_1}{RT\Delta X} (\Delta P - \Delta\pi), \quad (1)$$

where ΔP and $\Delta\pi$ are the static and osmotic pressure difference respectively. Ignoring ΔP with $\Delta\pi = v\phi RT(C_i - C_e)$, one can obtain

$$\tau = \frac{y-1}{a} - \frac{1}{2a} (1+R_{ei}) - \frac{b}{a} \ln \frac{ay^2-by-c}{a-b-c} + \frac{1}{2a\sqrt{b^2+4ac}} \left[\frac{b^2+2ac}{a} - b(1+R_{ei}) \right] \left[\ln \frac{2ay-b-\sqrt{b^2+4ac}}{2a-b-\sqrt{b^2+4ac}} - \ln \frac{2ay-b+\sqrt{b^2+4ac}}{2a-b+\sqrt{b^2+4ac}} \right] \quad (8)$$

where $a = 1+R_{ei}/\beta$, $b = 1+R_{ei}-R_{mi}(1+R_{ei}/\beta)$, $c = R_{mi}(1+R_{ei})$.

The parameter β represents the ratio of the concentration of the internal phase to that of the external phase. For $\beta=0$ or $\beta \rightarrow \infty$, the above equation

can be simplified. Predicted results in Fig. 1 show that y increases with increasing β , but when $\beta < 1$, the emulsion shrinking will happen. R_{mi} affects y in two respects. Firstly, raising R_{mi} results in the increase in membrane thickness and will decrease y ; secondly, the permeation area will increase with increasing R_{mi} due to the increase in emulsion volume at constant R_{ei} , and this will lead to the increase in y . Predicted results indicate that y increases with increasing R_{mi} implying that the later effect is more important.

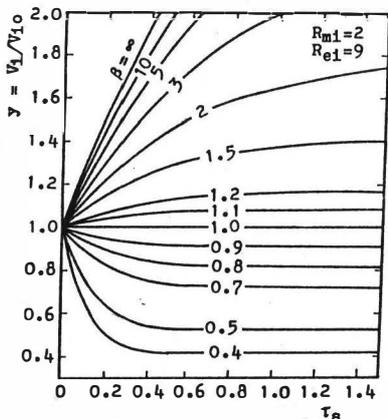


FIG. 1. Effect of β on y

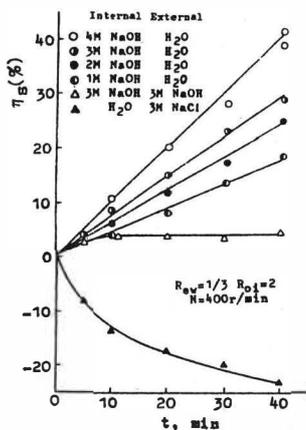


FIG. 2. Emulsion swelling

Experimental The experimental apparatus and the procedure used were the same as reported in a previous paper [3]. The W/O emulsion was prepared by using kerosene and paraffine as the membrane solvent, Span 80 (sorbitan mono-oleate) or E644 (polyamine) as the surfactant. The emulsion was then dispersed into the external phase. The changes of the emulsion volume with time were measured.

Results and Discussion

1. Effect of concentration gradient. As shown in Fig.2, the percentage swelling increases with increasing the concentration in internal phase; if the internal is water, and the external is 3M NaCl, the emulsion shrinks, this is in accordance with the model predictions shown in Fig. 1; and when the internal and the external phase have the same concentration, the swelling caused by entrainment is much smaller compared with that caused by permeation. This indicates that the effect of water permeation on swelling is more important than that of the entrainment.

2. Effect of the membrane viscosity. The viscosity was adjusted by adding different amount of liquid paraffine to kerosene. Results indicate that the swelling decreases with increasing the viscosity due to the decrease in K_g . Raising the membrane viscosity can restrain the swelling but will lead to the slow extraction rate and makes the breakdown of the emulsion difficult.

3. Effect of surfactants and carriers. The higher the concentration of the surfactants and carriers, the more the emulsion swelling. Similar results have also been reported by other authors [3-6]. These may be explained by the formation of the complexes between water and surfactant or water and carriers at the outer interface of the membrane and the complexes transport through the membrane into the internal phase so that the swelling can be accelerated. The effect of Span 80 on swelling is much larger than that of E644 as shown in Fig.3. It suggests that different surfactants have different capacities in transporting water molecules. The rate constants of permeation swelling in Table 1 calculated from the model indicate that K_s increases with increasing the concentration of internal phase, and the oxygen-containing surfactants or carriers have more effects on permeation swelling than nitrogen-containing surfactants or carriers.

4. Effect of entrainment. As can be seen from Table 2, when Span 80 is used, the entrainment swelling is larger than that when E644 is used. This is consistent with the effect of the surfactant on permeation swelling as discussed above. Also it can be seen that if the electrolyte solution is used, the entrainment is depressed, especially when Span 80 is used. It is our conjecture that the electrolytes reduce the thickness of the electro-double layer at the membrane/entrained droplet interface, and the droplet is easy to coalesce to form larger one which can be settled from the emulsion. Thus, the entrainment decreases.

Repeated coalescence and redispersion promote the entrainment swelling as shown in Fig.4. Since line b is in parallel with line c, it is deduced that the entrainment is only dependent on the times of coalescence and redispersion but have nothing to do with when the coalescence and redispersion happening. From these results it is concluded that the multistage mixer-settler seems unsuitable for the liquid membrane operations.

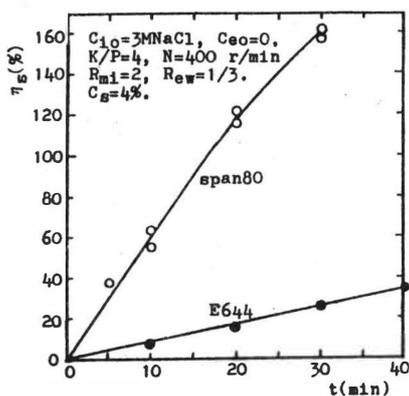


FIG. 3. Effect of surfactant on swelling

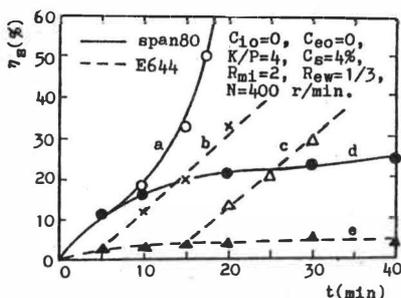


FIG. 4. Effect of repeated redispersion on entrainment swelling

- a, b - stop stirring for 1 min. at 5, 10, 15 min. respectively
- c - stop stirring for 1 min. at 15, 20, 25 min. respectively
- d, e - no redispersion

TABLE 1. Rate constant of permeation swelling

Run	Internal	External	Surfactant	Carrier	$K_S \times 10^{11} (m/s)$
1	1M NaOH	H ₂ O	E644	—	4.98
2	2M NaOH	H ₂ O	E644	—	7.34
3	3M NaOH	H ₂ O	E644	—	9.03
4	4M NaOH	H ₂ O	E644	—	12.8
5	3M NaCl	H ₂ O	E644	—	9.12
6	3M NaCl	H ₂ O	Span 80	—	88.5
7	H ₂ O	3M NaCl	E644	—	10.8
8	3M NaOH	H ₂ O	E644	TBP	13.8
9	3M NaOH	H ₂ O	E644	N503	10.8
10	3M NaOH	H ₂ O	E644	DIBK	10.3
11	3M NaOH	H ₂ O	E644	N1923	9.95
12	3M NaOH	H ₂ O	E644	DBC	11.1
13	3M NaOH	H ₂ O	E644	N235	8.57

$K/P = 4$, $C_S = 4\%$, $C_C = 1\%$, $R_{mi} = 2$, $R_{ew} = 1/3$, $N = 400$ r/min.

TABLE 2. Entrapment swelling

Surfactant	Internal phase	External phase	η_S (%)			
			10 min	20 min	30 min	40 min
E644	H ₂ O	H ₂ O	2.74	3.70	3.98	4.38
E644	3M NaOH	3M NaOH	3.98	3.47	3.40	4.42
E644	3M NaCl	3M NaCl	2.21	4.42	3.56	3.26
Span 80	3M NaCl	3M NaCl	6.40	16.3	16.2	13.7
Span 80	H ₂ O	H ₂ O	16.8	21.3	24.0	24.2

$K/P = 4$, $C_S = 4\%$, $R_{mi} = 2$, $R_{ew} = 1/3$, $N = 400$ r/min.

Notation

- | | | | |
|----------------|--|-------------|---|
| A | - permeation area, m ² . | T | - temperature, K. |
| C | - solute concentration, kmol/m ³ . | V | - volume, m ³ . |
| C ₁ | - solubility of water in membrane, kmol/m ³ . | \bar{V}_1 | - partial molar volume of water, m ³ /kmol. |
| C _C | - carrier concentration, wt%. | X | - distance, m. |
| C _S | - surfactant concentration in membrane, wt%. | y | - V_1/V_{i0} . |
| D ₁ | - Diffusivity of water in membrane, m ² /s. | β | - C_{i0}/C_{eo} . |
| K _S | - $D_1 C_1 C_{i0} \bar{V}_1^2 v \phi / \Delta X$, rate constant of permeation, m/s. | η_S | - $(VE/V_{E0} - 1) \times 100\%$. |
| K/P | - volume ratio of kerosene to paraffine. | v | - number of ions dissociated from a molecule of a solute. |
| ΔP | - pressure gradient, Pa. | π | - osmotic pressure, Pa. |
| R | - gas constant, J/kmol·K. | τ | - $3K_S t/R_1$, dimensionless time. |
| R ₁ | - radius of emulsion drops, m. | ϕ | - osmotic coefficient. |
| Rei | - V_{eo}/V_{i0} . | Subscripts | |
| Rew | - V_{Eo}/V_{eo} . | e | - external phase. |
| Rmi | - V_{mo}/V_{i0} . | E | - emulsion phase. |
| t | - time, s, min. | i | - internal phase. |
| | | m | - membrane phase. |
| | | o | - initial value. |

References

- Colinart P., Delepine S. et al. // J. Memb. Sci. 20. 167 (1984).
- Fujinawa K., et al. // Kagaku Kogaku Ronbunshu. 10(2), 226 (1984).
- Yan N.X., Huang S.A. et al. // Sep. Sci. Tech. 22(2 & 3). 801 (1987).
- Draxler J. and Marr R. // Ber. Bunsenges. Phys. Chem. 86. 64 (1982).
- Thien M.P., Hatton T.A. et al. // Preprints of ISEC'86. P. III-685.
- Yagodin G.A., Yurtov E.V. et al. // Ibid. P. III-677.

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Introduction. A liquid membrane can be created by using the organic phase of a water-in-oil-in-water emulsion to separate two aqueous phases as shown schematically in Fig. 1. This type of double emulsion, called emulsion liquid membranes (ELM), can combine the extraction and stripping steps of solvent extraction into a single operation. For example, a solute in the aqueous feed can be extracted into the membrane phase and subsequently stripped into the encapsulated aqueous phase.

Figure 2 illustrates acid stripping of copper from an anionic water-insoluble complexing agent (indicated by the clockwise circular arrows) which originally extracted copper from the aqueous feed. In this process, the movement of cupric ions from the feed to stripping solutions is balanced by of ELM countercurrent hydrogen ion transfer.

When leakage of the encapsulated phase occurs, previously extracted solute, as well as stripping reagents are released into the feed stream, thereby reducing the ultimate efficiency of the extraction. To promote large accumulations of solute in the internal phase, large reagent concentrations are used. Consequently, the fraction of internal droplets leaked can be small (1 to 5%) and still profoundly affect performance. Clearly, the amount of leakage expected and its minimization within operational constraints are important considerations for industrial applications. While

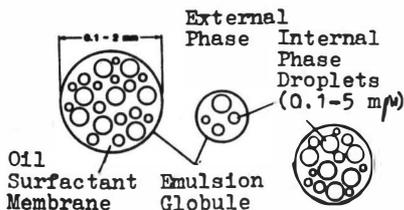


Fig. 1. Schematic diagram of ELM



Fig. 2. Liquid membrane extraction and stripping of copper

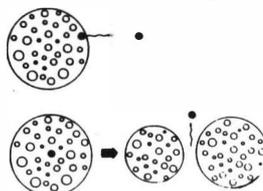


Fig. 3. Mechanisms of ELM leakage

there have been many previous studies of drop coalescence and stability in liquid-liquid dispersions, most are not pertinent to these relatively stable ELM systems.

Internal droplet leakage can arise through at least the two mechanisms diagrammed in Fig. 3. In the first case, droplets are rubbed off of the globule surface. For example, the oil membrane separating a trapped surface droplet from the bulk solution can thin and finally rupture releasing the droplet's contents. This mechanism might be promoted if osmotic swelling occurs as a result of water transport through the membrane.

A second mechanism is breakage of a larger emulsion globule into two or more smaller globules. In the process of tearing apart and forming new interfaces, some droplet leakage is likely. Teramoto et al. [1] report considerable leakage when the emulsion was dispersed at the start of their experiments. They attributed their observations to either initial leakage as globules formed or to internal phase solution that had never actually been encapsulated.

We have studied encapsulated-phase leakage during studies of ELM batch extractions of copper. Using lithium salt as a tracer, leakage was measured as a function of time for (1) two surfactants, (2) varying surfactant concentrations, and (3) different volume ratios of encapsulated and membrane phases. The effect of the complexing carrier species (LIX) when copper is and is not present was also investigated.

Experimental. The oleic membrane phase was prepared by stirring the prescribed amount and type of surfactant and the copper complexing agent into about 100 g of oil (S100N, an isoparaffinic, middle distillate from Exxon, USA). The surfactants used were two commercially-available nonionic polyamines, ECA 5025 (formerly called Paranox 106) or ECA 4360 (both from Exxon, USA). Differences in the two surfactant formulations are not evident from the chemical information sheets provided by the manufacturer. The complexing agent was the purified liquid ion exchanger, LIX65N (2-hydroxy-5-alkylbenzophenone oxime from Henkel). The internal aqueous solution of 3000 ppm lithium (as Li_2SO_4) and sulfuric acid in varying amounts (0.0, 0.5, 1.0 or 1.5 M) was encapsulated into the oil membrane phase by combining the prescribed amount of aqueous phase with about 100 grams of membrane phase in a commercial blender (Waring) at low speed for two minutes.

This emulsion was poured into one liter of solution under agitation in a two-liter, un baffled glass reaction vessel equipped with a sampling port. Typically, a two-inch diameter turbine impeller, placed

vertically in the reaction vessel, was rotated at 500 rpm using a variable-speed Lightnin stirrer.

Encapsulated-phase leakage was easily calculated from atomic absorption measurements of lithium in the bulk aqueous solution. Extraction experiments for lithium demonstrated that lithium does not partition into the membrane phase. All experiments were conducted at room temperature. Additional details are given elsewhere [2,3].

Results and Discussion. Comparative leakage and copper extraction experiments with equal weight percents (2.6 %) ECA 5025 and ECA 4360 were performed. Experiments with ECA 4360 showed greater encapsulated-phase leakage than those with ECA 5025. More importantly, ECA 4360 significantly interfered with copper extractions. Some inconclusive evidence suggests that ECA 5025 may actually enhance copper extraction [3]. Consequently, all further studies were conducted using only ECA.

Figure 4 compares percent leakage for 5 concentrations of ECA 5025. In these experiments, no copper or LIX was present, the volume fraction of emulsion to total volume (f_b) was 0.9, the membrane fraction of the emulsion (f_m) was 0.63, and the sulfuric acid concentration was 1.5 M. The leakage rate was nearly constant over the time period studied, decreasing as surfactant concentration increases. Increases in surfactant above 3 weight percent offered no further stabilization. When extrapolated to zero, all of the leakage lines appear to intercept near the origin, indicating insignificant spilling of internal solution that was not fully encapsulated during emulsification.

As shown in Figure 5, the percent leakage depends strongly on the volume fraction of membrane indicating the expected correlation with decreasing membrane thickness. In our experience, leakage rates greatly increase when the membrane fraction of the emulsion becomes less than 0.5. The data in Fig. 5 were measured in the absence of copper, 3 weight percent surfactant, a f_b of 0.9, and 1.5 M sulfuric acid.

Not surprisingly, the presence of the surface-active LIX carrier alters globule

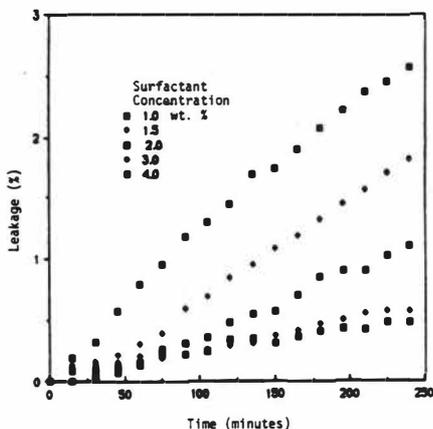


Fig. 4. Percent leakage for 5 concentrations of ECA 5025

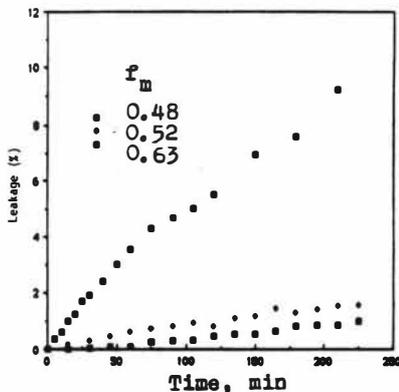


Fig. 5. Percent leakage as a function of membrane volume

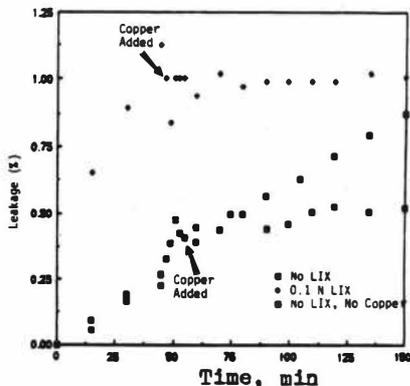


Fig. 6. Effect of LIX and copper on percent leakage

stability. Figure 6 reports leakage for four cases: (1) no LIX and no copper, (2) no LIX and 854 ppm copper (added after 60 minutes), (3) 0.1 M LIX and no copper, (4) 0.1 M LIX and addition of 854 ppm copper (as indicated at 45 minutes). For all three experiments shown in Fig. 6, the surfactant concentration was 3 weight percent, f_b was 0.9, f_m was 0.63, and H_2SO_4 was 1.5 M. More encapsulated phase leakage is observed when LIX65N is present in the membrane phase. However, when copper is added after 45 minutes, the droplet leakage rate dramatically decreases. This phenomenon has been observed consistently in our copper extraction experiments [2,3]. Interestingly, encapsulated-phase leakage is reduced by copper addition even when no LIX65N was present. The mechanism of this stabilizing affect is unclear. We are continuing to conduct leakage studies especially as related to osmotic swelling.

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References

1. Teramoto M., T. Sakai, K. Yanagawa, M. Ohsuga, and Y. Miyake // Sep. Sci. Tech. 18. 735 (1983).
2. Wang C.C.// Ph.D. Thesis, Colorado School of Mines, Golden, CO (1988).
3. Reed D.L.// M.S. Thesis, Colorado School of Mines, Golden, CO (1988).

A new hypothesis about the instability mechanism of supported liquid membranes (SLM's) is advanced: emulsion formation due to lateral shear forces. Experiments confirm that the removal of the LM-phase from the pores in the support is strongly affected by the salt concentration and the flow velocity of the water phases parallel to the membrane surface.

Introduction. The use of SLM's has recently been introduced as a promising alternative to traditional solvent extraction. Some advantages ascribed to this separation method, in which the extraction liquid is immobilized in the pores of a microporous support, are:

- little loss of extractant takes place; this makes it possible to use more expensive extractants;
- ions can be pumped "up-hill" in a single stage;
- the diffusion velocity through the liquid is high (as compared to that in solid polymeric membranes).

Despite these advantages SLM's are, at this moment, not widely used for practical separation processes. One of the main reasons, that SLM's have not yet left the laboratory, is the instability or the uncertain life-time of SLM's.

Not much has been published on the possible causes of SLM- instability. Besides trivialities like solubility of the LM-phase in the water phases and removal of the LM-phase from the pores in the support by a too large pressure difference over the membrane, an osmotic watertransport mechanism has been put forward by Danesi et al.([1]) and Fabiani et al.([2]). In this model the LM-phase is supposed to be removed from the pores by a flow of water through the membrane as a consequence of the combined effect of the solubility of water in the LM-phase and an osmotic-pressure gradient over the membrane.

We seriously doubt that the solubility of only a few percent of water in the organic phase can result in an osmotic waterflow, because there is no continuous pathway present for the water phase in the membrane, necessary for the osmotic forces to be effective. Therefore we believe that another mechanism must be responsible for the LM-phase removal from the pores and we think that the formation of emulsions can explain a lot of instability phenomena in the SLM-papers mentioned above and in other SLM-systems. We will illustrate our theory with experiments based on the removal of decanol from the pores. This solvent is chosen because it produces SLM's with a relatively instable character.

Experiments and results. The experimental set-up is shown in figure 1A. In figure 1B the dimensions of the permeation module are presented; the water phases are flowing in a tangential mode along the membrane. To prevent the molecular dissolution of decanol in the waterphases, all the water phases were saturated with decanol before starting the experiments.

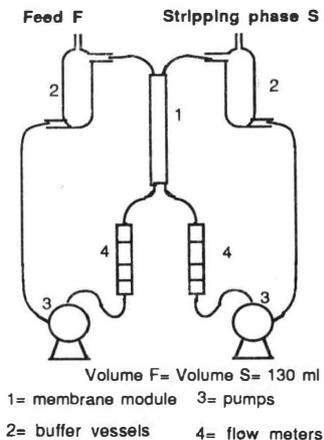


Fig 1A. Experimental set up

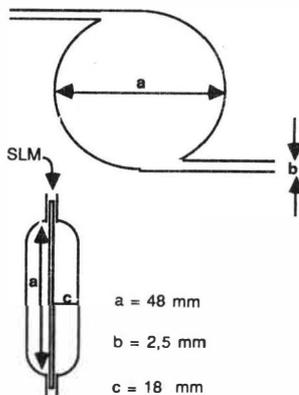


Fig 1B. Dimensions of the membrane module

In the experimental permeation tests the SLM's were composed of Accurel^R-supports (Enka; thickness: 90µm; porosity: 75%; average pore size: 0,1 µm), decanol was used as solvent and quaternary ammonium salts (10 w%) as carriers. The compositions of the feed and the stripping phase, both flowing at a volume velocity of 2,3 ml/sec. through the cell-halves, were 0,0025 M NaNO₃ and 4,0 M NaCl respectively.

All the membranes showed fairly similar instability-effects. Independent of the kind of carrier that has been used, the SLM's started to leak after 40 to 60 hours; this was expressed as a sudden increase of the chloride- concentration in the feed and some watertransport from the feed to the stripping phase.

In a period of 7 days about 80 % of the LM-phase had been removed from the membrane. The same phenomena occurred when no carrier was used. Also stopping the flow in the stripping phase part of the cell had no influence on this behaviour. However, when there was no flow of the feed, the membranes showed no chloride transport in 14 days and only 40% of the decanol was removed from the pores in that period.

This was the basis for further research on the conditions by which decanol is being washed out of the pores. To increase the instability effects Celgard^R-supports (Celanese; thickness: 25 µm; porosity: 45 %; pore dimensions: 0,04 µm) are used. In order to exclude the effects of a possible direct water transport through the membrane, the feed and the stripping phase were taken at identical compositions. No carrier is used. The quantity of decanol, removed from the support (at the contact areas between SLM and water phases) during a period of 7 hours was determined as a function of two variables: i the salt concentration of both water phases and ii the volumetric flow through the cell-halves. Figure 2 shows the influence of the NaCl- concentration in the water phases on the decanol-removal at a constant water flow of 5,5 ml/sec. Figure 3 shows the removal of decanol from the SLM's as a function of the water flow velocity, at a constant NaCl-concentration in the water phases of 0,5 M.

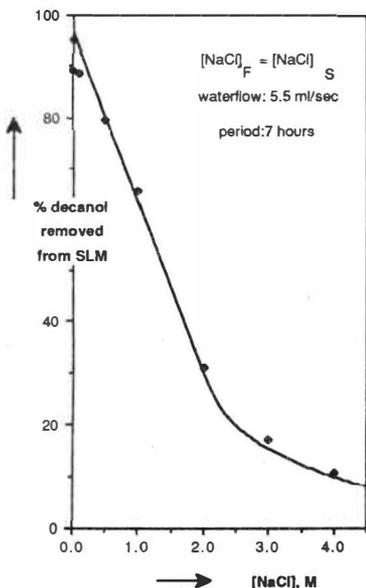


Fig. 2. Decanol removal as a function of [NaCl]

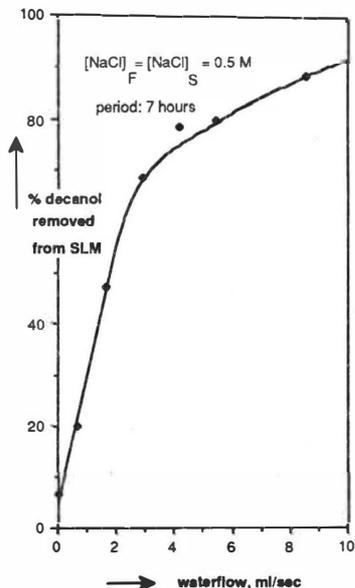


Fig. 3. Decanol removal as a function of waterflow velocity

Discussion and conclusion . Figure 2 and 3 clearly show that for the removal of decanol from the pores in the support no osmotic pressure gradient, and therefore no direct water transport, is necessary. The washing out effects of the LM-phase are caused by a high flow rate of the water phases combined with a low salt concentration. In accordance with the permeation experiments this will lead to a leaky membrane.

The dependence of the loss of decanol on the water flow rate and on the salt concentration indicates that we are dealing with emulsion formation. This is confirmed by two simple experiments. When an amount of decanol is hand shaken for a while, in a test-tube, with a 4 M NaCl-solution we see that the demixing almost immediately results in 2 clear phases. On the other hand, in a similar experiment, the separation of demi-water and decanol gives a turbid water phase, that clarifies very slowly. It is not difficult to realize that the rapid flow of a water phase with a low salt concentration in a SLM-proces has, at the interface with the organic phase, the same effect on emulsion formation as the shaking activity in a test-tube experiment. This emulsion formation at the low salt-concentration feed side will lead to SLM-degradation. Presently we are involved in developing SLM's with stabilities which are of practical importance; the first results are promising.

References

1. P.R. Danesi, L. Reichley-Yinger and P.G. Rickert// *Journal of membrane science*, **31** (1987), 117-145.
2. C. Fabiani, M. Merigiola, G. Scibona and A.M. Castagnola// *Journal of membranes science*, **30** (1987), 97-104.

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In pertraction \mathcal{N} through liquid membranes a continuous aqueous phase is contacted with an emulsion, in which a second aqueous phase is dispersed in an organic phase. This composite emulsion is stabilized by surfactants.

We tested an analogous arrangement of this process with solid paraffin as an organic solvent. In the melted solvent a reaction agent was dissolved and the second aqueous phase was dispersed. After cooling solid particles were formed, which contained small liquid drops. When pertraction had been finished, the solid dispersion was again melted and organic and aqueous phases were separated.

An expected disadvantage of pertraction with solid particles is that the process is slower than emulsion pertraction. We have compared the rate of pertraction with the solid dispersion with both the transfer rate in a solid phase and the rate of emulsion pertraction.

A dispersion was prepared at 65-70°C by mixing an aqueous solution of a stripping agent, the melted paraffin and an organic reaction agent. The emulsion was poured in orifices of a pre-cooled porcelain plate. Cylindrical solid particles were formed and eventually cut in pieces.

We investigated pertraction of sulfuric acid from an aqueous solution to a second aqueous phase containing sodium hydroxide and measured the process rate. Organic phase contained technical trialkylamine (TAA) as a carrier, dissolved in paraffin. Cylindrical particles (5x5 mm) were used, bases of cylinders were glued by pure paraffin. Pertraction proceeded in a batch arrangement in a mixed vessel. The initial compositions of phases are given in Tabl.1. Results of experiments are shown in Fig.1, where c_A - concentrations of sulfuric acid in liquid phase (measured) and q_A - in solid phase (computed) are plotted against time. In the same Figure c_B - measured concentrations of hydroxide in the aqueous phase formed after melting of the particles, are plotted.

For the description of the process, the advancing front diffusion model was used [2]. A solution of the Fick's second law for cylindrical symmetry with the pseudo-steady-state assumption leads to the following equation describing the movement of the reaction front

$$4 T = Z^2 \ln Z^2 - Z^2 + 1, \quad (1)$$

where the dimensionless time and the dimensionless position of the advancing reaction front are

$$T = q_{AR} D_{ef} t / R^2 q_B \quad Z = z / R \quad (2)$$

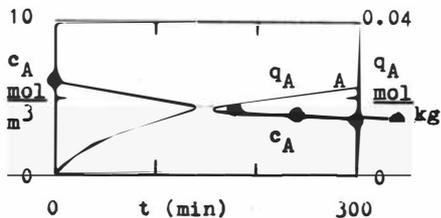
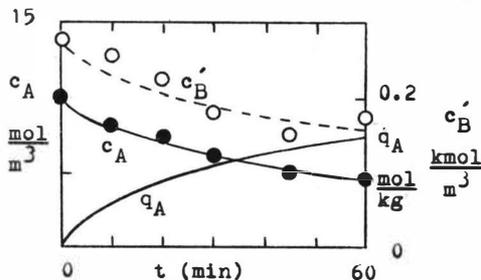


Fig. 1. Pertraction of H_2SO_4 (syst.1)

Fig. 2. Sorption of H_2SO_4 (syst.2)

Table 1. Initial compositions of phases

System	Cont. aqueous phase	Globules		Globules/cont. phase (kg/m^3)
		TAA	disp. aqueous phase	
1	0.01M H_2SO_4	11%	47% (2.75M NaOH)	32
2	0.006M H_2SO_4	21%	---	107
3	0.002M $K_2Cr_2O_7$ H_2SO_4 (pH 1.6)	11%	51% (0.1M NaOH)	95

Here R is the cylinder globule radius, the radial coordinate of reaction front is z , q_{AR} is the concentration of transported component in the globule at interphase per unit mass of dispersion, q_B is the equivalent concentration of the internal reagent per unit mass of dispersion, t is time. A material balance yields

$$V (c_A^0 - c_A) / m q_B = 1 - Z^2, \quad (3)$$

where V is the volume of the continuous aqueous phase, m is the mass of the solid dispersion, c_A is the molar concentration of component A in the continuous phase, c_A^0 is the original value of this concentration.

From the experimental data, the effective diffusion coefficient was estimated, as $D_{er} = 1.8 \times 10^{-10} m^2 s^{-1}$. The lines in the Fig. 1 correspond to this value of the diffusion coefficient.

To compare the rates of diffusion, the globules without the dispersed water phase were tested. The compositions of the phases are given in Tabl. 1 (system 2), the results are plotted in Fig. 2. According to penetration theory, the equation describing the solute transport is

$$\ln (c_A^0 / c_A) = (4 m K / R V) (D t / \pi)^{1/2}. \quad (4)$$

From the experimental equilibrium data the distribution ratio $K = q_{AR} / c_A = 1.5 \times 10^{-2} m^3 kg^{-1}$ is approximately constant in the region of concentrations used. From the experimental data the value of the diffusion is $D = 7.3 \times 10^{-12} m^2 s^{-1}$. The lines in the Fig. 2 correspond to the equation (4) and this diffusion coefficient.

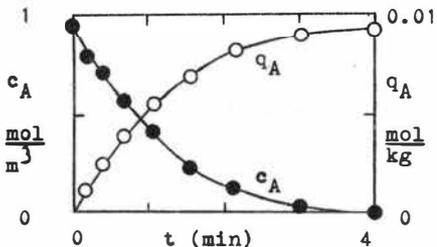


Fig. 3. Pertraction of chromium in emulsion [3]

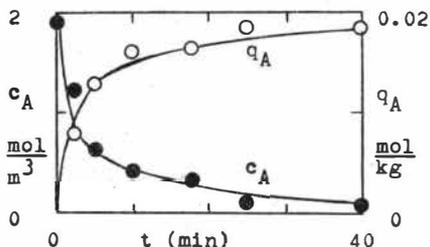


Fig. 4. Pertraction of chromium (system 3)

For comparison, the diffusion coefficient of sulfuric acid in water in infinite dilution, computer from Nernst equation, is $D^0 = 2.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

To compare the process with solid particles with emulsion pertraction, the results of Hochhauser and Cussler [3] were used. These authors pertracted chromium (VI) from an acid solution to a solution of sodium hydroxide with tridodecylamine as a carrier. Their results, published in graphical form, are shown (after unit conversion) in Fig. 3. Solute A is taken as $\text{H}_2\text{Cr}_2\text{O}_7$. Results of our analogical measurements are given in Fig. 4. The initial composition of phases is given in Tab. 1 (system 3).

Using a simplified film model, Hochhauser and Cussler found the effective value $(DA/L)_{ef} = 3 + 8 \times 10^{-8} \text{ m}^3 \text{ s}^{-1}$. A is the interfacial area and L is the membrane thickness. With an analogous arrangement of experiments and with the same model we estimated for solid dispersion $(DA/L)_{ef} = 2.5 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$. In this case we used particles of an irregular shape having a mean size of 0.5 - 3 mm.

For illustration we present results of flow pertraction in a cascade of four mixed prismatic vessels, with 6x6 cm square bases. The continuous phase flowed through the cascade, while globules of the solid dispersion remained in the vessels. In Fig. 5 the results of the measurements are shown under the following conditions: the continuous phase volume in each vessel 216 ml, the mass of the solid dispersion in each vessel 10 g, the volumetric flow of the continuous phase 0.6 ml s^{-1} , the original molar concentrations of the solute in all vessels $c_{A1}^0 = 0$. Sulfuric acid was added to pH 1.6. In Fig. 5 are shown time dependent concentrations of the solute (taken as $\text{H}_2\text{Cr}_2\text{O}_7$) in the continuous phase in the first vessel and in the output from the cascade.

We tested systems with solid reaction agents which would be unsuitable for emulsion pertraction. We investigated pertraction of Cu^{2+} from ammoniacal solution (pH 9) of CuSO_4 to a solution of sulfuric acid (1M) and pertraction of NH_4 from a solution of NH_4OH to a solution of phosphoric acid (1M) with stearic acid as a carrier. The composition of globules was 29% dispersed aqueous phase. In these systems

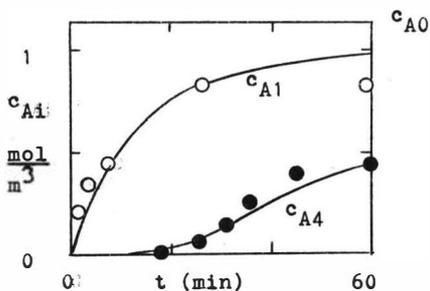


Fig.5. Flow pertraction of chromium in stage cascade (system 3)

Table 2. Pertraction with stearic acid

system	A	c_A^0 mol m ⁻³	m/V kg m ⁻³	t min	c_A mol m ⁻³	q_A mol kg ⁻¹
4	Cu ²⁺	4.1	80	60	2.3	0.022
5	NH ₄ ⁺	76.1	100	45	60.7	0.150

pertraction with solid dispersion was easily realized. The conditions of batch pertraction and the results are shown in Tab.2.

Results of experiments have shown that the realization of this process was easy. An obvious disadvantage is that the process is slower than the pertraction in liquid. However, the process has the following advantages: no surfactants are necessary, the dispersion is stable, a long contact time is possible, the decomposition of the solid dispersion is easy, the separation of the phases is easy, volatile organic solvents are not needed and solid extraction agents can be used. Such pertraction could be an alternative separation process for concentrating of compounds present in aqueous solutions in low concentrations in cases when a long contact time causes no inconvenience or is even appropriate.

References

1. Š.Schlosser, E.Kossaczky // J.M embr. Sci. 6.83 (1980).
2. T.A.Hatton, D.S.Wardius // I&ECHE J. 30,934 (1984).
3. A.M.Hochhauser, E.L.Cussler // I&ECHE Symp.Ser. N 152. Vol. 71. 136 (1975).

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The distribution coefficients of germanium between aqueous and organic phases were determined by means of several commercial liquid ion exchangers with regard to the recovery of germanium from aqueous leaching solutions. The complex formation was investigated with regard to its reversibility in three-phase stirred cells.

Because of the lack of the direct reversibility of the complexes, the extraction of germanium with CCl_4 from HCl-solutions - a process which is well known from the analytical chemistry - , was transferred to the three-phase-stirred cells.

Only few detergents are stable at the high HCl concentrations necessary for the extraction. Paranox 100 turned out to be the most suitable detergent for the formation of emulsion liquid membranes under these conditions. This made possible the use of the emulsion liquid membrane technique for the recovery of germanium. Fig. 1 shows that the maximum achievable degree of germanium extraction strongly depends on the HCl concentration in the feed.

A complete extraction in a single stage equipment is only pos-

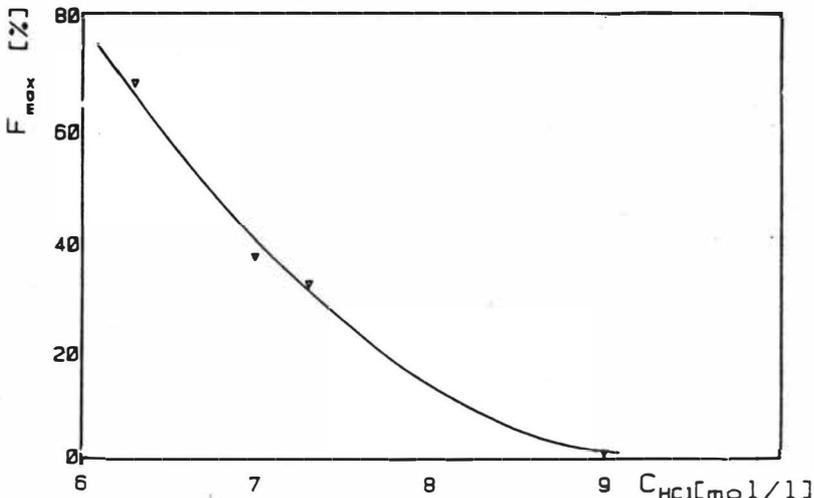


Fig. 1. Maximum achievable residues of germanium as a function of the HCl-concentration

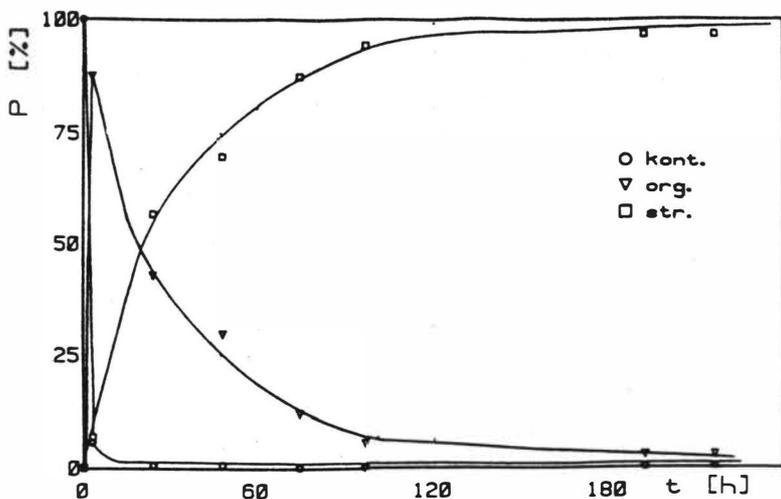


Fig. 2. Three-phase extraction of germanium from 9 M HCl. Germanium concentration in the continuous phase (kont), org. membrane phase (org) and stripping phase (str) as a function of time

sible by at least 9 M HCl. In Fig. 2, the concentrations of germanium in the feed, organic and stripping phases are shown at 9 M HCl as a function of the extraction time, measured in a three-phase stirred cell with very small interfacial areas.

Technical fly ash leaching solutions were used also. In Table 1, the compositions of two solutions are given that were used for the extraction investigations. For the germanium extraction, the following system was used:

Organic phase: 9.0 vol-% CCl_4 , 0.4 vol-% PARANOX, 15.0 vol-% xylene and 75.6 vol-% EXSOL D 80.

Stripping phase: 1 M NaOH.

Ratio of aqueous to organic phase = 2:3.

Fig. 3 shows the germanium residue in the leaching solutions 1 and 2 (see Table 1) and in a model solution with 100 ppm Ge. The variation between them is due to the concentration dependence of the germanium distribution coefficient. During these extractions only germanium is extracted. The accompanying elements remain in the leaching solution.

The influence of the holdup of the emulsion phase, the composition of the stripping and membrane phases as well as the stirrer speed on the degree of extraction was investigated using emulsion liquid membranes in a laboratory stirred tank.

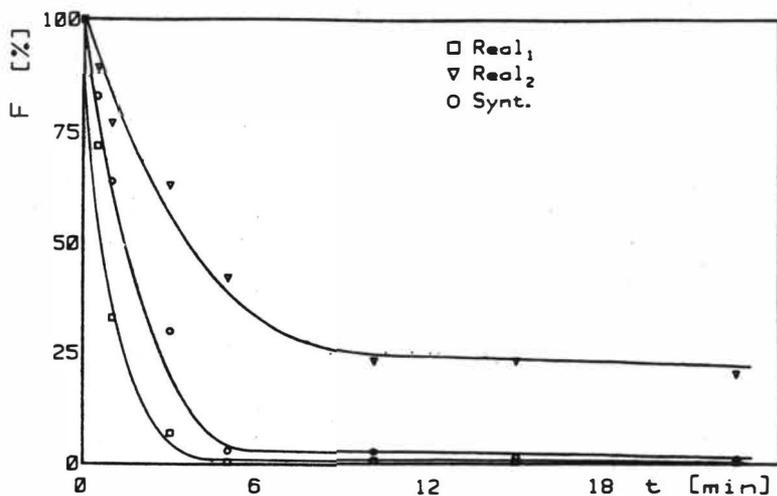


Fig. 3. Germanium extraction with emulsion liquid membrane as a function of time. Real leaching solutions (Real 1 and 2), model solution synt

Table 1. Composition of the leaching solutions

metal	concentration	solution 1	solution 2
Ge	mg/l	85.0	300.0
Cu	g/l	26.3	19.4
Zn	g/l	10.9	11.2
Fe	g/l	11.9	5.61
As	g/l	4.3	11.9
Mo	g/l	0.9	0.63
Na	mg/l	440.0	340.0
Ca	mg/l	200.0	122.0
Al	mg/l	300.0	139.0
Si	mg/l	23.0	58.0
Ag	mg/l	14.0	4.0
Cl ⁻	mol/l	7.0	7.0
Mg	g/l	3.2	1.9
H ₃ O ⁺	mol/l	7.0	7.0

Practically a 100 % extraction of germanium was obtained within some minutes without any coextraction of the accompanying elements (Cu, Zn, Fe, Ag, Mo, K, Al, Si, As) which are present at much (partly by one to two order of magnitude) higher concentrations in the leaching solution than in germanium.

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Introduction. The LM technique is considered as a novel separation and concentration method.

The purpose of the work is to study both experimentally and theoretically the nitric acid membrane extraction process and to analyse the possibility of LM technique application for the purpose of nitric acid regeneration from waste solutions.

Theory. One-dimension molecular diffusion of nitric acid in a non-stirred system consisted of two semi-infinite aqueous phases divided by a plane LM could be described by a system of parabolic differential equations:

$$D_1 \frac{\partial^2 C_1}{\partial x^2} = \frac{\partial C_1}{\partial t}, \quad D_2 \frac{\partial^2 C_2}{\partial x^2} = \frac{\partial C_2}{\partial t}, \quad D_3 \frac{\partial^2 C_3}{\partial x^2} = \frac{\partial C_3}{\partial t}. \quad (1)$$

Let's suppose that the reactions of transported complex formation and destruction at the LM boundaries are both instantaneous. The initial and boundary conditions are formulated as follows

$$C_1 = C_{10}, \quad C_2 = 0, \quad C_3 = 0 \quad \text{at } t = 0;$$

$$D_1 \frac{\partial C_1}{\partial x} \Big|_{x=0} = D_2 \frac{\partial C_2}{\partial x} \Big|_{x=0}, \quad D_2 \frac{\partial C_2}{\partial x} \Big|_{x=\delta} = D_3 \frac{\partial C_3}{\partial x} \Big|_{x=\delta}, \quad (2)$$

$$C_1(x=-\infty) = C_{10}, \quad C_3(x=\infty) = 0, \quad \alpha_1 C_1 \Big|_{x=0} = C_2 \Big|_{x=0}, \quad \alpha_2 C_3 \Big|_{x=\delta} = C_2 \Big|_{x=\delta}$$

It's possible to resolute (1) with regard for (2) analytically by means of Laplas operation technique. The expressions obtained for the solute quantity transferred across the LM boundaries look rather complicated

$$M_{12} = 2Q \frac{\sqrt{D_2}}{1-A^2} \left\{ (1-BA) \left(\sqrt{\frac{t}{\pi}} + 2 \sum_{k=1}^{\infty} (-A)^k \left[\sqrt{\frac{t}{\pi}} \exp\left(-\frac{k^2 \delta^2}{D_2 t}\right) - \frac{k\delta}{\sqrt{D_2}} \operatorname{erfc}\left(\frac{k\delta}{\sqrt{D_2 t}}\right) \right] \right) + (A-B) \left(\sqrt{\frac{t}{\pi}} \exp\left(-\frac{\delta^2}{D_2 t}\right) - \frac{\delta}{\sqrt{D_2}} \operatorname{erfc}\left(\frac{\delta}{\sqrt{D_2 t}}\right) + \sum_{k=1}^{\infty} (-A)^k \left[\sqrt{\frac{t}{\pi}} \left(\exp\left(-\frac{\delta^2(1+k)^2}{D_2 t}\right) + \exp\left(-\frac{\delta^2(1-k)^2}{D_2 t}\right) \right) - \frac{\delta}{\sqrt{D_2}} \left((1+k) \operatorname{erfc}\left(\frac{\delta(1+k)}{\sqrt{D_2 t}}\right) + (1-k) \operatorname{erfc}\left(\frac{\delta(1-k)}{\sqrt{D_2 t}}\right) \right) \right] \right\}, \quad (3)$$

$$M_{23} = Q(1-B) \sqrt{D_2} \sum_{k=0}^{\infty} (-A)^k \left[2 \sqrt{\frac{t}{\pi}} \exp\left(-\frac{\delta^2(1+2k)^2}{4D_2 t}\right) - \frac{\delta^2}{\sqrt{D_2}} (1+2k) \operatorname{erfc}\left(\frac{\delta(1+2k)}{2\sqrt{D_2 t}}\right) \right],$$

$$A = B \cdot \frac{1 - \alpha_1 \sqrt{\frac{D_2}{D_1}}}{1 + \alpha_1 \sqrt{\frac{D_2}{D_1}}}, \quad B = \frac{\alpha_2 \sqrt{\frac{D_2}{D_3}} - 1}{\alpha_2 \sqrt{\frac{D_2}{D_3}} + 1}, \quad Q = \frac{\alpha_1 C_{10}}{1 + \alpha_1 \sqrt{\frac{D_2}{D_1}}}.$$

Still they are useful for computer calculations.

In some particular cases which are generally realized under experimental conditions eqns. (3) could be simplified. At $\alpha_1 \ll 1$ and $\alpha_2 \ll 1$ the second one comes in the form

$$M_{23} = \frac{\alpha_1 C_{10} D_2}{\delta} t - \frac{\alpha_1 C_{10} \delta}{6} - \frac{2\alpha_1 C_{10} \delta}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D_2 n^2 \pi^2}{\delta^2} t\right). \quad (4)$$

After the expiry of some transition time $t_t = \frac{\delta^2}{6D_2}$ it becomes a linear function with the slope $\text{tg} \alpha = \frac{\alpha_1 C_{10} D_2}{\delta}$. This remote part of the kinetic curve corresponds to the quasi-stationary regime.

If $\alpha_1 \gg 1$ and $\alpha_2 \gg 1$ the transport rate is limited by the solute diffusion in the source phase. The relative kinetic function

$$M_{23} = 2C_{10} \sqrt{D_1} \sqrt{\frac{t}{\pi}} \quad (5)$$

could be linearized in coordinates $M(\sqrt{t})$.

For the LM process simulations in cases of source and receiving phases stirring a formal mass transfer equation

$$j \left(\frac{1}{\beta_1} + \frac{1}{\alpha_1 \beta_2} + \frac{\alpha_2}{\alpha_1 \beta_3} \right) = C_{10} \quad (6)$$

has been applied.

Experimental. TBP or TAA were used as HNO_3 carriers. Permeation measurements in three-phase systems with solid supported or bulk LM were carried out in conductometric diffusion cells with stirring and without one. For the stirred cell with solid supported LM partial mass transfer coefficients $\beta_1 = \beta_3 = 0.04$ cm/s had been determined previously according to the method described in [1]. A LM matrix was selected among Nucleapore, PALL or ASYPCR membranes. Experiments on HNO_3 regeneration from waste water were carried out in the pertractor with the bulk LM.

Results and discussion. The distribution coefficients of HNO_3 between its aqueous solutions and TBP in n-decane were first determined: $\alpha_1 = 0.07 - 0.8$ at $C^{\text{TBP}} = 0.4 - 2.0$ M, $C_{10}^{\text{HNO}_3} = 0.01 - 0.2$ M. For the unstirred system HNO_3 transport is satisfactorily simulated by eqn. (4). Transition time being very short (< 0.03 s.), kinetic curve looks as a straight line coming practically from the zero point. Diffusion in the LM is the rate-limiting step. Permeation proceeds in the quasi-stationary regime. These conclusions are the more valid for the stirred system, HNO_3 flux being insensitive to the mixing intensity.

Diffusion coefficients determination by the slope of $M_{23}(t)$ - function results in the similar values $D_2^{\text{HNO}_3} = (1.3 - 1.7) \cdot 10^{-6}$ cm²/s

for all matrixes tested with $d \gg 0.2 \mu$. If $d < 0.2 \mu$ diffusion appears to be hindered, $D_2^{HNO_3}$ -values being significantly reduced. Some increase in these values at low TBP concentration in membrane phase is probably due to the wearening of the moving particles interaction with each other as well as their interaction with the matrix walls. It's worthwhile to point out that $D_2^{HNO_3}$ -values calculated by means of Wilkie-Cheng correlation method are few times overestimated.

For the transport systems with TAA as a carrier and alkaline receiving solution $\alpha_1 \gg 1$ and $\alpha_2 > 1$, HNO_3 diffusion in the source phase limiting the overall permeation rate. The process rate was found to be independent on the matrix porosity due to the continuous organic liquid film formation on the solid supported membrane surface. It was also shown that under the definite conditions the spontaneous interfacial convection could be developed in a LM system with TAA.

As far as HNO_3 regeneration from waste solutions by means of LM technique is concerned the better results (extraction degree more than 95%, concentration factor more than 5) were obtained for TAA membranes as compared with TBP ones. An aqueous suspension of calcium hydroxide was utilized as a receiving phase in this process.

Symbols

A and B - dimensionless parameters; C_1, C_2, C_3 - solute concentration in phases 1, 2, 3, respectively, g/cm^3 ; C_{10} - initial solute concentration in phase 1, g/cm^3 ; D_1, D_2, D_3 - solute diffusivity in phases 1, 2, 3, respectively, cm^2/s ; d - matrix pores diameter, μ ; j - flux across membrane, $g/cm^2 \cdot s^{-1}$; LM - liquid membrane; M_{12}, M_{23} - solute quantity transferred across membrane boundaries, g/cm^2 ; Q - compound parameter, g/cm^3 ; t - time, s ; x - distance coordinate, cm ; α_1 and α_2 - distribution coefficients; β_1 and β_3 - mass transfer coefficients in phases 1 and 3, respectively, cm/s ; δ - membrane thickness, cm ;

Reference

1. Ivakhno S.Yu., Afanasiev A.V., Yagodin G.A. Membrannaya extractsiya neorganitcheskih veshchestv. Moskva: VINITI AN SSSR, 1985. 127 s.

TRANSFER RATE AND SEPARATION OF Sr^{2+} and Cs^+ BY
SUPPORTED LIQUID MEMBRANES UTILIZING SIZE-SELECTIVE
SYNERGISTIC CARRIERS

6-20

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In the present work we describe for the first time a SLM containing synergistic carriers, one of which is a crown-ether, suitable for practical alkali metals and alkali earths separation from strong acid aqueous solutions. The exemplary SLM reported here in detail separates Sr^{2+} from Cs^+ from 0.2 M HNO_3 solutions.

SLM Description and Results The membrane utilizes the two commercially available compounds shown in Figure 1, dissolved in n-dodecane, as carriers. One of the major novelties of this new SLM system is represented by the possibility of using n-dodecane as diluent for the carriers. Diluents of this type are necessary to ensure the proper stability of the SLM [1]. Chlorinated diluents, nitrobenzene and low boiling point aromatic solvents cannot be used in practical SLM systems as they chemically attack the support and have physico-chemical properties leading to unstable liquid supported membranes. In addition, this new SLM is particularly interesting since McDowell et al. [2] have shown that the synergistic effect appears to be size-selective, i.e. in many cases it is the greatest when the crown-ether cavity corresponds to the diameter of the ion being extracted (transported). A new family of practical SLM's, with a broad range of selectivities for alkali and alkali earth metals which can be adjusted by the proper selection of the crown-ether cavity size, is therefore available.

The design of a suitable SLM system requires high extractability into the membrane phase of the cation to be separated at the feed side of the membrane. On the contrary much lower extractability must occur at the strip side of the membrane to assure a sufficiently large concentration gradient inside the membrane. Selected distribution ratios (D) of Cs^+ and Sr^{2+} between HNO_3 solutions and n-dodecane solutions of the carriers are shown in Table 1. The experimental distribution data

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TABLE 1

Extraction of Sr^{2+} and Cs^{2+} by HD, CE and their mixtures in n-dodecane from HNO_3 at 25°C

a)

Organic Phase: $3 \times 10^{-3} \text{ M}$ CE, no HD		
Aqueous Phase	D (Sr^{2+})	D (Cs^+)
HNO_3 0.2 M	2.5×10^{-3}	4×10^{-4}
HNO_3 6.0 M	$<1 \times 10^{-3}$	$<10^{-4}$

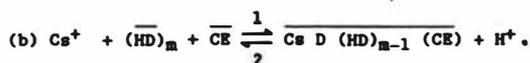
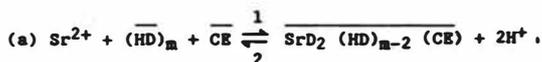
b)

Organic Phase: 0.2 M HD, no CE		
Aqueous Phase	D (Sr^{2+})	D (Cs^+)
HNO_3 0.2 M	17	1.8
HNO_3 6.0 M	1.7×10^{-2}	1.3×10^{-2}

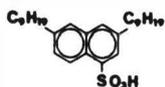
c)

Organic Phase: 0.2 M HD, $3 \times 10^{-3} \text{ M}$ CE		
Aqueous Phase	D (Sr^{2+})	D (Cs^+)
HNO_3 0.2 M	1.7×10^3	1.8
HNO_3 6.0 M	1.2	1.3×10^{-2}

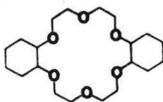
indicate that selective extraction of Sr^{2+} with respect to Cs^+ takes place from $[\text{HNO}_3] = 0.2\text{M}$ when CE is present. The synergic effect of CE and HD on Sr^{2+} extraction is evident. More extensive liquid-liquid distribution studies in a wide concentration range of HD, CE and HNO_3 have shown that the extraction-stripping reactions can be to a first approximation and in a limited concentration range described by the equations:



SUPPORTED LIQUID MEMBRANE CARRIERS



DIBUTYLPHENYL
SULFONIC ACID
HD



DICYCLOHEXYL
18 CROWN 6
CE

Ionic Diameter

Sr^{2+} 2.26 Å

Cs^{+} 3.38 Å

CE Cavity Diameter

(2.6 - 3.2) Å

Fig. 1

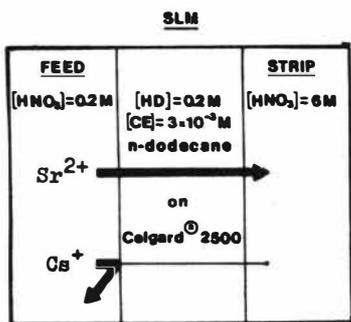


Fig. 2

Scheme of Supported Liquid Membrane (SLM) used in this work

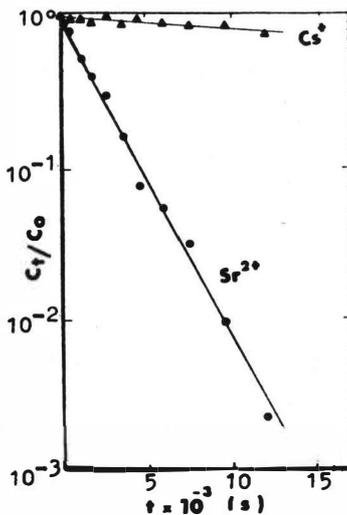


Fig. 3

Semilogarithmic plot of the feed conc. of Sr^{2+} and Cs^{+} vs time (s)
 C_t = conc. at time t, C_o = conc. at time zero

The bar indicates organic (membrane) phase species. The SLM systems, based on the chemistry described by equations (a) and (b), is schematically shown in Figure 2. Reaction 1 is responsible for the extraction of the cations into the SLM at the feed-SLM interface.

Reaction 2 for the stripping of the cations from the SLM at the SLM-strip interface. The flux of Sr^+ ions from feed to strip is accompanied by a counter flux of H^+ ions from strip to feed. The results of a typical transport experiment are shown in Figure 3 as semilogarithmic plots $\log(C_t/C_0)$ vs t (sec). C_t and C_0 are the concentration of Sr^{2+} or Cs^+ in the feed solution at time t and time zero. As the radiotracers ^{137}Cs and ^{85}Sr were used, the concentrations of Sr^{2+} and Cs^+ at the various times were measured radiometrically and simultaneously by a multichannel analyzer. The equipment and measuring procedures were the same as those described in references [3]. The support for the liquid membrane (Celgard 2500^R) was a flat-sheet 2.5×10^{-3} cm thick microporous polypropylene film with effective pore size of 0.04 microns and 45% nominal porosity (ϵ), manufactured by Celanese Plastic, Charlotte, North Carolina, U.S.A.

The geometrical membrane area (A) was 1.80 cm^2 and the volume of feed and strip solutions (V) was 4.0 cm^3 . The transport data have been analyzed according to the theories and models developed by Danesi [3], using the equations:

$$(c) \ln(C_t/C_0) = -P \frac{A \cdot \epsilon}{V} t,$$

$$(d) P = \frac{D}{D\Delta_a + \Delta_0},$$

P is the cation permeability coefficient (cm/sec), D is the metal cation distribution ratio at the feed side and Δ_a and Δ_0 are diffusional parameters described in [3]. From equations (c) the following permeability coefficients were calculated: $P(\text{Sr}^{2+}) = 2.4 \times 10^{-3}$ (cm/sec) and $P(\text{Cs}^+) = 9.8 \times 10^{-5}$ (cm/sec). The corresponding SLM separation factor, $P(\text{Sr}^{2+})/P(\text{Cs}^+)$, is 25. The data indicate that in a single contact 99% of the initial Sr^{2+} can be recovered, together with 15% of the initial Cs^+ . Better selectivities can be obtained by adjusting the concentrations of CE, HD and HNO_3 .

The exemplificative results shown here demonstrate the great potential of these SLM's for the recovery and separation of Sr^{2+} and Cs^+ from HNO_3 solutions in system of analytical and industrial importance.

References

1. P.R. Danesi, L. Reichley-Yinger and P.G. Rickert //J. Membr. Sci. 1987, Vol. 31, P. 117.
2. W.J. McDowell, B.A. Moyer, G.N. Case and F.I. Case //Solv. Extr. Ion Exch. 1986, Vol. 4, P. 217.
3. P.R. Danesi //Sep. Science and Techn. 1984-85, Vol. 19, P. 857 and reference therein.

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INTRODUCTION

Liquid ionexchange membranes have been proposed as an attractive new technology for the elimination and recuperation of metals from dilute solutions. Our attention was drawn on a problem concerning zinc removal from a nickelsulphate solution.

The nickelsulphate solution contained 58 g/l of nickel as nickelsulphate with 600 ppm zinc as an impurity which had to be removed. Precipitation of the zinc, or treatment by solid ionexchange lead to unsatisfactory results. The use of liquid ionexchange to solve the problem was considered.

In this paper the results obtained from laboratory experiments using the liquid membrane technique are presented. Both solid supported- and liquid emulsion membranes were tested.

SOLID SUPPORTED LIQUID MEMBRANES

It is known from the literature that zinc shows a good permeation behaviour in the system : zinc-di(2 ethylhexylphosphoric) acid - sulphuric acid (1-2). These findings were confirmed by our experiments on this permeation system (3). From these former results, obtained with a pure zincsulphate solution, it was shown that with the support used (Accurel tubing 1.2*1.6 ; porosity 75 %) and a membrane composition of 30 vol % DEHPA in kerosene, complete removal of zinc was possible at a reasonable flux. The same kind of experiments were performed with the nickelsulphate solution.

Experimental

The permeation system was constructed with the support mentioned earlier. The microporous hollow support, impregnated with 30 vol % of DEHPA in Shellsol K, was fitted into a glastube of 6 mm diameter and had a length of 105 cm. The feed solution (500 ml: 620 ppm Zn ; 58,4 g/l Ni) was pumped in a recycling mode through the innerside of the tubing while a 2 M sulphuric acid stripsolution (50 ml) was recirculated at the other side of the membrane. The initial pH of the feed solution was 5,47. For this run no pH adjustments were done. The plugflow velocity of the feed solution in the tubing was $1 \text{ cm} \cdot \text{sec}^{-1}$.

Results

The results are shown in figure 1 [(Me) is in ppm] During the experiment the hydrogen ion concentration of feed solution steadily increased as mass-transfer took place. The pH dropped from 5,47 to 2,09 at the end of the experiment.

The obtained data were treated by regression analysis and from the slope of the curve the initial flux was calculated

and showed to be $136 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{hour}^{-1}$. At the end of the experiment the strip solution contained practically all of the zinc: 6,2 g/l (Final zinc concentration in the feed was 3 ppm) but also 5,9 g/l of nickel, which is 1 % of original amount of nickel in the feed solution.

Another run under constant pH conditions of the feed solution was started. A similar permeation module as for the first run was used. 300 ml of feed and 100 ml of 2 M H_2SO_4 strip solution were circulated through the system.

The feed solution was pumped with a plugflow velocity of $3.4 \text{ cm} \cdot \text{sec}^{-1}$ through the tubing and the pH in the feed vessel was kept at a constant level (pH = 4).

The results are shown in figure 2.

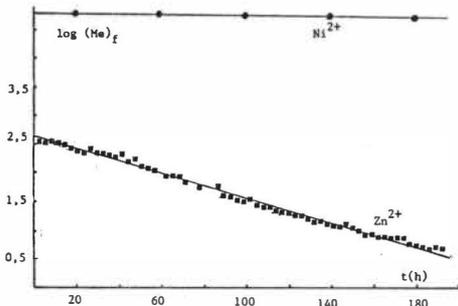


Fig. 1. log metal concentration as a function of time. Membrane: 30 vol.% DEHPA in Shellsol K. Recycling mode without pH₁ adjustment. Lin. flow velocity: $1 \text{ cm} \cdot \text{s}^{-1}$

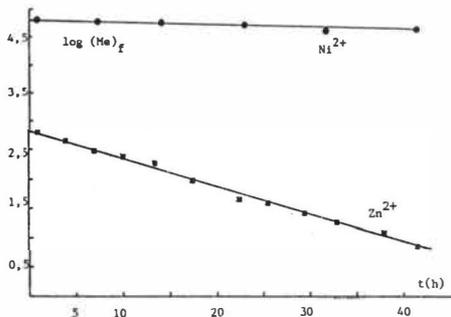


Fig. 2. log metal concentration as a function of time. Membrane: 30 vol.% DEHPA in Shellsol K. Recycling mode. Constant pH: Lin. flow velocity: $3.4 \text{ cm} \cdot \text{s}^{-1}$

The zincflux calculated from these data showed to be $520 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$. The final concentration of zinc in the feed was 5 ppm and the nickel content was 56,9 g/l, which means that 1,9 % of nickel was coextracted under these conditions.

LIQUID EMULSION MEMBRANES

Liquid emulsion membranes for the treatment of diluted zinc solutions also received considerable attention in the literature last years (4,5,6).

A first series of experiments using this type of liquid membrane was done with a pure zinc solution containing 600 ppm zinc as zinc sulphate. Various membrane compositions were tested. Figure 3 shows the results obtained with SPAN 80 and di-2 ethylhexylphosphoric acid in Shellsol K. The emulsion contained 2 M

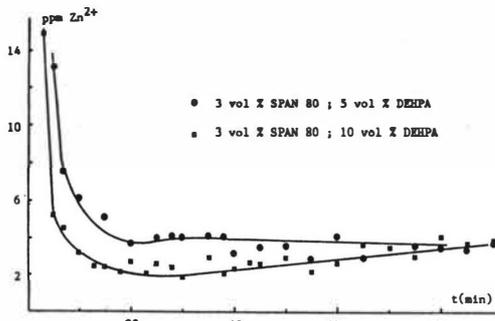


Fig. 3. Evolution of zinc in the feed as a function of time. Diluent: Shellsol K. Emulsion: strip/solvent = 1/2. Emulsion/feed = 1/5. Initial zinc concentration: 600 ppm

sulphuric acid in a ratio aqueous to organic phase of 1/2. The ratio of emulsion to feed was 1/5. These results show that zinc can be almost completely eliminated from the feed using this technique: down to 2 ppm with 10 % DEHPA and less than 4 ppm with 5 % DEHPA. The same kind of experiments

were also done with the feed under consideration. Figure 4 shows the results obtained. With the emulsion membranes used, at the phase ratios mentioned, the final concentration of zinc that could be obtained was 20 ppm with 5 vol % DEHPA and 12 ppm with 3 vol %

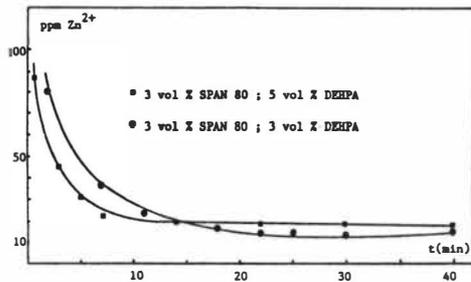


Fig. 4. Evolution of zinc concentration in the feed as a function of time. Feed: 620 ppm Zn; 58 g/l Ni. Emulsion: strip/solvent = 1/2; Emulsion/feed = 1/5

DEHPA in the liquid membrane. This is considerably higher than the concentrations obtained with the pure zincsulphate solution. This is due to the fact that coextraction of nickel takes place which leads to a faster and more drastic drop in pH of the feed solution.

After electrostatic splitting of the loaded emulsion, the strip solution was analysed for zinc and nickel. With the membrane containing 5 vol % DEHPA we found 5050 ppm zinc and 4795 ppm nickel. For the membrane with 3 vol % DEHPA, the concentration of zinc and nickel was respectively 4540 ppm and 2700 ppm. A considerable swelling of the emulsion was also noticed : 77 vol % for the membrane with 5 vol % DEHPA and 100 vol % for the one with 3 vol % DEHPA.

CONCLUSIONS

It was shown that the elimination of zinc from a concentrated nickelsulphate solution is possible using liquid membranes. With supported liquid membranes almost complete removal of zinc is obtained.

Using emulsion membranes, batch experiments showed that the final concentration of zinc in the feed under consideration is higher than with supported membranes and stagewise contact either in mixer-settlers or column extractors should be used for complete removal of zinc.

Further experiments should be carried out in order to look for higher selectivity in both permeation systems.

ACKNOWLEDGEMENTS

The authors wish to thank Enka Belgium and Obernburg (G.D.R.) for the supply of the Accurel Microporous support.

REFERENCES

1. L.Fernandez , J.Aparicio , M.Muhammed // Journal of membrane science, 27 (1986), 77-91.
2. L.Fernandez , J.Aparicio , M.Muhammed // Proc. ISEC '86, P. 611-618 ; DECHEMA Frankfurt A/Main,
3. M.Verhaege , M.Vanhullebusch , D.Vanrobaeys // Proc. Summerschool on extraction 7-11 sept. 1987. PROGEC - France ,
4. D.Melzner , K.Schügerl et al. // Hydrometallurgy, 13 (1984), 105-123.
5. J.Draxler, R.Marr // Chem. Eng. Process, 20 (1986), P. 319-329.
6. D.Lorbach , R.Marr // Chem. Eng. Process , 21 (1987), P. 83-93.

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INTRODUCTION

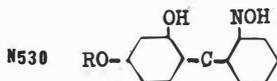
Solid supported liquid membrane is a new separation technique. Comparing with liquid surfactant membrane, supported liquid membrane avoids the problem with the stability of emulsion, demulsion and flooding. Because extraction and strip can be carried out simultaneously, there is no problem with loading. This technique is suited for very dilute solutions and has very high enrichment factors. Therefore, it has become attractive in the field of hydrometallurgy and waste water treatments[1-6].

The goal of the present work was to investigate the effects of liquid pH, flow rates of solutions and concentrations of carrier in the membrane on the flux of copper by using a flat sheet supported liquid membrane, and to propose a calculational method for copper permeation.

EXPERIMENTAL

The membrane solution used for copper permeation was N530-kerosene.

A flat sheet film (Selgard 2400, thickness is 25 μm , porosity 0.38 and



pore diameter 0.02 μm) was used as a supporter of membrane solutions.

Fig.1 shows the experimental device. Membrane extractor consisted of a rectangular tank having 0.26cm in wide, 17cm in length, and 4cm in high. There was a channel surrounding the membrane where it contained membrane solution to stabilize the membrane properties.

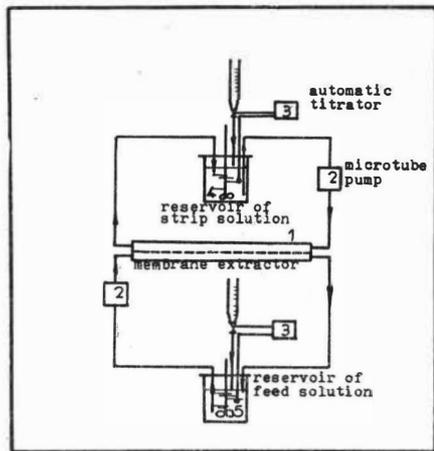


Fig 1. Liquid membrane circuit

The membrane solutions were recycled from the reservoirs through the module with two microtube pumps. After a known time, solution concentrations in reservoirs were sampled (sample volume=0.05ml), copper concentrations were analyzed by colorimeter. The volumetric flow rates were 0.0104-0.025 m/s for feed solution, and 0.025-0.0375 m/s for strip solution. The pH of feed solution were varied from 1.5 to 4.0, and pH=1.0 for strip solution in the experiments. pH were controlled by automatic titrators with sodium hydroxide and sulphuric acid. The concentrations of carrier were varied from 0.1 to 0.35 in volume. The temperature of the experiments was kept at 25 $^{\circ}\text{C}$.

automatic titrators with sodium hydroxide and sulphuric acid. The concentrations of carrier were varied from 0.1 to 0.35 in volume. The temperature of the experiments was kept at 25 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

The permeation flux of copper, N , can be calculated from the measurement of Cu concentrations vs time. Experimentally determined values for Cu flux varied from 0.01 to 0.0281 kmol/m² s, depending on flows, pH of aqueous solutions and concentrations of carrier.

1. Effect of pH

Fig. 2 shows the relationship between pH of feed solution and flux keeping ReE and ReS constant. The flux of copper can be found to be almost independent of pH when pH > 3. The Cu flux is proportional to pH when pH < 3 for the feed solution. When pH of extraction solution equals to that of strip solution, the permeation rate is certainly zero.

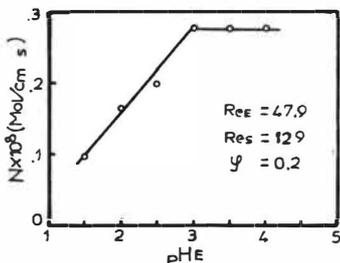


Fig 2. Permeate flux of Cu as a function of pH_E

2. Effects of ReE

The experimental results are shown in Fig. 3. The increases of ReE dramatically reduced the Cu flux.

The extraction and stripping of complex CuR₂ can be represented by a reversible reaction [7]



The chemical reactions occur in aqueous zones adjacent to the interfaces, where the subscript A and O denote the aqueous and organic phases, respectively [8, 9]. Since the increase of feed flow rate reduces the thickness of boundary layer, the reaction space decreases. It might be the reason that permeation rate is controlled by chemical reaction instead of diffusion resistance in the boundary layer of extraction side.

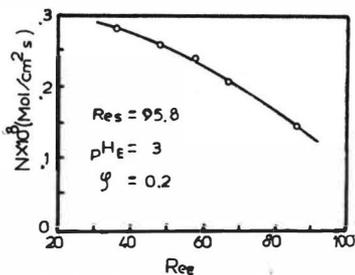


Fig 3. Effect of Re_E on flux of Cu

3. Effect of ReS

The experimental results are shown in Fig.4. It is clear that the flux of copper increases with increasing ReS. The process might be controlled by diffusion of Cu in the boundary layer of strip side.

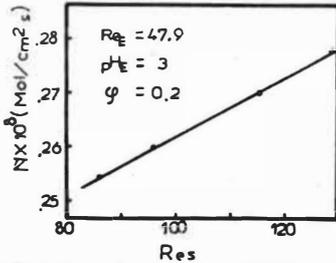


Fig. 4. Permeate flux as a function of ReS

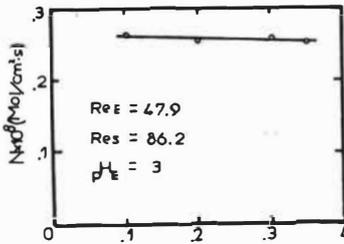


Fig. 5. Effect of ϕ on flux of Cu

4. Effect of carrier concentrations

It can be seen in Fig.5 that there are two regions: Cu flux maintains constant when $\phi > 25\%$; Cu flux decreases with ϕ increasing when $\phi > 25\%$. This might result from the effect of viscosity of membrane solution.

DATA TREATMENT

The reaction zones located at the interfaces with thicknesses of δ_E and δ_S , which denote extraction and stripping zones respectively. Furthermore, δ_E and δ_S vary inversely as ReE and ReS, where

$$ReS = \frac{de U_S \rho_S}{\mu_S}, \quad ReE = \frac{de U_E \rho_E}{\mu_E}$$

Assuming that the diffusion of complex CuR₂ in the membrane solution is a control process comparing with other components, and it can be represented by following equation:

$$N = k_t ([CuR_2]_{Ei} - [CuR_2]_{Si}) \quad (2)$$

Tanaka[6] proposed the equations for extraction

and stripping reaction rate of Cu with LIX65N:

$$r_E = 6.0 \times 10^{-8} [Cu^{++}]_{Ei} ([RH]_{Ei} / [H^+]_{Ei}) \quad (3)$$

$$r_S = 2.5 \times 10^{-8} [CuR_2]_{Si} [H^+]_{Si} \quad (4)$$

Considering that $[Cu^{++}]_{Ei}$ is independent of Cu flux according to the experiments, we use $[CuR_2]_{Ei}$ instead of $[Cu^{++}]_{Ei}$. Therefore, above equations can be modified as follows:

$$r_E = k_E [RH]_{Ei}^a / ([CuR_2]_{Ei}^b [H^+]_{Ei}^c) \quad (5)$$

$$r_S = k_S [CuR_2]_{Si}^d [H^+]_{Si}^e \quad (6)$$

The basis equation for the flux of copper permeation can be obtained from equation (5), (6) and (2), assuming the partition coefficients of CuR₂ in two interface are constant:

$$N^2 = \frac{\alpha}{1 + \beta} \quad (7)$$

where

$$\alpha = [RH]_{Ei}^a / ReE^b [H^+]_{Ei}^c, \quad \beta = ReS^d / [H^+]_{Si}^e \quad (8)$$

Because $Re_S \gg 1$, and $[H^+]_S$ did not change in our experiments, the equation can be written by using pH instead of $[H^+]_E$, we obtained

$$N = \sqrt{\frac{\alpha}{\beta}} = K \frac{[RH]_O^a [PH]_E^d}{Re_E^b Re_S^c} \quad (9)$$

The experimental data can be treated based on above equation.

After regression, a semi-empirical equation was obtained:

$$N = 3.66 \frac{DH^{1.39} Re_S^{0.194}}{Re_E^{0.726} \phi^{0.022}}, \quad pH \leq 3$$

$$N = 14.7 \frac{Re_S^{0.227}}{Re_E^{0.726} \phi^{0.022}}, \quad pH > 3$$

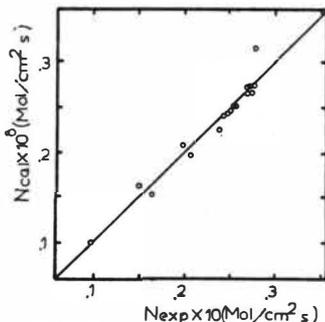


Fig. 6. Comparison of experimental and calculated results

(10)

The comparison between experimental and calculated results is shown in Fig. 6.

CONCLUSION

The flux of copper is strongly effected by feed flow rate for the solid supported liquid membrane with N530. It can be explained that the reaction takes place in the space near the membrane surface. Therefore, the velocity effect on Cu flux has to be taken into account. The semi-empirical equation proposed under the conditions may be used to predict copper flux for solid supported liquid membrane.

NOTATION

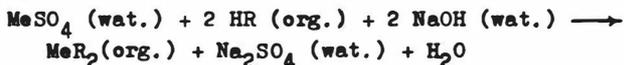
a, b, c, d, e, K - constant.	δ - thickness [m].
d _e - hydraulic diameter [m].	μ - viscosity [Ns/m].
F - surface [m ²].	ρ - density [kg/m ³].
kt - mass transfer coefficient of CuR ₂ [m/s].	ϕ - concentration of carrier [M].
k - constant of reaction rate.	Subscript
N - flux of copper [kmol/m ² s].	E - extraction.
r - rate of reaction [kmol/m ² s].	S - strip.
Re - Reynold number.	i - interface.
u - velocity [m/s].	

REFERENCES

- Largman T. et al. // Hydrometallurgy, 1978, 3, 153.
- Babcock W.C. et al. // ISEC'80, Vol 2, R80.
- Danesi P.R. et al. // Solvent Extraction & Ion Exchange, 1984, 2(6)781.
- Chiarizia R. et al. // Ibid. 1984, 2(3)478.
- Danesi P.R. et al. // Sep. Sci. & Tech. 1982, 17(9)1183.
- Takahashi K. et al. // J. of Chem. Eng. of Japan, 1985, 18(3)205.
- Whewell R.J. et al. // Hydrometallurgy, 1979, 4, 109.
- Rod V. et al. // Chem. Eng. Res. Des. 1985, 63, 89.
- Hanson C. // ISEC'74, R2401(1974).

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Extraction separation of heavy nonferrous metals was studied in detail by means of carboxylic acids from both theoretical and practical points of view. At Chemical-metallurgical Institute of Kazakh Academy of Sciences there was developed an extraction technology to utilize valuable components from spent copper electrorefining solutions with naphthenic acid solution in kerosene [1]. It has been successfully tested on Balkhush mining-metallurgical plant. The technology has not been yet introduced because metal extraction by means of carboxylic acids is accompanied with salt formation in the raffinates by the reaction



utilization of which is a complex task.

Later on this technology was elaborated: electro dialysis method has been used for alkali and acid regeneration from raffinates. Combination of two- and three-chambered electro dialyses resulted in sufficient energy consumption decrease (1000-1400 kwhr / t NaOH) with high salt decomposition (90-95%) [2]. The investigation in twenty two-chambered electro dialysis apparatus shewed that working with raffinates energy consumption is 7-10 % higher due to the presence of dissolved naphthenic acid in comparison with synthetic sodium sulphate solutions.

Recently the processes with ion-exchange membranes, namely, the method of extraction in membrane apparatuses, have been widely developed. The authors have studied liquid extraction of copper, nickel and zinc with decane and mbenzine solutions of caproic and naphthenic acids in electrochemical system with ion-exchange membranes (Fig.1).

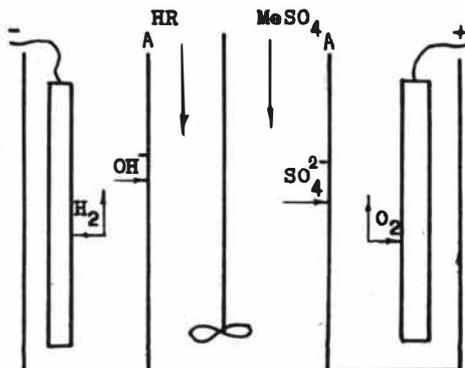


Fig.1. Electrochemical liquid extraction scheme

The Figure shows that contrary to a simple extraction metal recovery into extract is carried out without any neutralizing agents. Sufficiently high electrical conductivity of water-organic suspension is ensured by O:W (3-5):1 system voltage being 10-40 v. Cell voltage depends also on current density varied in the range of 100-200 A/m² and on extraction chamber thickness. Electric power consumption amounts to 2000-6000 kwhr/t of extracted metal with its current efficiency 85-98 and 90-99% extraction rate.

This method was tested for copper and nickel separation out of the precipitates of sulphate-ammonium technology of electrolyte refining from nickel. The precipitate was dissolved in water with solid-liquid= 1:3 ratio and ions of copper and nickel were separately extracted from the solution in electrochemical membrane cell by 1 M solution of naphthenic acids. After the extraction the remained in the solution ammonium sulphate can be recycled for nickel deposition from the electrolyte (Fig.2). High-grade copper and nickel vitriols are produced out of the reextracts.

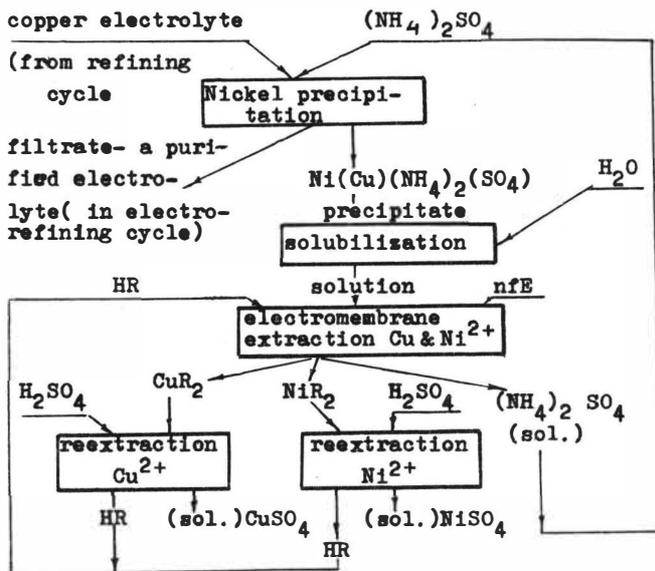


Fig.2. Principal technological copper and nickel extraction scheme

References

1. A.C. N° 400174 (USSR). The method of copper and nickel separation by extraction /Buketov E.A. et al. B.I. 1974. N23.
2. A.C. N° 916601 (USSR). The plant for sulphuric acid and alkali production /Sharipov M.Sh., Zharmenov A.A., Mustafinova A.S. B.I. 1982. N 12.

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The liquid membrane process (LMP) with a surfactant and a carrier is a promising process for separating metal cations of low concentrations from aqueous solutions. The present contribution contains investigations for the separation of chromium from aqueous solutions, which is of great importance in the electroplating industry.

Experimental

The following system of materials was chosen:

External phase III volume V_3 , aqueous solution of CrO_3 .

Membrane phase II volume V_2 , n-decane with soluted tri-n-octylamine (TOA) as carrier and Rofetan OM (an ester mixture of unsaturated natural fatty acids with a chain length of C_{18} to C_{22}) as surfactant.

Internal phase I volume V_1 , aqueous solution of NaOH.

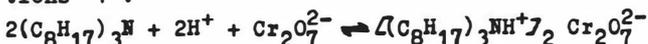
Analysis of chromium was carried out by titration with a 10% aqueous solution of potassium iodide. Generation of emulsion: V_1 and V_2 were stirred by a double-bladed propeller stirrer (diameter 20 mm) in a conical device of 0.2 l volume. Contactor for mass transfer: $V_1 + V_2 + V_3$ were stirred by a glass stirrer (diameter 55 mm) in a cylindrical device of 0.75 l volume. Temperature $22^\circ\text{C} \pm 2$.

Test programme with the parameters investigated

Parameter investigated	Range	Value*
pH value of the external phase	1.5...3.5	1.8
initial concentration c_0 of Cr^{6+} in $V_3, \text{kg/m}^3$	0.1...0.8	0.4
carrier concentration in the membrane phase vol%	1.17...5.6	3.0
surfactant concentration in the membrane phase vol%	0.4...1.9	1.5
concentration of NaOH in the internal phase	0.1...1.0	0.15N
volume ratio $V_3 : V_1$	5...50	10
volume ratio $V_1 : V_2$	0.2...1.0	1
generation of emulsion: contact time, s	60...1800	60
rotations, s^{-1}	33...60	33
rotations in the contactor with mass transfer, s^{-1}	1.5...6.0	3.3

* If the parameter in question is not investigated.

The mass transfer in the contactor involves the following reactions 1 :



Interface III-II from left to right side and interface II-I opposite.

It is a cocurrent transport (metal ions and H^+ ions from the external phase into the internal phase).

The samples were taken from the contactor after 1, 3, 5, 10, 20 and 30 minutes. The results were represented in diagrams for times up to 10 minutes, since contact times of more than 10 minutes only resulted in minor changes.

Results

The system of materials being selected, essential factors affecting the mass transfer in the external phase, membrane phase, internal phase, and the effect of the volume ratios will be discussed.

External phase

At high concentrations of H ions ($pH < 3$), few dichromate ions are present, and the reaction with TOA can take place [2]. pH values of 1.5 to 2.2 are recommendable, cf. Fig.1. At high initial concentrations of Cr , mass transfer decreases with increasing time of contact, since the driving force is reduced by the reagent consumed, cf. Fig. 2. As regards the technological design, a countercurrent column is recommended. Plotting $\ln c/c_0 = f(t)$ for small contact times up to 5 minutes gives straight lines of different slopes. This is in correspondence with the results obtained by other authors, cf. [3] and [4].

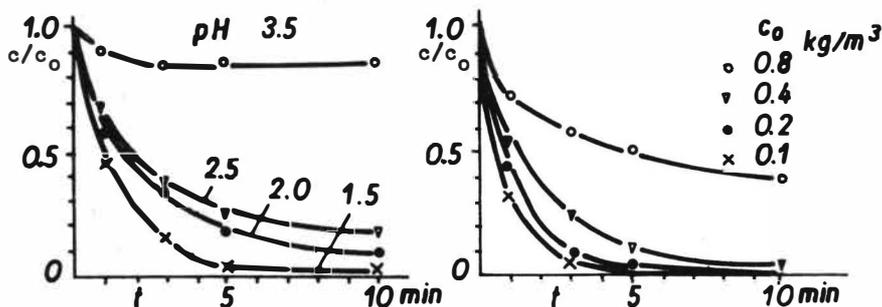


Fig.1. Influence of pH value, other parameters see Table

Fig.2. Influence of initial concentration c_0 of Cr^{6+} , other parameters see Table

Membrane phase

The selection of the carrier and the surfactant has a great influence on mass transfer and macro drop stability in the contactor. When the carrier and the surfactant have been defined, the concentrations are of importance. Increased carrier concentration promotes mass transfer, since a greater amount of ions react at the interface, cf. Fig.3. At carrier concentrations greater than 4 vol%, the stability of the

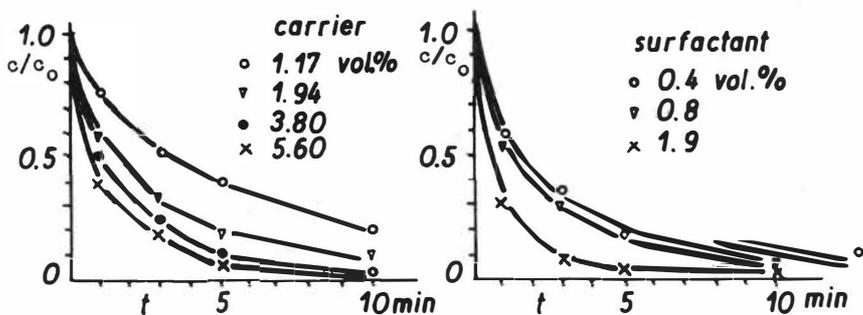


Fig.3. Influence of carrier concentration, other parameters see Table

Fig.4. Influence of surfactant concentration, other parameters see Table.

emulsion is greatly disturbed. A greater surfactant concentration increases the macro drop stability, which promotes mass transfer, cf. Fig.4.

Internal phase

NaOH and Na_2CO_3 were tested as reagents for the internal phase. Best results were obtained with NaOH. The effect of the NaOH concentration is represented in Fig.5.

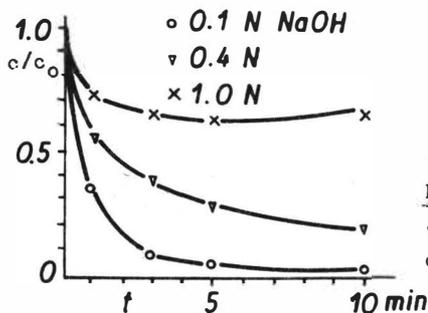


Fig.5. Influence of concentration of NaOH in the internal phase, other parameters see Table

Volume ratios

The ratio $V_3 : V_1$ is the decisive factor which determines the possible enrichment of the transferred metal in the internal phase. Increasing ratios $V_3 : V_1$ and $V_3 : V_2$ have a negative effect on mass transfer, cf. Fig.6. In many cases, a constant ratio $V_3 : V_2$ of about 10 is favourable for an increasing ratio $V_3 : V_1$.

Breakdown of macro drops

The choice of the system of materials is the factor which has the greatest influence on the breakdown rate. In systems of materials showing a tendency towards macro drop breakdown, an increasing volume

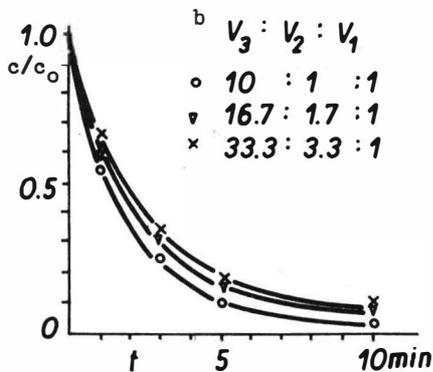
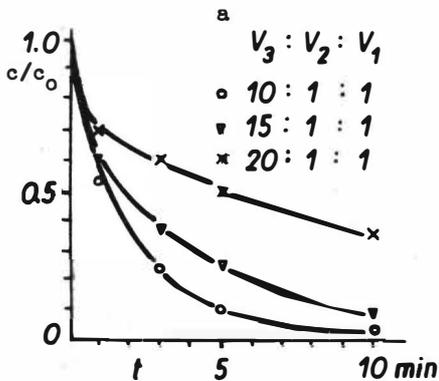
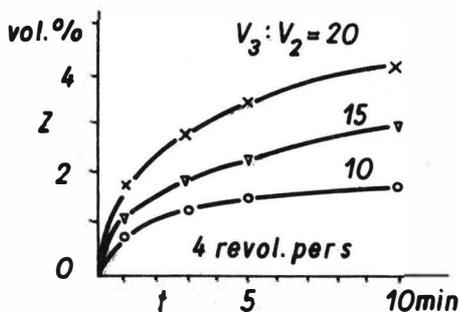


Fig.6. Influence of volume ratio $V_3 : V_1$, other parameters see Table.

a: $V_2 : V_1 = 1$
 b: $V_3 : V_2 = 10$

Fig.7. Breakdown rate Z at $V_2 : V_1 = 1$ vs. contact time t , external phase 0.2 N NaOH, internal phase water distilled



ratio $V_3 : V_2$ and increasing mechanical load through the mechanical energy applied lead to an increased breakdown rate, results for the investigated system see Fig.7.

Modelling

The following conditions were established for modelling:

1. Reactions at the interface proceed rapidly, hence no resistance exists. This has been confirmed by kinetic investigations with the help of radioactive tracers.

2. The liquid membrane is considered as a plane layer.

3. Diffusion in the membrane phase is the decisive resistance.

The efficiency G of metal in the absence of macro drop breakdown is represented by

$$G = 1 - \frac{c}{c_0} = 1 - e^{-s t} \quad \text{with } s = \frac{D A c_3^2}{l V_3 c} \quad (1)$$

Including the breakdown of macro drops, the mass flow of the metal dM/dt is composed of two expressions:

$$\frac{dM}{dt} = \frac{dM_m}{dt} - \frac{dM_b}{dt} \quad (2)$$

The model based on equns. (1) and (2) is represented in detail in [5]. The model contains an adaption parameter s , see equn. (1), and two adaption parameters for different initial concentrations of Cr. Good agreement between experimental and calculated values was achieved.

Conclusions

1. Mass transfer of chromium with TOA as carrier and Rofetan OM as surfactant is favourable under the conditions shown in Table in the last column. The separation of chromium after 5 minutes time of contact is more than 95% at initial concentrations up to 0.5 kg Cr per m^3 .
2. LMP involves mass transfer in the contactor and separation of the emulsion as important process stages. The separation of the emulsion is strongly affected by the nature and the concentration of the surfactant. This enables the conditions to be varied to a certain degree, in agreement with point 1.

The authors thank Prof. Mühl for helping to select the systems of materials.

Symbols used

- A (m^2) - interfacial area.
c (kg/m^3)-Cr⁺⁶ concentrations of the external phase at the contact time t .
 c_{32} (kg/m^3)-Cr⁺⁶ concentration at the interface.
 c_0 (kg/m^3)-initial concentration of Cr⁺⁶ of the external phase.
D (m^2/s)diffusion coefficient.
I (m) - width of the diffusion layer.
M (kg) - mass transfer of Cr⁺⁶.
t (min) - contact time.
Z (vol%) -breakdown rate.

Indices

- b - breakdown.
mt - mass transfer.
1 - internal phase.
2 - membrane phase.
3 - external phase.

References

1. Deptula C. // J.Inorg.Nucl.Chem. 1968. V.30. P.1309-1316.
2. Ishimori T. // J.Atom.Energ.Soc.Japan. 1963. V.5. P.89.
3. Marr R., Bart H. // Symp.Hydrometallurgy'81, Manchester. Proceedings. London, 1981, D.3.
4. Martin T.P., Davies G.A. // ISEC-80. Paper 80-230.
5. Weiss S. and Castaneda Zepeta A. // 5th Intern. Summer School "Modelling of Heat and Mass Transfer Processes." 1985. P.147-171.

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Organic cumene solutions containing mixtures of Cyanex 471 (up to 4% w/v) and di-2-ethylhexyl-Phosphoric Acid, DERPA, (up to 4% v/v) supported in flat porous films (teflon) have been employed as liquid membranes to pump silver ions against their concentration gradient between two aqueous solutions of different composition.

Using batch experiments, the membrane system (extraction and stripping process) was studied under a variety of chemical conditions including strong silver complexing agents (i.e. EDTA, thiosulfate, thiocyanate and ammonia), which, in all cases, strip the metal from the organic silver-loaded solutions. In spite of these results only NH₃ aqueous solutions (0.25 M) were able to properly function as stripping solution when the liquid supported membrane was placed to work in the separation experiments.

Potentiometric measurements were used to monitor the silver mass transfer process. More of 90% of the silver was separated in less than two hours. The results of these experiments also includes the effect of reacting species concentration as well as the hydrodynamic conditions employed. The influence of the diffusion process in the mass transfer rate is also discussed.

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Mass transfer of palladium through liquid supported membranes is accomplished by using Cyanex 471 (tri-isobutyl-thiophosphine) dissolved in cumene as carrier. The use of a catalyzed extraction reaction based on the ligand trans-effect (1) has overcome previous reported lack of succes in applying Cyanex 471 to the extraction of Palladium (II) by supported liquid membranes (2). The study includes the choice of appropriate conditions to both aqueous and stripping solutions. Feed solutions containing Pd(II) $10E-5$ to $10E-4$ M, SCN- $10E-4$ to $5.10E-5$ M and pH=2.5 were employed against stripping solutions of general composition: 0.01 to 0.1 M SCN- and pH=2.5. In both solutions chloride concentration was kept constant at 1.0 M through all the experiments. The membrane consisted of Cyanex 471 in cumene solutions up to $10E-3$ M supported in a flat porous teflon membrane (Millipore).

The effect of chemical parameters (i.e. concentration of the reacting species) as well as hydrodynamic conditions (i.e. stirring speed) in the mass transfer rate are discussed.

References

1. Al-Bazi S.J. and Freiser H. // *Solv. Extr. Ion Ex.* 4(6), 1121 (1986).
2. Walker R.D. // *Energy Research Abstr. Num.* 8877. 10(5) (1985).

STUDY OF THE MASS TRANSFER PROCESS ON THE SEPARATION OF
Ti(IV) BY A SSLM USING TRIBUTYLPHOSPHATE (TBP) IN CUMENE
AS A CARRIER

6-27

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A solid supported liquid membrane process has been employed on the separation of Ti(IV) from high concentrate chloride solutions. This process is based on the Titanium extraction by TBP dissolved in cumene. For this purpose, a Millipore flat membrane (GVHPO9050) of 125 μ m thickness and 75% porosity has been used. The feed solutions consisted on mixtures LiCl-HCl up to 10M total chloride concentrations containing up to 140 ppm of Ti(IV) while the stripping solutions were charged with $Mg(NO_3)_2$. The carrier, consisting on TBP-Cumene organic solutions (TPB ranging from 40 to 80% v/v and 4% dodecanol as modifier), was placed in the lyophilic membrane support.

Under this conditions the study has been undertaken in order to characterize the mass transfer process of Titanium. The influence of chemical and hydrodynamic parameters on the Titanium mass transfer rate has been determined. In this sense, the Titanium concentration, the hydrochloric acid concentration, the TBP membrane content, the interfacial contact area and the rpm of the impellers have been varied in order to determine their contribution. The results, expressed in terms of Titanium permeability, point out that the determining step on the mass transfer is due to the diffusion process at both aqueous and organic films.

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Since the introduction of liquid emulsion membrane by Li[1], the technical applicability of this Liquid-Membrane-Permeation (LMP) process and its economic superiority to solvent extraction was found feasible for several pilot plants for recovery of uranium [2], copper [3], mercury [4] and zinc [5] from liquid streams. LMP is commonly regarded as a rate process, which is controlled only by the residence time in the mass transfer apparatus contrary to solvent extraction which is equilibrium limited process. In conventional solvent extraction, the processes of extraction and stripping are separated, whereby in LMP these two steps are combined to one single step. This is achieved by producing a water-in-oil emulsion.

While the main work reported on the use of liquid surfactant membrane is directed on the separation and preconcentration of uranium, copper, mercury, zinc, chromium and cobalt [1-7], few papers [8-10] were published on the extraction of the lanthanides by this technique. In this respect, Jiang et al [8] and Zhu et al [9] carried out limited investigations on the extraction of Eu(III) and La(III) from HCl media using LMP containing HDEHP. Teramoto et al.[10], studied the extraction of selected lanthanides from hydrochloric acid medium using the mono-(2-ethylhexyl) ester (PC-88A) as a carrier. The present investigations cover the extraction of several lanthanides from nitric acid medium using HDEHP as active carrier. The different parameters affecting the transport of these elements were studied and discussed.

Experimental

Di-(2-ethylhexyl) phosphoric acid (HDEHP) was obtained as a practical reagent from Fluka AG, Switzerland. Tween-85, a non ionic surfactant, was supplied from Shell Company, Egypt. Cyclohexane was El-Nasr Chemical Company product, Egypt. All other chemicals and reagents were A.R. grade and obtained from Merck.

The emulsion was prepared by mixing 25 cm³ of 0.1M HDEHP in cyclohexane with 1 cm³ of Tween-85. To this solution, 25 cm³ of the stripping aqueous nitric acid solution was added followed by vigorous mixing using stirring at a rate of 5000-7000

rpm for 20 min. provided with a special designed bladed impeller.

The extraction experiments were carried out in a thermostated glass vessel and the mixing was achieved by magnetic stirrer at 150 rpm. The concentration of the different lanthanides was determined complexometry by EDTA and Eriochrome black-T as indicator or radiometrically using the respective radioactive tracers.

Results and Discussion

Liquid membrane permeation process using the liquid cation exchanger HDEHP can generally proceed through the following steps; i- diffusion of the metal and counter ions through the stagnant film of the external aqueous phase, ii- complex formation between the metal cation and the liquid cation exchanger at the external surface of the W/O emulsion drop; iii- diffusion of the complex and chelating agent in the peripheral oil layer of the W/O emulsion drop, iv- diffusion of the complex and the chelating agent through the interstitial oil membrane phase and v- stripping of the metal at the interface between the oil membrane phase and the internal aqueous phase droplet containing the stripping solution.

Based on this basic concept of the process, the different factors affecting the transport of lanthanum was investigated to understand the transport process. Unless otherwise stated, the concentration of the lanthanide ions in the outer phase was 0.8 gm metal per litre of 0.1M HNO_3 solution, the aqueous phase: emulsion phase volume ratio was 20:1, the stripping solution in the aqueous phase was 1M HNO_3 and the working temperature was $30 \pm 1^\circ\text{C}$.

Effect of Aqueous : Emulsion Phases Ratio

The effect of aqueous to emulsion phase ratio on the extraction of lanthanum is given in Fig. 1. In this respect, after 5 min, the extraction percent (% E) decreased by increasing the aqueous phase volume. After 10 min, the % E for 5:1 aq. : emul. decreased, whereby the sequence for the uptake remained the same. The decrease in % E with increasing the aqueous phase volume is in agreement with basic principles of solvent extraction. The decrease observed for the 5:1 ratio suggests that with high residence periods for small aqueous volume the emulsion could disturb the chemical compositions of the aqueous phase with subsequent decrease in the % E of lanthanum.

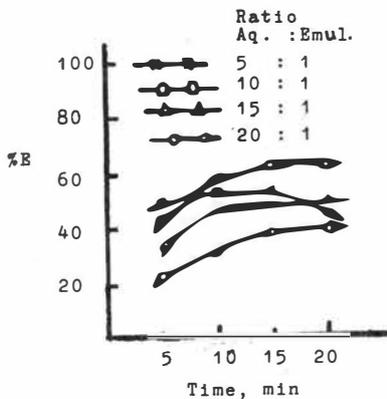


Fig. 1

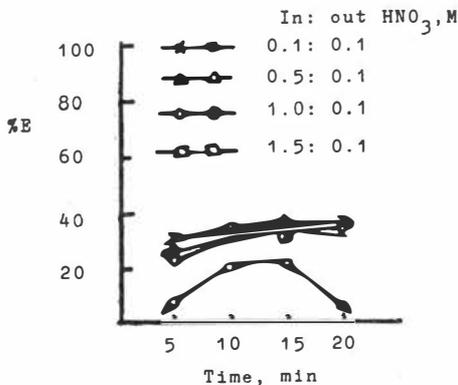


Fig. 2

Effect of Inner Phase Concentration

The effect of nitric acid concentration on the emulsion phase was studied and the obtained results are represented in Fig. 2. It is clear that by increasing nitric acid concentration into the emulsion phase as stripper, the % E increases up to 1.0M HNO_3 , followed by slight decrease when HNO_3 molarities reach 1.5 M. Such decrease, again, can be related to the diffusion of the acid to the aqueous solution with subsequent decrease in the extractive power of the membrane, HDEHP, active layer.

Effect of Outer Phase Acid Concentration

Decreasing the nitric acid molarity in the aqueous phase increased the % E of lanthanum within the first 5 min of the extraction; Fig. 3. After 15-20 min, the extraction sequence was reversed. This can be explained in terms of the diffusion of the stripping aqueous solution in the emulsion to the outer aqueous phase. Subsequently, the metal ions will be back diffused to the outer phase.

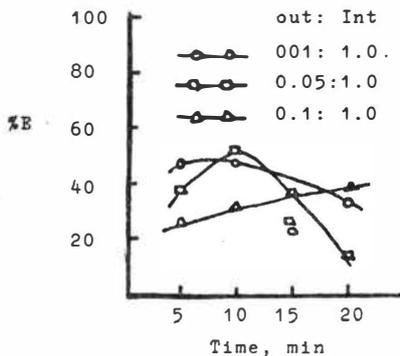


Fig. 3

Effect of Metal Ion Concentration

Increasing the metal ion concentration decreased the % E; Fig. 4. At high concentration, 0.8-1.0 g La/L, however, the % E slightly changed.

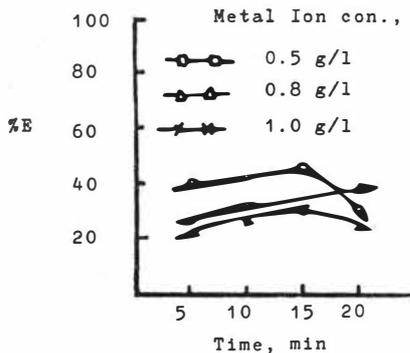


Fig. 4

Effect of Temperature

By decreasing Temperature, the lanthanum extraction percent increased; Fig. 5. This is in parallel to the solvent extraction of lanthanides by HDEHP where the extraction increases by increasing temperature [11].

Transport of Different Lanthanides

The transport of the lanthanides : La, Sm, Gd and Er and their analogue : Sc and Y were investigated; Fig. 6. The % E of the different metals took the sequence : Sc > Er > Sm > Gd > La > Y. This sequence was changed to Sc > Sm > Er > Gd > La > Y at a reaction period of 20 min. This shows the kinetic contribution in the sequence of extraction.

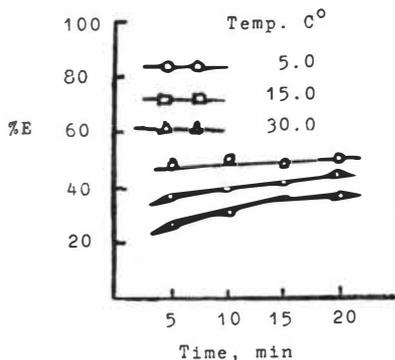


Fig. 5

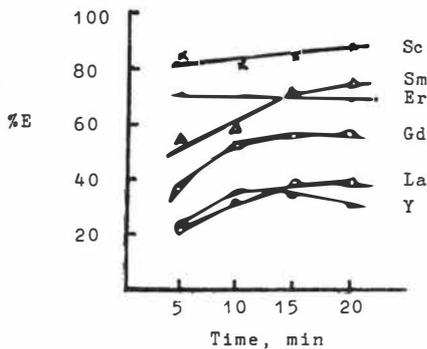


Fig. 6

Conclusion

The aforementioned investigations show that from nitric acid solution, different lanthanides can be extracted by liquid emulsion membrane using HDEHP as a carrier. The extraction is varied by different variables affecting the extraction and stripping as well as the rate of the transport process. Modeling of the permeation process is required taking into account the leakage of the metal ions to the aqueous feed phase, especially when the time of transport is relatively high.

References

1. Li N.N. // U.S. Patent 1968. Vol. 3. P. 410 and P. 794.
2. Hayworth H.C., Ho W.S., Burns W.A., Jr., Li N.N. // Sep. Sci. Technol. 1983. Vol. 18. P. 493.
3. Li N.N., Cahn R.P., Naden D., Lai R.W.M. // Hydrometallurgy. 1983. Vol. 9. P. 277.
4. Kitagawa T., Nishikawa Y., Frankenfeld J.W., Li N.N. // Environ. Sci. Technol. 1977. Vol. 11. P. 602.
5. Prötsch M., Marr R. // Proc. ISEC'83. 1983. P. 66.
6. Fuller E.J., Li N.N. // J. Membr. Sci. 1984. Vol. 18. P. 25.
7. Strozobicki J., Charewicz W. // Hydrometallurgy. 1980. Vol. 5. P. 243.
8. Jiang C., Yu J., Zhu Y. // J. Chem. Ind. Chem. Eng. (China). 1982. P. 225.
9. Zhu Y., Jiang C., Wang S., Lui Z., Yu J. // Proc. ISEC'83. 1983. P. 58.
10. Teramoto M., Sakuramoto T., Koyama T., Matsuyama H., Miyake Y. // Sep. Sci. Technol. 1986. Vol. 21. P. 229.
11. Raieh M., Zakareia N., Aly H.F. // J. Radioanal. Chem. 1979. Vol. 52. P. 285.

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1. Introduction

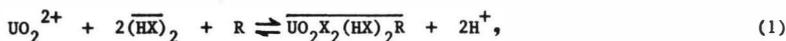
Since it was known that the wet-process phosphoric acid is containing a considerable amount of uranium originated from the phosphate ore, a few studies have been performed for the recovery of uranium from the phosphoric acid solution. (3)

In this work, the separation of uranium from the synthetic solution of phosphoric acid containing a certain amount of uranium by the surfactant liquid membrane process was carried out, and a model of mass transfer of uranium was made based on the extraction-stripping system. In most of the existing models, the rate-controlling step was considered to be complex formation and/or diffusion across the membrane, and decomplexation of stripping was assumed to be instantaneous. However, it was found that stripping is also a rate-controlling step in the recovery of uranium from the phosphoric acid. (4) The results that mass transfer rate is increased with the temperature imply the above phenomenon because the complexation of uranium by DEHPA-TOPO used in this system as a carrier is favored by low temperature, whereas stripping is favored by high temperature.

In the model presented here, therefore, both the diffusion of uranyl complex and stripping were considered as the simultaneous rate-controlling steps.

2. Uranium Transfer Mechanism

The uranium recovering mechanism by liquid surfactant membrane process is based on the reaction in both membrane and internal phases. Uranium can be effectively extracted with the synergistic combined extractant of di (2-ethyl hexyl) phosphoric acid (DEHPA) plus tri-octyl phosphoric oxide (TOPO) by forming a membrane-soluble complex as follows:



where $\text{HX} = \text{DEHPA}$, $\text{R} = \text{TOPO}$.

The uranyl complex permeates through the membrane to the internal phase boundary, where it is stripped by reduction with ferrous iron contained in the internal phosphoric acid as follows:



The introduction of fluorides into the internal solution was found to increase both the extent and the rate of uranium (VI) reduction by iron (II). (1,2)

3. Experimental

Before extraction W/O (water in oil) emulsions were prepared by adding an appropriate amount of internal solution drop by drop to the mineral oil (SN-100) containing the complexing agent (DEHPA-TOPO) and surfactant (SPAN 80) with vigorous stirring.

The emulsion was added in the external solution without uranium under the agitation of 200-300 rpm and then concentrated uranium solution was poured instantaneously. In the W/O/W system, the reduced uranium can be leaked out from the internal phase to the external phase by the breakage of emulsion. Hence, 2g/l of NaClO₃ was added in the external solution in order to oxidize the uranium (IV) to uranium (VI) which is an extractable form by the extractant.

The sizes of the emulsion drops were measured by a photographic method, and the concentrations of uranium and leaked iron in the external phase were analyzed by means of the inductively coupled plasma-optical emission spectroscopy (Plasmascan Model 710).

The change of iron concentration with time was used for determining the breakage rate of the emulsion.

4. Development of Model

4.1 Effective mass transfer coefficient

In the stripping process, the mass flux of uranium into the internal phase can be expressed by

$$J = \frac{k E C_m}{q} = Ka C_m, \quad (3)$$

where k is the mass transfer coefficient when the reducing agent is absent in the internal phase whereas E is the enhancement factor in the presence of chemical reaction, and q is the distribution coefficient (org/aq) of uranium at the interface 2. The parameter $kE/q (=Ka)$ in the above equation (3) is defined by the effective mass transfer coefficient.

4.2 Mathematical description

The uranium concentration in the external phase can be described as the following equation:

$$-V_e \frac{dC_e}{dt} = n \left\{ 4\pi R^2 \left(D_m \frac{\partial C_m}{\partial r} \right)_{r=R} \right\} - n \xi \left\{ \frac{4}{3} \pi R^3 \phi \bar{C}_i \right\} \quad (4)$$

$$C_e = C_{e0} \quad (t = 0)$$

the second term of the right-hand side in equation (4) indicates the leaking out rate of the internal uranium by the emulsion breakage.

Since n and \bar{C}_i are expressed as follows :

$$n = \frac{3V_d}{4\pi R^3}, \quad \bar{C}_i = \frac{3}{R} \cdot \int_0^R C_i r^2 dr.$$

Equation (4) can be rewritten by

$$-\left(\frac{V_e}{V_d}\right) \frac{dC_e}{dt} = \frac{3D_m}{R} \left(\frac{\partial C_m}{\partial r}\right)_{r=R} - \frac{3\xi\phi}{R^3} \int_0^R C_1 r^2 dr \quad (5)$$

On the other hand, the concentration of uranyl complex within an emulsion drop can be described as follows :

$$\frac{\partial C_m}{\partial t} = \frac{D_m}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_m}{\partial r} \right) - \frac{Ka}{1-\phi} C_m \quad (6)$$

$$C_m(0, r) = 0 \quad (t=0), \quad C_m(t, R) = mC_e \quad (r=R), \quad \frac{\partial C_m}{\partial r} = 0 \quad (r=0)$$

The uranium accumulation rate in the internal phase has the stoichiometric relationship with the consumption rate of the reducing agent, that is,

$$\frac{dC_1}{dt} = -\frac{1}{b} \frac{dC_R}{dt} = \frac{Ka}{\phi} C_m \quad (7)$$

If the equation (7) is substituted in equation (5), the following equation can be derived

$$-\frac{dC_e}{dt} = 3 \left(\frac{V_d}{V_e}\right) \left[\frac{D_m}{R} \left(\frac{\partial C_m}{\partial r}\right)_{r=R} - \frac{Ka\xi}{R^3} \int_0^R \left\{ \int_0^T C_m dt \right\} r^2 dr \right] \quad (8)$$

$$C_e = C_{e0} \quad (t = 0)$$

5. Computer Simulation and Results

Equations (6) and (8) were solved numerically by means of the Crank-Nicolson method.

The value of Ka was determined by the curve fitting with the experimental and predicted results.

The experimental condition and the corresponding values of the system parameters are summarized below :

Experimental condition	External solution : 5M H ₃ PO ₄ (500 ppm U, 2g/l NaClO ₃) Internal solution : 5M H ₃ PO ₄ (1M F ⁻ , 15g/l Fe ²⁺) W/O = 1/1 (φ = 0.5) V _d /V _e = 1/3 Viscosity of liquid paraffin = 10 cp Surfactant = 5 wt% SPAN 80 Stirring Speed = 210 rpm Temperature = 60°C
Values of Parameters	ξ = 9.1 × 10 ⁻⁴ /sec D _m = 1.5 × 10 ⁻⁶ cm ² /sec Ka = 1.4 × 10 ⁻² /sec

The predicted and experimental results are compared with the changes of V_d/V_e in Fig.1. The dotted line illustrates the rate of mass transfer without regarding the resistance of stripping. As shown in this figures, the predicted and experimental results are in fairly good agreement.

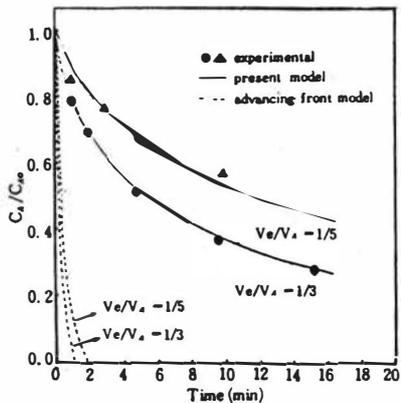


Fig. 1. Comparison of the experimental and predicted results for the extraction rate; $\phi=0.5$, $v=9.1 \times 10^{-4}$ (1/sec), $m=3.4$

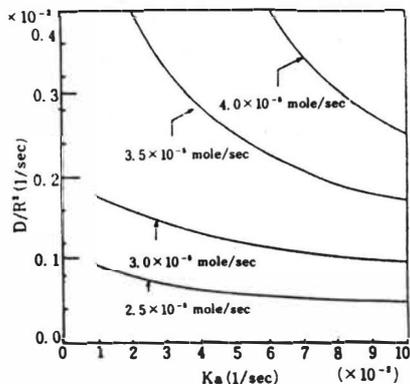


Fig. 2. Contour map of the initial mass transport rate with the parameters of D/R^2 and Ka .

Fig. 2 shows the contour map of the initial mass transfer rate with the simultaneous changes of D_m/R^2 and Ka . These parameters have the same unit, which indicates both of them are measures of the relative influence on the mass transfer rate. As shown in Fig. 2, they have nearly same extent of influence. However, the rate of mass transfer is more sensitive to the size of Ka as the value of D/R^2 is increased, which means the effect of resistance of the stripping step.

7. References

- (1) C.F. Baes // *J.R. J. Phys. Chem.* **60**, 805 (1956).
- (2) C. Plaza, M. Lamache // *Electrochimica Acta.* **26**, 45 (1981).
- (3) F. J. Hurst, D. J. Crouse, K. B. Brown // *Ind. Eng. Chem. Process Des. Develop.* **11**(1), 122 (1972).
- (4) H. C. Hayworth, W. S. Ho, W. A. Burns, Jr., and N. N. Li // *Separation Sci. Tech.* **18**(6), 494 (1983).
- (5) J. W. Frankenfeld, R. P. Cahn, N. N. Li // *Separation Sci. Tech.* **16**(4), 185 (1981).

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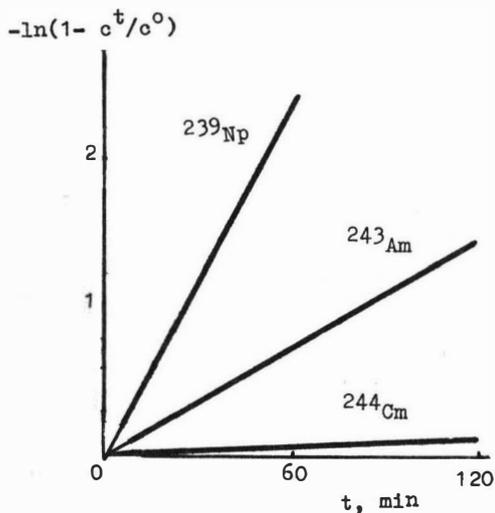
The most effective separation methods of transplutonium elements (TPE) are based on search and use of conditions for their stabilization in unusual oxidation states [1]. In particular, the methods have been developed to obtain stable compounds of Am(IV), Am(V) and Am(VI) in solutions of various inorganic complex forming agents for americium purification from other TPE by solvent extraction. The main disadvantage of solvent extraction application in this case is, as a rule, a high reduction rate of americium in organic phase. This limitation can be overcome when using extraction through thin organic membrane with subsequent reduction reextraction into receiving aqueous solution.

To optimize the process of americium membrane extraction combined with americium oxidation it is necessary to solve a system of equations describing the kinetics of redox-processes in phases and specific features of mass-transfer through membrane. An exact theoretical solution of such system of equations is quite difficult to obtain. Nevertheless published previously empirical parameters, calculated from the data on kinetics of americium oxidation in various media and kinetics of interphase transfer in two- and three-phases extraction systems, can be used for practical aims.

In the present work the kinetics of induced by amines and alkylphosphoric acids membrane transfer of various valent forms of americium from phosphate, polyphosphate and polyphosphotungstate solutions has been studied. Electrolysis of a solution and registration of its absorption spectrum were carried out simultaneously using spectroelectrochemical cell [2]. The membrane extraction cell consisted from two compartments separated by a supported liquid membrane. Circulation of donating and receiving solutions provided by peristaltic pump.

A typical kinetic curve of the process displaying Am(VI), Np(VI) and Cm(III) distribution in system of 1M HClO₄, 10⁻²M H₃PO₄ - 0,5M HDEHP, decane - 1M HClO₄, H₂O₂ is shown in Fig. The kinetics of membrane extraction of americium depends on the rate of its oxidation to the hexavalent state. This fact and low stability of the latter in organic solutions results in a comparatively slow rate of mass transfer through membrane. So the value of permeability coefficient of americium, which is proportional to the slope of linear dependence (see Fig.), is some lower, than that of neptunium, the oxidation rate of which on

these conditions is high. At the same time the permeability coefficient of americium essentially exceeds that of stable in trivalent state curium. As specific rate of membrane extraction of Am(III) and Cm(III)



Typical kinetic curves

in the discussed system are very close ≈ 37 , the higher observed membrane flux of americium as compared to that of curium(III) proves that namely organic complexes of hexavalent americium give the main contribution to its mass transfer through membrane.

Thus, membrane extraction proves to be a quite perspective method for selective isolation of transplutonium elements during the chemical processing of irradiated targets. For practical realizing of this periodical process simple but reliable and remarkably controlled equipment can be create.

References

1. Lebedev I.A., Myasoedov B.F. // Radiokhimiya. 1982.Vol.24.P.700.
2. Kulyako Yu.M., Trofimov T.I. et al.//Radiokhimiya. 1987. Vol.29. P.494.
3. Novikov A.P., Myasoedov B.F. // Solv.Extr. and Ion Exch. 1987. Vol.5. P.117.

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The liquid membrane processes are widely used for cationic metals. Only a few works have been reported involving separation of anionic species. From the practical point of view metals which form stable anions were studied [1-4]. An experimental investigation was presented on the facilitated transport of CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, CrCl_4^- , CrCl_5^{2-} , CrCl_6^{3-} , ZnCl_3^- , ZnCl_4^{2-} , ReO_4^- , TcO_4^- , V (VI). Aliquat 336 was used in all cases as a carrier. The liquid membrane idea for evaluation of anions by anion sensitive electrodes was used for several years [5].

This paper deals with emulsion membrane extraction of anions (TcO_4^- , Cl^- , SCN^-) facilitated by Aliquat 336 with various anions in inner solutions.

The surfactant SPAN 80 was product Atlas Chemical Industries; Aliquat 336 (methyl tricaprlyl ammonium chloride) was a product of General Mills, n-alkanes came from (USSR). Other chemicals used were of analytical reagent grade.

A turbine type impeller of our own construction [6] was used for preparation of the liquid membranes with volume of membrane : inner solution ratio = 1 : 1 and at mixing rate 4 000-5 000 r.p.m. for 10 min. The extraction in multiple W/O/W emulsion was performed in a glass vessel filled with 25 or 50 cm³ of outer solution stirred with a magnetic bar (50 mm x 10 mm) stirrer at 200-450 r.p.m.

The radionuclide ^{99m}Tc was used as a tracer for the metal. The concentration of SCN^- in solution was determined as a complex with Fe^{3+} by photometric method. The concentration of Cl^- in solution was determined by photometric method with the mixture of $\text{Hg}(\text{SCN})_2, \text{Fe}^{3+}$ [7].

Results of the membrane extraction of pertechnetate with Aliquat 336 as a carrier in systems where co-counter ions in a stripping solution and a feed solution was SCN^- or ClO_4^- at different concentration has been described in our paper [8]. The maximum yield in membrane extraction of TcO_4^- were calculated from extraction data at the condition similar to extraction of pertechnetate in a boundary feed-membrane; membrane-stripping solution. The situation is change for the system in which the membrane extraction of pertechnetate is performed with competition of NO_3^- in outer solution. In fig.1 results of emulsion membrane extraction of pertechnetate from 0.1 M HNO_3 in outer (feed) solution and 1 M NaCl, 1 M NaNO_3 , 1 M NaClO_4 , 1M KSCN in inner solution with membrane 0.5 % Aliquat 336, 3 % SPAN 80 in n-alkane are summarized. The extractibility of pertechnetate increases in order from $\text{Cl}^- < \text{NO}_3^- < \text{ClO}_4^- < \text{SCN}^-$. The comparison with solvent extraction shows no advantage of membrane extraction from the point of the ions preconcentration. It is evident that in the system where anion is with low extractibility in the stripping solution, the membrane extraction appear to be only an extraction without any effect of the inner phase. The maximum preconcentration efficiency is reached for SCN^- and ClO_4^- anions in inner solutions.

The minimum on the curve can be seen in the case of SCN^- and ClO_4^- stripping solutions. It was caused not by breaking of the emulsion but mutual transport of ions from one phase to another one. The kinetic nature of this phenomenon can be presumed.

According to Gindins' results [9], the extractability of anions with quaternary ammonium is in order $\text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^-$ and can be correlated with $\Delta G^\circ_{\text{hydr}}$ of anions. The position of SCN^- and TcO_4^- in this series is very close to perchlorate.

In fig.2 the results of membrane extraction of SCN^- (0.01 and 0.001 M) are shown. Preconcentration was good namely in the solution with lower concentration of SCN^- .

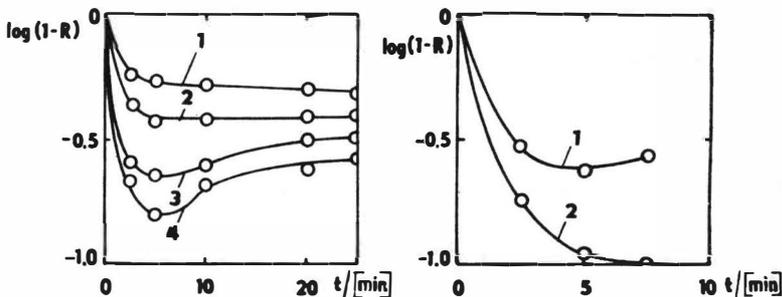


Fig.1. Membrane extraction of perchlorate: Membrane 0.5% Aliquat 336 in n-alkane, 3% Span 80; outer solution $^{99\text{m}}\text{TcO}_4^-$ in 0.1 M HNO_3 ($V_{\text{II}}:V_{\text{I}}=0.1$, $V_{\text{M}}:V_{\text{II}}=1$)

Fig.2. Membrane extraction of rhodanide: membrane 0.5% Aliquat 336 in form ClO_4^- , 3% SPAN 80 in n-alkane; inner solution 0.1 NaClO_4 ($V_{\text{II}}:V_{\text{I}}=0.1$, $V_{\text{M}}:V_{\text{II}}=1$); outer solution 1-0.01 M NaSCN , 2-0.001 M NaSCN

In fig.3 the emulsion membrane extraction of chloride is presented. Membrane consisted of Aliquat 336 in the form of ClO_4^- with 3% SPAN 80 in n-alkane. 1 M NaClO_4 was used as inner solution. The recovery of chloride membrane extraction increases with decreasing of Cl^- concentration. This dependence is in accordance with concentration difference between outer and inner solutions. In the case of Donnan equilibrium the recovery should be higher. These results can be interpreted by a strong ClO_4^- in outer solution influence on distribution ratio D_{Cl^-} in the boundary of outer solution and membrane. No transport of Cl^- from outer to inner solution through liquid membrane (0.5% Aliquat 336; 3% SPAN 80) in the case of 1 M NaNO_3 inner solution was observed.

Fig 4,5 show the emulsion membrane extraction of chloride from solution with various concentration of NaCl with the membrane consisting of 0.5% Aliquat 336; 1.5% LIX 64N; 3% SPAN 80 and inner solution 0.2 M NaNO_3 and 0.2 M CH_3COONa respectively. The presence of LIX 64N as a additive has positive influence on the transport of Cl^- . Acetate anion with hydration energy higher than Cl^- and lower extraction constant [9] is suitable to secure gradient and the exchange reaction. The preconcentration of chloride is in accordance with

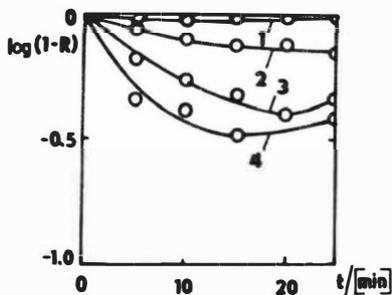


Fig.3. Membrane extraction of chloride :Membrane 0.5% Aliquat 336 in form ClO_4^- 3% SPAN 80 in n- alkane;inner solution 1 M NaClO_4 ($V_{II}:V_I=0.1$, $V_M:V_{II}=1$) outer solution:1-0.1 M NaCl,2-0.01 M NaCl,3-0.001 M NaCl,4-0.0001 M NaCl

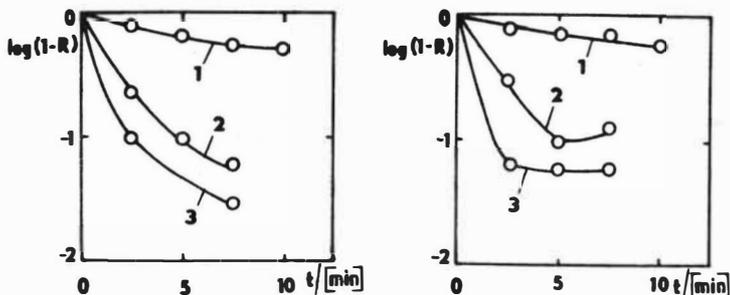


Fig.4. Membrane extraction of chloride: Membrane 0.5% Aliquat 336,3% SPAN 80 1.5% LIX 64N in n-alkane;Inner solution 0.2 M NaNO_3 ($V_{II}:V_I=0.1$ $V_M:V_{II}=1$);outer solution 1-0.01 M NaCl,2-0.001 M NaCl,3-0.0001 M NaCl

Fig.5. Membrane extraction of chloride :Membrane 0.5% Aliquat336 , 1.5% LIX 64N, 3% SPAN 80 in n-alkane;inner solution 0.2 M CH_3COONa ($V_{II}:V_I=0.1$ $V_M:V_{II}=1$);outer solution 1-0.01 M NaCl,2-0.001 M NaCl,3-0.0001 M NaCl

Donnan equilibrium.The explanation of LIX 64N influence on the transport of chloride is under the study.

It has been demonstrated,that the liquid emulsion membrane extraction can be used for preconcentration of anions.LIX 64N additive enables to used a strippand with high hydratation energy.Future work is needed to investigate the role of LIX 64N on anion transport across the membrane.

References

1. E.J.Fuller,N.N.Li//J.Membr.Sci. **18**(1984). 251.
2. A.G.Bouvier,R.J.Mard// th Intern.Congress CHISA,Prague, 1981.
3. J.Strzelbicki,W.A.Charewicz,A.Mackiewicz//Separ.Sci.Technol.**12**(1984)321.
4. O.Loicono,E.Drioli,R.Molinari//J.Membr.Sci. **28**(1986),123.
5. Ru Qin Yu//Ion-Selective Electrode Rev.**8**(1986),153.
6. A.Svec,P.Rajec//Chem.listy.**77**(1983)206.
7. T.M.Florence,Y.J.Farrar//Analyt.Chim.Acta,**54**(1971)373.
8. P.Rajec,F.Macosek,J.Belán//J.Radioanal.Nucl.Chem. **1**(1986)71.
9. L.M.Gindin,Extraktzionnye procesy i ikh primenenie,Moskva:Nauka,1984.

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Separation of various solutes by supported liquid membranes (SLM) is very attractive because of their high selectivity and permeability. However, SLM is not always stable because the membrane solution absorbed in the pores of the porous polymer support membrane dissolves in the feed and strip phases. In this paper, we present a new type of liquid membrane, that is, a flowing liquid membrane (FLM) in which the liquid membrane solution containing a carrier flows in a thin channel. FLM was found to have both high stability and high permeability compared with the conventional SLM.

We carried out the separation of benzene from cyclohexane by FLM. Furthermore, a spiral-type flowing liquid membrane module was developed, and it was found that they could successfully separate and concentrate heavy metal ions such as Co(II), Ni(II), Cr(VI) and Zn(II).

Separation of Benzene from Cyclohexane The experimental apparatus is shown in Fig.1. The aqueous liquid membrane solution containing silver nitrate as a carrier flows in a thin channel between the feed phase (benzene, cyclohexane or their mixture) and the strip phase (dodecane), and these phases are separated by microporous PTFE membranes whose pores are filled with the organic solution. Because the solubility of benzene in the aqueous membrane phase is low, and also because the diffusional resistance through the pore is much higher than that through the flowing aqueous membrane phase, the overall resistance in the present membrane system is much lower than that for the case where hydrophilic porous membranes are used. Figure 2 shows the effect of the flow rate of membrane phase, v_M on the mass transfer coefficient of benzene in the membrane phase, k_{MB} obtained from the physical permeation experiments using water as a membrane solution. k_{MB} is proportional to v_M to the power of about unity. When v_M is high, the mass transfer coefficient is about 20 times that of SLM. Therefore, FLM has excellent mass transfer characteristics. Figure 3 shows the effect of $AgNO_3$ concentration on the permeation rate of benzene and cyclohexane when SLM (0.12mm, cellulose filter paper) was used. Since Ag^+ reacts with benzene reversibly, but does not react with cyclohexane, the permeation of benzene is selectively facilitated. As the concentration of $AgNO_3$ increases, the permeation rate of benzene J_B increases

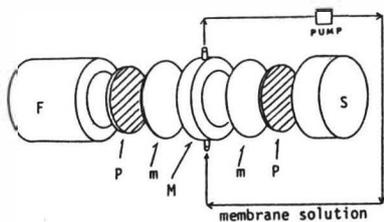


Fig.1. Schematic diagram of FLM

F: feed phase, S: strip phase, m: support membrane
 M: membrane solution phase, P: spacer

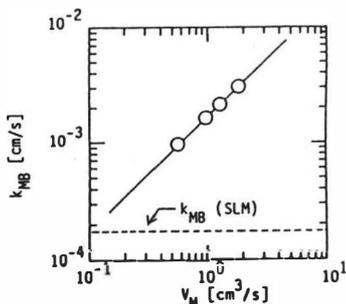


Fig.2. Relation between k_{MB} and v_M

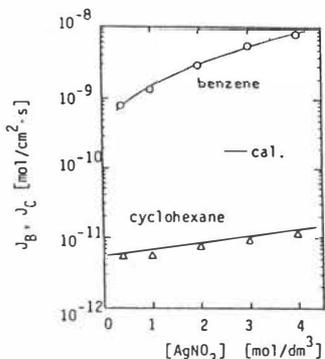


Fig. 3. Effect of $[AgNO_3]$ on J_B and J_C

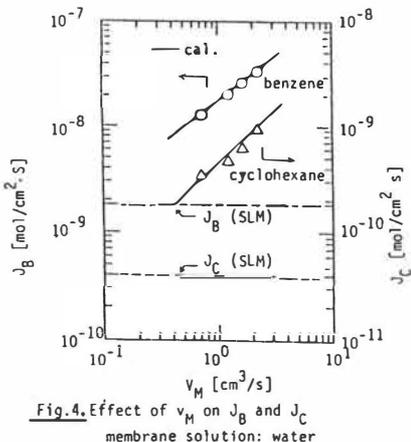


Fig. 4. Effect of v_M on J_B and J_C
membrane solution: water

because the facilitation factor increases. The physical permeation rate of cyclohexane J_C also slightly increases due to the increase in its solubility in the membrane phase under the condition that $[AgNO_3] + [NaNO_3] = 4 \text{ mol/dm}^3$. The flux ratio J_B/J_C reaches about 600 when $[AgNO_3] = 4 \text{ mol/dm}^3$. The effect of v_M on J_B and J_C obtained by FLM in which water was used as a membrane phase is shown in Fig. 4. In this case, the diffusional resistance in the membrane solution phase is dominant, and so both J_B and J_C are about 20 times those of SLM. Figure 5 shows the relation between v_M and the permeation rates when $[AgNO_3]$ is 4 mol/dm^3 . The dependence of J_B on v_M is less than first order because the contribution of the resistance in the organic phase appears as J_B increases. So the selectivity decreases with increasing v_M . However, J_B/J_C is still as high as about

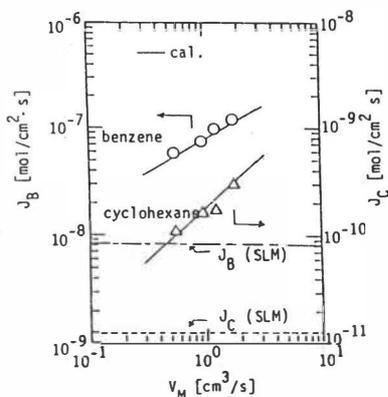


Fig. 5. Effect of v_M on J_B and J_C
membrane solution: 4 [M] $AgNO_3$

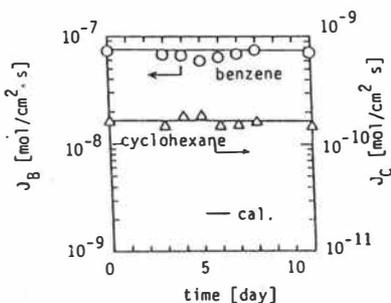


Fig. 6. Time-course of J_B and J_C

400 even at high v_M . Both J_B and J_C are also much larger than those through SLM. As shown in Fig. 6, the fluxes are almost kept constant for more than 10 days, suggesting that FLM has excellent stability.

The permeation rates were analyzed on the basis of the mass transfer with chemical reaction [1]. The calculated results shown by the solid lines in Figs. 3-6 agree well with the experimental results.

Removal of heavy metal ions by spiral-type flowing liquid membrane module

The schematic diagram of the module, which is the modification of the spiral-type supported liquid membrane module [2], is shown in Fig.7. The support films and mesh spacers were spirally wound around the tubes through which feed, strip and membrane solutions were supplied. Two modules, module A and B were produced. Module A (support: microporous polypropylene, total length of support: 4.8m, diameter of the module: 9cm, height: 19cm) was used for the removal of Co(II) and Ni(II), and module B (support: microporous PTFE, total length of support: 8m, diameter : 12cm, height: 19cm) for Cr(VI) and Zn(II).

Figure 8 shows the effect of the feed flow rate, v_F on $[Co]_{Fout}/[Co]_{Fin}$ when PC-88[®] dissolved in dodecane was used as the membrane solution. Although the experiments were carried out in a once-through mode for the feed solution, more than 99% of Co(II) was successfully removed when $[Co]_{Fin}$ was low. The cause of such high recovery is that at low cobalt concentration, diffusion of cobalt in the feed phase limits the permeation rate. Another important cause is that the flow pattern of the feed phase is approximately plug flow. Figure 9 shows the effect of the feed concentrations on $[Co]_{Fout}/[Co]_{Fin}$ and $[Ni]_{Fout}/[Ni]_{Fin}$ in the simultaneous permeation of Co(II) and Ni(II). Since the distribution ratio of cobalt is much larger than that of nickel, cobalt is selectively removed when the feed metal concentration, $[M]_{Fin}$ is high and the diffusional resistance in the membrane solution phase is dominant. On the other hand, when $[M]_{Fin}$ is low, the permeations of both cobalt and nickel are almost limited by the diffusion in the feed phase, which results in low selectivity. As shown in Fig.10, as v_M increases, k_{MB} reaches the constant value regardless of v_M because the rate is limited by the resistance through the pores of the two support membranes. As v_M decreases, the resistance in the stagnant film of the membrane solution phase becomes large and k_M decreases. In this region, the diffusional resistance in the membrane solution phase can be controlled by adjusting v_M . This is one of the advantages of the flowing liquid membrane. Figure 11 shows the effect of v_M on $[M]_{Fout}/[M]_{Fin}$ under the condition corresponding to the data showing lowest selectivity in Fig.9. When $v_M=0$, the resistance in the membrane solution phase becomes large, which brings about the decrease in the permeation rates of metal ions. However, the degree of the decrease of

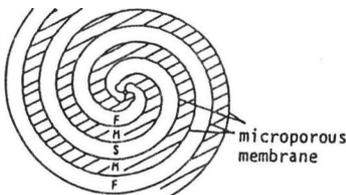


Fig.7. Spiral-type flowing liquid membrane module. F: feed solution, M: flowing liquid membrane, S: strip solution

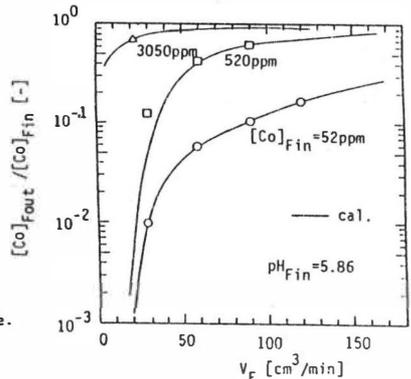


Fig.8. Effect of v_F on $[Co]_{Fout}/[Co]_{Fin}$

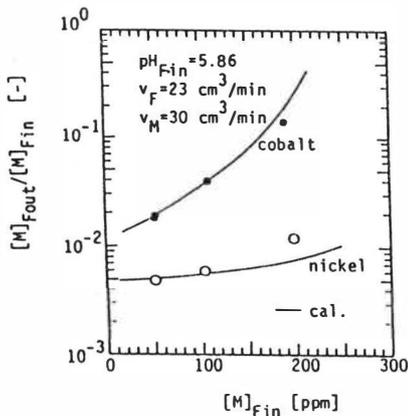


Fig. 9. Relation between $[M]_{Fout}/[M]_{Fin}$ and $[M]_{Fin}$

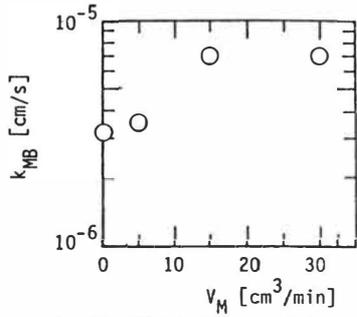


Fig. 10. Effect of v_M on k_{MB}

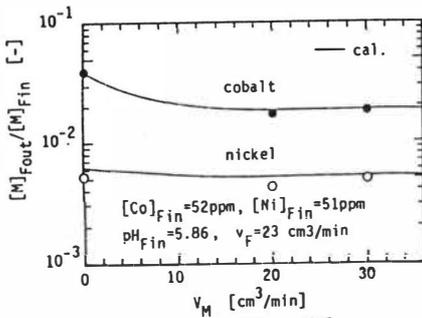


Fig. 11. Effect of v_M on $[M]_{Fout}/[M]_{Fin}$

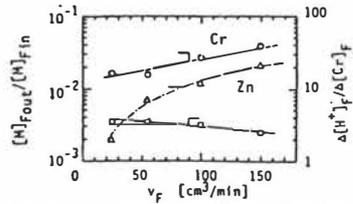


Fig. 12. Effect of v_F in the recovery of Cr(VI) and Zn(II). Recovery of Cr; membrane phase: tri-n-octylamine 30%, 2-ethylhexyl alcohol 5%, Shellsol AB 65%, feed solution: $[Cr]_{Fin}=50ppm$, $pH_{Fin}=2.5$, strip solution: 0.1MNaOH. Recovery of Zn; membrane phase: D2EHPA 50%, dodecane 50%, feed solution: $[Zn]_{Fin}=50ppm$, $pH_{Fin}=3.0$, strip solution: ZnH_2SO_4

nickel is larger than that of cobalt because nickel has much lower distribution ratio than cobalt. So the selectivity improves with increasing v_M . The solid lines in Figs. 8, 9 and 11 are the calculated results based on the design equations of the module [2, 3].

As shown in Fig. 12, Cr(VI) (carrier: TOA) and Zn(II) (carrier: D2EHPA) were also successfully removed by modul B, and the ratio of $\Delta[H^+]_F (= [H^+]_{Fin} - [H^+]_{Fout})$ to $\Delta[Cr]_F (= [Cr]_{Fin} - [Cr]_{Fout})$ is about theoretical value of 2.

References

1. Teramoto M., Matsuyama H., Yamashiro T., Katayama Y. // J. Chem. Eng. Japan, 1986. Vol. 19. P. 419.
2. Teramoto M., Matsuyama H., Takaya H., Asano S. // Sep. Sci. Technol. 1987 in press; Proc. ISEC'86 1986. Vol. 1. P. 986.
3. Matsuyama H., Katayama Y., Kojima A., Washijima I., Miyake Y., Teramoto M // J. Chem. Eng. Japan, 1987. Vol. 20: P. 213.

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Pertraction (permeation) through liquid membranes is a separation process which has been introduced from laboratories into pilot plants or even to industry. This is especially the case of liquid emulsion-type membranes. Various types of mechanisms of separation effect and mass transfer through liquid membranes of different kinds have been discussed in works [1-3].

In Fig.1 is depicted the three phase system in pertraction into emulsions. The fact itself that a double dispersion is under discussion indicates the complexity of the system. The emulsion which is in an intensive contact with the feed must be sufficiently stable what necessitates the utilization of suitable surfactants. The stability of these emulsions in the pertraction is ensured by a relatively rigid adsorption film on phase interfaces (see Fig.1). It was shown that the resistance of this film against mass transfer is significant [3-6]. Its properties influence both the stability of the emulsion during pertraction [7] and the breaking of the emulsion in an electric field [3, 4,7]. The adsorption film is in fact the fourth phase of the pertraction system. Its properties significantly influence the course of pertraction. Mass transfer in this four-phase system can be further influenced by the kinetics of chemical reactions on the phase interfaces and/or in the volume of the phases.

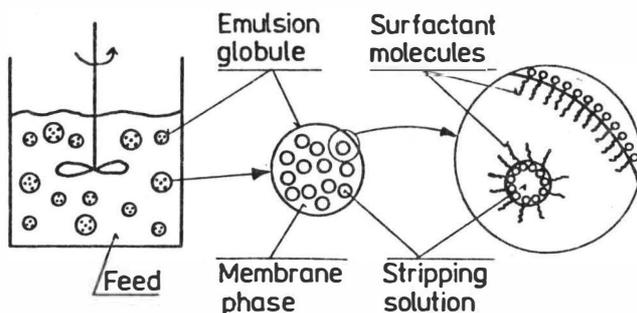


Fig.1. Scheme of the pertraction into emulsion

The characterization of such a complex system as well as the modeling of mass transfer in it are very difficult. The obtaining of all necessary data is very laborious and beyond the power of individuals or small teams. At present, accessible results for various systems have been obtained under insufficiently defined conditions and are far from being complete. This fact does not allow for instance to combine results of various authors and to use them in testing pertraction models.

Hence, it seems to be useful to take steps to standardize the test systems as well as the methods for studying pertraction. Standardization together with the obtaining of reliable data would help in:

- a. the study of the mechanism of mass transfer in pertraction and its modelling
- b. the comparison of equipments and their scale-up
- c. the comparison of various surfactants
- d. the comparison with other separation processes.

Experiences gained by standardization of test systems for solvent extraction [8-10] could be utilized.

Nowadays in separation of aqueous solutions there seems to be a need to use test systems especially for two types of pertraction. In the study of pertraction without chemical reaction in the membrane especially ammonia, phenol or amines (e.g. aniline) are employed as permeants. From the viewpoint of application, the pertraction of ammonia into emulsion of phosphoric acid is prospective. This system would be a suitable test system.

Pertraction with chemical reaction in the membrane, most often with coupled counter-transport, has been used in separation of metals. Among the preferably studied metals belong copper, zinc, uranium and cobalt. Pertraction of zinc has been already commercialized [1]. Zinc and bis-(2-ethylhexyl)phosphoric acid as a carrier are more serious candidates for the test system in the solvent extraction [9,10]. Therefore, it will be suitable to consider this system also for the pertraction.

Hydrocarbon solutions of the emulsifier and if need be a carrier (ligand) and an additive are used as the membrane phase. Various hydrocarbons and/or their mixtures (e.g. isoparaffinic or kerosene fractions) are employed. It is suitable to use the dodecane fraction of n-alkanes which is better defined and easily accessible. This fraction together with n-dodecane for the basic measurements seems to be a suitable candidate for test systems of both types of pertraction.

The problem is the standardization of the emulsifying agent. Hitherto, practically only technical products were utilized. These are insufficiently defined. Most often sorbitan monooleate (SPAN 80) and

polyamine of succinimine type (e.g. ECA 4360) were used. The former is unsuitable from the point of view of industrial application. The properties of polyamine ECA 4360 from various batches significantly differ [4,7]. In the first stage, until more suitable surfactants are at disposal it would be a solution to organize the distribution of samples from one deposited gretaer sample, probably ECA 4360. In pertraction but also in the breaking of the emulsion in an electric field the properties of the emulsion from freshly prepared membrane phase significantly differ from the steady properties after several regenerations of the membrane phase, see Fig.2 and 3.

Recently the interest in separation of hydrocarbon mixtures by pertraction through aqueous liquid membranes has increased. Therefore, it is necessary to pay attention to a suitable test system also in this area.

For the characterization of the pertraction system one needs to know not only the properties of the bulk phases, their volume ratios and size distribution of drops in the emulsion as well as size distribution of globules of the emulsion but also the properties of the adsorption films. The properties of the emulsion, e.g. its stability depend also on the age of the emulsion what is related to relatively slow adsorption kinetics of the surfactants.

The breaking of the emulsion and its swelling during pertraction affect the course of pertraction. Less attention is paid to the change of pH in the feed solution which influences the concentration of permeant and/or its distribution coefficient. The latter often depends on the surfactant type and its concentration [4,11]. The surfactant can affect also the kinetics of the chemical reaction on the phase interfaces.

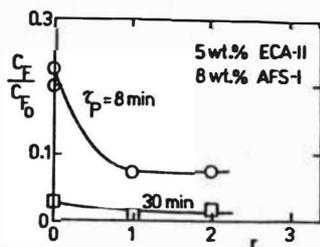


Fig.2. Influence of the number of regenerations of the membrane phase on the batch pertraction of ammonia into the emulsion of phosphoric acid. Conditions as in paper [7]

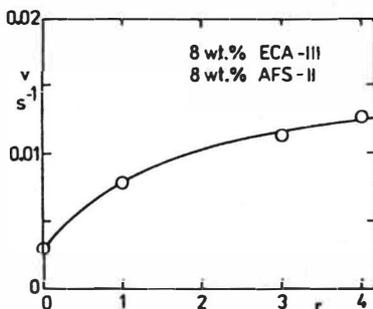


Fig. 3. Influence of the number of regenerations of the membrane phase on the normalized initial rate of the batch deemulsification in an electric field 20 kV, 50 Hz. Conditions as in paper [7]

Both the geometry of the pertractor and the frequency of the mixer significantly influence the pertraction kinetics. Similar conditions are in the preparation of the emulsion. The standardization of these equipments would be also profitable especially with regard to obtaining data for their scale-up.

This paper cannot involve all problems in their complexity. The main aim is to evoke interest in this topic and inspire a discussion.

REFERENCES

1. J.Draxler and R.Marr// Chem.Eng.Process. 20(1986), 319.
2. R.Marr, A.Kopp.//Chem.Eng.Tech. 52(1980), 399.
3. Š.Schlosser, E.Kossaczky//J.Radioanal.Nuclear Chem. Articles. 101(1986), 115.
4. Š.Schlosser, E.Kossaczky//Preprints ISEC'86. Vol.III,P.935. München, Sept.1986.
5. Š.Schlosser, E.Kossaczky. New view on mechanism of mass transfer in pertraction into emulsions /in Slovak // Preprints 14th Conf. OSCHI. P.121-8. Jasná, May 1987.
6. Š.Schlosser, E.Kossaczky, V.Hayden. Interfacial phenomena in pertraction through emulsion-type liquid membranes, Paper N D4.2, 10 p.// 9th Int.Congres CHISA'87. Praha, Aug.1987; submitted for publication in J.Membr.Sci.

7. Š.Schlosser, E.Kossaczký. Liquid membranes stabilized by polymeric surfactants // Synthetic Polymeric Membranes. p.571-80. W.de Gruyter Co., Berlin, 1987.
8. T.Míšek, R.Berger, J.Schröter /eds. //Standard test systems for liquid extraction. 2nd ed. EFCE Publ.series N 46. Rugby, 1985.
9. M.J.Slater. The possible use of D2EHPA/metal as a liquid-liquid extraction test system, paper presented at the EFCE Working Party meeting in Prague, April 1987.
10. H.J.Bart, M.Koncar, R.Marr. Problem of test systems in reactive liquid-liquid extraction. Paper N D6.2 //9th Int.Congress CHISA'87. Praha, Aug.1987.
11. R.S.Baird, A.L.Bunge, R.D.Noble// Am.Chem.Eng.J., 33(1987). 43.

**METAL
EXTRACTION**

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Only on the 60-s due to development and introduction into practice of highly efficient extraction-separation methods it has become possible to obtain large quantities of individual Rare Earth Elements(REE) with unique properties that provides their usage in most modern fields of science and technology.

On the early 50-s there appeared real foundations to develop industrial extraction technology of REE separation. This happened after publication of pioneer papers by Warf, Peppard, Wiver et al., which presented high extractive efficiency of Tributylphosphate (TBP), the forefather of a large class of organophosphoric extractants.

In the USSR systematic study of REE separation began in 1951 at the Institute of Physical Chemistry of the USSR Ac.of Sci. Primary investigations were aimed at developing the methods of separation of radioactive REE; since the middle 50-s this transformed into separation of natural REE. These years were marked by investigations of the basic regularities of REE extraction by TBP in acid and neutral nitrate systems, as well as designing multi-stage extractors; various methods of extraction processes were worked out and their mathematical description was presented. All the REE of the Ce subgroup were obtained in the individual form. Some of the above results were published in the period 1959-1965 [7-6].

In the early 60-s the Institute of Physical Chemistry in cooperation with some other institutions worked out and introduced an industrial technology of REE extraction. This technology is being continuously developed since then.

At present extraction methods provide industrial production of all the individual REE up to 99.999 and more per cent purity and are the dominating technological processes in the USSR and abroad.

Successful realization of REE extraction would not have been possible unless the complex approach have been applied, viz. investigation of the extraction system and extraction methods, designing of multi-stage extractors, development of definite technological processes of REE extraction from different types of raw material.

The main difficulty in REE extraction technology is associated with extraction of elements in their three-valency state. A possibility to transfer three-valent lanthanides into two- and four-valency state would provide ideal conditions for their selective extraction. Unfortunately, only two elements, i.e. Ce(IV) and Eu(II), are comparatively stable in water solutions in oxidized and reduced states without stabilization.

Various position of Y within the lanthanides row in various extraction systems also presents a possibility of its selective isolation. Under certain conditions Ce(IV) can be extracted by nearly all the applied extractants. But for practical purposes one can confine himself to simple extractants, such as TBP and D2EHP [7-9].

Industrial extraction purification of Eu(II) by D2EHP after its reduction by amalgamated Zn was performed during the processing of basthnezite in the USA [10].

There exist two ways to solve the problem of Y extraction from the lanthanides group. The first one is based on successive isolation of this element in two extraction systems with different Y position in the lanthanide extraction row (Fig.1-3). This method is preferable in complex processing of raw material.

The other method consists in selective isolation of Y in case its position in the extraction row comes out of the lanthanide group; this method is based on simultaneous working of minimum two reagents in one or in different phases. Selective extraction methods are most valuable for obtaining high-purity Y out of its concentrates. To realize the first method it is necessary to have in one phase a mixture of two reagents with reverse dependence between the change of lanthanide distribution ratio value and their atomic number under condition of simultaneous shift of Y location towards heavy lanthanides for one reagent and towards light lanthanides for the other. It is evidently seen in case of extraction by a mixture of quarternary ammonium bases and carboxylic acids in the nitrate medium (Fig.4,5) [11].

For the second case it is necessary to have similar dependences between distribution ratio changes and the lanthanide atomic number under condition of simultaneous shift of Y disposal within the extraction row and the row of complex formation. For example, the extraction systems: TBP-NH₄NCS-LnCl₃ [12], SO-NH₄NCS-LnCl₃ [13]; phosphonate-LnBr₃-LiBr [14]; HD2EHP-EDTA-LnCl₃ [15] (Fig.6).

The well-known "Talspick" process of separation actinides and lanthanides is based on this principle.

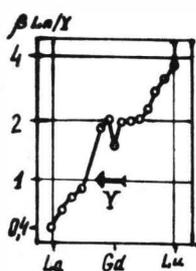


Fig. 1. TBP-NH₄NCS-LnCl₃

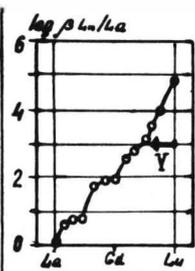


Fig. 2. TODD-NH₄NCS

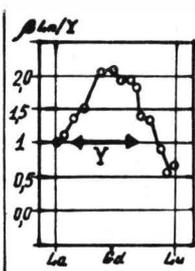


Fig. 3. TBP-ISOPr₄SnO₃-Ln(NO₃)₃

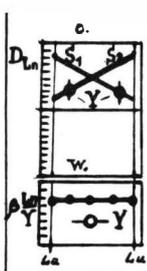


Fig. 4

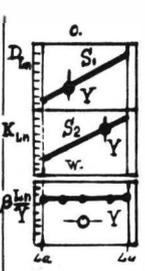


Fig. 5

If one disregards the general technical requirements for extractants, which should be obligatory observed, then the choice of corresponding extraction system for REE separation in their main three-valency state must be determined by three technological factors, namely the value of the neighbouring elements separation factor (in producing pure substances) should not be less than 1.5 (since the necessary number of separation stages sharply increases); The extractant loading should not be less than 25-30 g/l but it is better to have 100-150 g/l (Ln_2O_3). Unfortunately, we don't have a universal extractant equally effective for the whole REE group, thus different extractants and extraction systems are used in separation processes. Practically all technological problems of separation can be solved by one and the same extractant, for example TBP, if a series of various systems is used, viz. 1. TBP- $\text{Ln}(\text{NO}_3)_3$; 2. TBP- $\text{Ln}(\text{NO}_3)_3$ - $\text{M}(\text{NO}_3)_x$; 3. TBP- $\text{Ln}(\text{NO}_3)_3$ - HNO_3 ; 4. TBP- $\text{Ln}(\text{NO}_3)_3$ -EDTA; 5. TBP- LnCl_3 - NH_4NCS . But for practice, it is much better to have two or even four reagents TBP, HD2EHP, quaternary ammonium bases, and carboxylic acids, which present four different classes of agents. Some extractants require corresponding deluents and modifiers to be used to ensure higher adaptability and stability to extraction systems.

Every extractant has its peculiarities, its chemistry, and its optimal applicability when it will demonstrate its highest selectivity. We also should take into account the peculiarities of chemical behavior of lanthanides in their long row of 15 elements. In standard cases more effective extractants will demonstrate higher selectivity since they easily enter the inner lanthanide sphere destroying the hydratic sphere and forming corresponding solvates or complexes (for example, helato-forming reagents). (Fig.7-9). Increasing of lanthanide salt concentration and introducing salting out agents which dehydrate lanthanide ions with natural increasing of difference between their activity coefficient, as well as total saturation of the organic phase and, correspondingly, with increasing of selectivity (Fig.10-13). For low effective extractants the whole selectivity effect is reached due to affecting the water phase. The selectivity of extractants which have two reac-

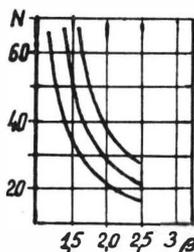


Fig. 6

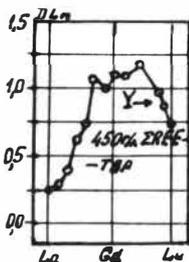


Fig. 7

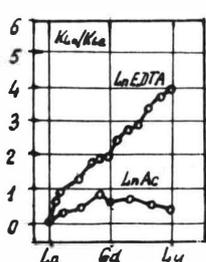


Fig. 8

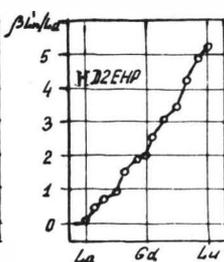


Fig. 9

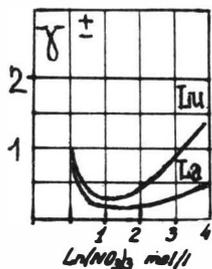


Fig. 10

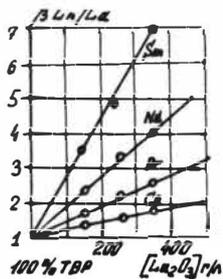


Fig. 11

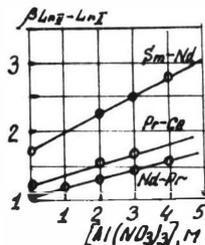


Fig. 12

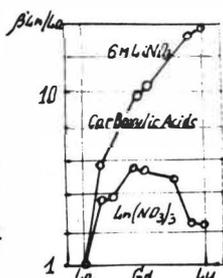


Fig. 13

Fig. 1-13. Main regularities of the extraction of rare earth elements (lanthanide and actinide) groups forming different types of extraction complexes, is controlled by more complicated factors. For example, organophosphoric acids (see separate communication). Application of mixed systems (extractant-water soluted complexone) in separation processes also manifests its peculiarities. Such systems will be examined in detail in a separate report. The main condition in reaching maximum selectivity of extraction systems with complexones is to use either low-selectivity extractants or extractants with reverse relation of changing of distribution coefficient values within the lanthanide row as compared with the complexone. At present we have rather large set of extractant systems to solve the problem of REE separation. Though the task of obtaining of more effective and selective extractants still remains urgent for specific problems in the technology of REE separation.

The process of REE separation can be performed only as a multi-stage process with application of corresponding multi-stage extractants. The experience shows that the most reliable type of the extractor is a mixer-settler [16]. Extraction apparatus of a mixer-settler type (regardless of the method of mixing the phases, transportation among the stages and settling regime) should meet the following requirements: all the stages must be hydraulically independent, each stage should have a regulated overflow of the heavy phase; the mixer chamber should be isolated from the settler chamber and should have a naturally forced emulsion overflow. Taking into account the positive role of high sluggishness of REE separation process from the point of view of analytical monitoring, control and stability of the working regime of the extraction cascade, we consider a box mixer-settler with large containing volume the most suitable construction. The latter condition is extremely necessary when applying the method of total reflux and other non-stationary methods in which accumulation and extraction of pure components is performed just from the extractor's cells. For certain operations centrifugal extraction apparatus, also of a mixer-settler type, can be applied very effectively.

Countercurrent
Extraction process

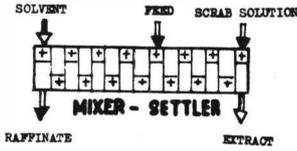


Fig. 14

Total Reflux

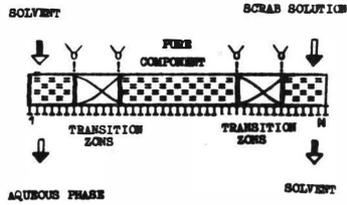


Fig. 15

Fraction Countercurrent
Process of Separation

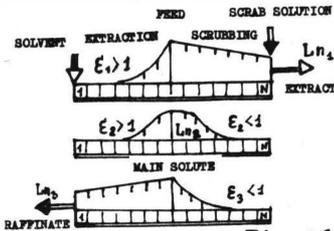


Fig. 16

Total Reflux with
Addition Mixers

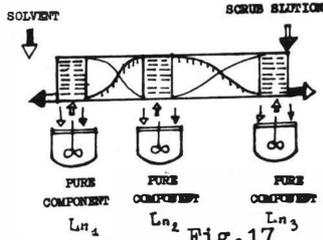


Fig. 17

Extractor with
Addition Mixer

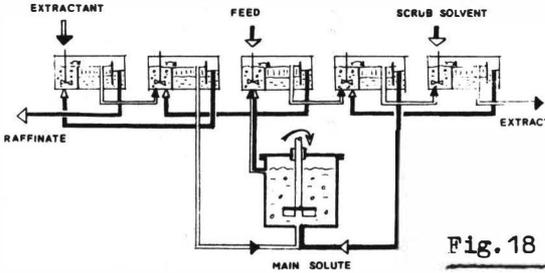


Fig. 18

Semicontercurrent
Extraction Process

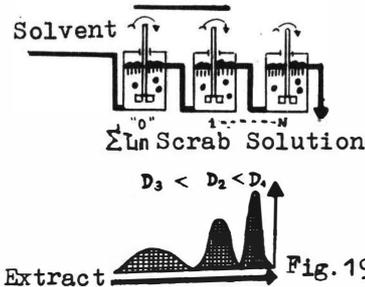


Fig. 19

Fig. 14-19. Typical extraction methods of separation of rare earth elements

The main method of REE separation is a continuous countercurrent process (Fig.14). But in many cases preference should be given to non-stationary separation processes such as the process of total reflux (Fig.15,16), fractional countercurrent with various collectors for purified components either in the form of measuring tanks at the cascades outflow or special devices in the chain of extraction stages [17] (Fig.17,18). In certain cases it is useful to apply the method of semi-countercurrent separation (Fig.19).

Table 1. Values of separation coefficients of rare earth elements for typical extraction systems [18-24]

Ln _I /Ln _{II}	TBP - Ln(NO ₃) ₃		Carboxylic acids			
	450 g/l Ln ₂ O ₃	150 g/l Ln ₂ O ₃ 5N Al(NO ₃) ₃	Versatic Ln(NO ₃) ₃	Secondary branched Ln(NO ₃) ₃	LnCl ₃	
Ce-La	1.9-2.0	2.5-3.2	2.9	2.7	2.6	
Pr-Ce	1.6-1.7	1.8-2.0	1.5	1.9	2.0	
Nd-Pr	1.4-1.5	1.8-2.0	1.3	1.9	2.0	
Sm-Nd	1.9-2.2	2.8-3.0	2.2	2.7	2.4	
	TBP -HNO ₃			HD2EHP	Quarternary ammonium bases	
	8M HNO ₃	11M HNO ₃	11.5M HNO ₃	Ln(NO ₃) ₃	Ln(NO ₃) ₃	
	Sm-Nd	2.100	2.90	4.20	5.2-5.0	-
	Su-Sm	1.30	1.45	1.85	2.0-1.9	1.5-1.9
	Bd-Su	1.18	1.30	1.70	1.8-1.7	1.4-1.8
Tb-Gd	1.30	1.50	1.65	4.6-2.6	-	
	TBP-EDTA-NH ₄ NO ₃		D2EHP		TOPO, T1MHPO	
	Ln(NO ₃) ₃	Ln(NO ₃) ₃	LnCl ₃	NH ₄ NCS, LnCl ₃		
	Gd-Eu	1.4	1.8-1.7	1.5	1.8	
	Tb-Gd	2.3-1.9	4.6-4.1	6.8	2.8	
	Dy-Tb	1.9-1.6	2.8-2.6	3.2	2.5	
	Ho-Dy	2.4-1.9	2.0-2.2	2.5	2.9	
	Er-Ho	2.5-1.9	3.5-2.5	3.0	4.0-2.2	
	Tm-Er	2.4-1.7	2.5-3.0	3.0	3.8-3.0	
	Yb-Tm	3.5-2.5	2.0-2.5	3.0	3.5-2.8	
	Lu-Yb	2.4-2.0	2.5-2.0	2.5	3.5-2.5	

Despite the differences in composition of primary raw material there are standard operations to be obligatory performed. They are the following: 1. Isolation of pure sum of REE; 2. Group separation along the borders: Sm-Nd, Gd-Tb, Er-Ho; 3. Selective extraction of Ce(IV) and Eu(II); 4. Isolation of Y; 5. Separation of lanthanides in their main three-valency state.

For technological processing of REE there can be used different extraction systems, different extraction methods and different sequence of separating operations. Eventually it is defined by conjuncture requirements, composition of the raw material and sometimes by some specific conditions of the interprise performing the extraction process.

References

1. Brezhneva N.E., Korpusev G.V. et al. Khimiya radioelementov i radiatsionnykh prevrasheni. Moskva: Atomizdat, 1959. S.57-74.
2. Brezhneva N.E., Korpusev G.V. et al.//Trudy II Mezhdunarodnoy konferentsii atomnoy energii. Zheneva, 1964. P.512.
3. Korpusev G.V. et al.//Ekstraktziya. Moskva: Gosatomizdat, 1962. Vyp.I. S.125-142.
4. Korpusev G.V.//Ibid. Vyp.II. S.117-140.
5. Korpusev G.V. et al. Redkozemelnye elementy. Moskva: Izd.AN SSSR, 1963. S.195-210, 211-223, 224-239.
6. Korpusev G.V.//Khimiya oskolochnykh dolgozhivushikh elementov. Moskva: Atomizdat, 1979. S.111-179.
7. Korpusev G.V. et al.//ZhNKh. 1962. Vol.7, N 9. P.2254.
8. Levin V.I., Korpusev G.V. et al.//Atomnaya energiya. 1959. Vol.15, N 2. P.138-146.
9. Peppard D.F., Ferraro J.R.//J.Inorg. Nucl.Chem.1959.Vol.10.P.275.
10. Lanthanides and Actinides/Ed.K.W.Bagnall. gl.1. Separation Chemistry of the Lanthanides and Transplutonium Actinides.
11. US patent. N 3757687.
12. US patent. N 3821353.
13. Mikhailichenko A.I. et al. Avt.svid.SSSR N 472566. B.I. N 47 (1981).
14. US patent. N 3615171.
15. US patent. N 4109358; N 4201747.
16. Korpusev G.V., Tsylov Yu.A.//Zvetnye metally. 1965. N 2, P.66.
17. Korpusev G.V., Krylov Yu.S. Avt.svid.SSSR N 540653. B.I. N48 (1976).
18. Korpusev G.V. et al. Avt.svid.SSSR. N 135646. B.I. N3. (1961).
19. Korpusev G.V. et al. Avt.svid.SSSR. N 158419. B.I. N 21 (1963).
20. Korpusev G.V. et al. Avt.svid.SSSR. N 189588. B.I. N 1 (1971).
21. Korpusev G.V. et al. Avt.svid.SSSR. N 564900. B.I. N 28 (1978).
22. Korpusev G.V. et al.//ZhPhKh. 1984. Vol.42. P.2984.
23. Korpusev G.V. et al.//Radiokhimiya. 1981. Vol.23. P.810-816.
24. UK patent N 1026791 (1966).

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Extraction and separation of niobium, tantalum and titanium from sulphate solutions containing no other ligands except sulphate ions is of great interest because of the high stability of the solutions.

In the present work we used as extractants the neutral oxygen-containing solvents - tributyl phosphate (TBP), petroleum sulphoxides (PSO), phosphoric acid hexabutyltrisamide (PAHETA) and trialkylphosphineoxide (TAPO), and organophosphorus acids - di-2-ethylhexylphosphoric acid (D2EHFA), octylphenyl-2-ethylhexylphosphoric acid (OP2EHFA), dioctylphenylphosphoric acid (DOPPA), and isododecylphosphetanic acid (IDDPFA). All the extractants correspond to the "commercial" grade. In some of the experiments we used purified D2EHFA.

In studying the extraction of metals we observed marked differences in equilibrium attainment time. For metal extraction by using neutral extractants TBP and PSO stirring within less than 5 minutes proves sufficient, whilst in the case of TAPO and PAHETA a longer time is necessary (Fig.1a). The time of equilibrium attainment in the extrac-

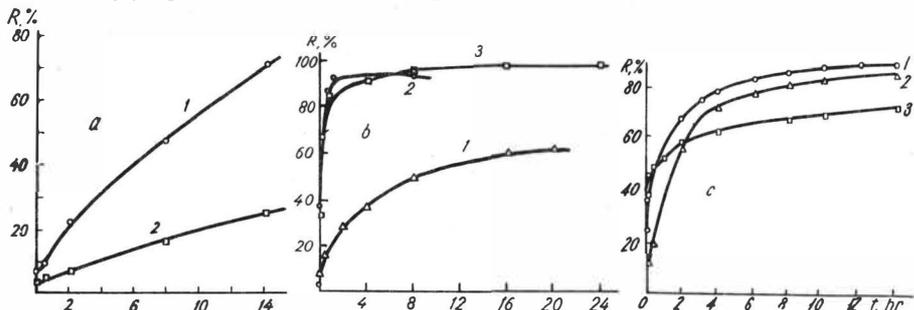


Fig.1. Extraction kinetics of metals

a) by 20% TAPO of Nb(1) and Ti(2) from 1M H₂SO₄; b) by 10% DOFPA of Ti(1) and Nb(2) and by 30% IDDPFA of Ti(3) from 1M H₂SO₄; c) by D2EHFA of Ti(1,2) from the solutions of TiOSO₄ and (NH₄)₂TiO(SO₄)₂ in 1M H₂SO₄ and Ta(3) in 3M H₂SO₄; (1,2) 50% D2EHFA, (3) 20% D2EHFA in o-xylene

tion of titanium with DOPPA and IDDPFA is, correspondingly, 20 and 24 hours (Fig.1b).

When using D2EHFA, both "commercial" and "purified", we noted marked differences in equilibrium attainment time. A complete extraction of niobium, tantalum and titanium by D2EHFA is achieved after 30 min of stirring. When extraction is carried out by the use of a pure extractant, equilibrium sets in slowly (Fig.1c). This appears to be

associated with the formation of condensed films at the interface.

We have studied the effect of the H_2SO_4 content on metal and acid extraction. With the content of $H_2SO_4 \leq 4M$ no sulphate ion is observed to be present in the extracts of organophosphorus acids. Under similar conditions the extraction of H_2SO_4 in TAPO and PAHBTA is 1-4%. The aqueous solution containing about 10M H_2SO_4 , up to 4% of H_2SO_4 goes over into organophosphorus acid extracts and up to 8-12% of H_2SO_4 in the case of TAPO and PAHBTA. To an even greater extent is extracted H_2SO_4 by PSO and TBP. Extraction of H_2SO_4 by TBP rises from 9 to 37% with an increase of the H_2SO_4 content in the solution from 4 to 10M. An increase in H_2SO_4 extraction by PSO from 8 to 43% occurs with an increase of the H_2SO_4 content from 1 to 6M.

Extraction of titanium(IV) by PSO in the absence of a free acid is insignificant (4.1) and is observed to increase up to 92.1% under 6M H_2SO_4 (Fig.2a, curve 1). A high extraction of titanium by TBP occurs

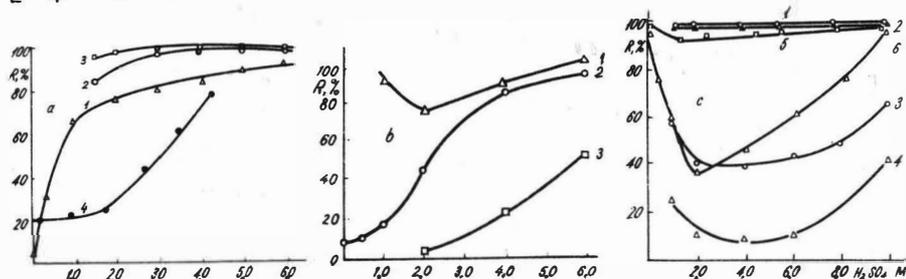


Fig.2. The effect of H_2SO_4 concentration on metal extraction

a) by PSO of Ti(1), Nb(2), Ta(3), Ti(III)(4);

b) by 20% TAPO of Nb(1), Ti(2), Ta(3);

c) by D2EHPA of Nb(1,3), Ta(2,4), Ti(5,6). Extractant: 50% D2EHPA commercial(1,2), 20% D2EHPA(3,4), 100% D2EHPA(5), 50% D2EHPA(6)

under a significantly higher content of H_2SO_4 (about 11M). Niobium and tantalum extraction by PSO within a wide range of H_2SO_4 concentrations from 1.5 to 5.0M exceeds 80%(Fig.2a, curve 2,3). Extraction of titanium(III) (Fig.2a, curve 4), as could be expected, proceeds much worse than that of titanium(IV). A high degree of extraction of niobium by TAPO and PAHBTA from solutions with a low concentration of H_2SO_4 points to the possibility of extraction of hydrolyzed niobium forms.

Metal extraction by TAPO and TBP from solutions with a single metal is observed to increase in the series $Ta < Ti < Nb$. Maximum differences in metal extraction by TAPO have been recorded under about 2M H_2SO_4 (Fig.2b). In the case of metal extraction by PAHBTA the extraction of niobium and tantalum is much higher than that of titanium. From the 8M H_2SO_4 solution as much as 95.7, 90.1 and 25.4% of niobium, tantalum and titanium is extracted, correspondingly.

Metal extraction by IDDDPA and commercial D2EHPA is insignificantly dependent on the H_2SO_4 concentration and amounts to 94-100% for H_2SO_4 2-10 M (Fig.2c). Dependence of metal extraction by purified D2EHPA upon the H_2SO_4 content is more sophisticated (Fig.2c). A minimum at the curves within the 2-4M H_2SO_4 region can be explained by complications in the mechanism of metal extraction.

With the H_2SO_4 concentration rising from 0.5 to 10M the extraction of titanium by DOPPA and OP2EHPA declines from 41.5 to 5.7 and from 86.3 to 14.6% respectively. Niobium extraction by DOPPA and OP2EHPA declines less perceptibly (from 97 to 43.1 and 95 to 81.9% respectively), thus pointing to the possibility of metal separation.

The identified differences in the kinetics and conditions of niobium and tantalum extraction disappear when we go over from solutions containing a single metal to process solutions. One of the main reasons behind changes in the behaviour of metals proves to be the formation of mixed sulphate complexes of niobium and titanium. We have demonstrated the relationship between the $TiO_2 : Nb_2O_5$ ratio and the degree of extraction of niobium into the extract. In case the molar ratio $TiO_2 : Nb_2O_5$ declines from 6 to 2 the niobium extraction by PSO from 6M H_2SO_4 solutions increases from 78.2 to 93.5% and that by TBP from 10M H_2SO_4 solutions - from 68.6 to 91.2%. From process solutions the extraction by TBP is observed to increase in the series $Ta < Ti < Nb$. From the 8 M H_2SO_4 solution the degree of extraction of niobium, tantalum and titanium by TBP amounted to 81.9, 6.5 and 32.1%, respectively. PSO, similarly to IDDDPA and D2EHPA, proves to be a collective extractant of the three metals.

Of great practical interest appears to be the extraction of metals under the ratio of phase volumes $V_o : V_{aq} < 1$. This enables solution flows to be reduced and metals to be concentrated. The degree of concentration of metals in the case of extraction by 40% D2EHPA is about 8 times and in the case of 20% IDDDPA - 4.6 times. A high extraction of niobium, tantalum and titanium by TAPO, PAHETA and PSO continues to be retained up to the ratio $V_o : V_{aq} = 1:5$ (extraction - 62.5-87.7%).

An additional concentration of metals is possible at the stage of their stripping by fluoride solutions. As regards D2EHPA-extracts, a particularly complete stripping of metals is achieved with the use of HF and NH_4F solutions. From PSO-extracts titanium and iron can be more easily back-extracted, compared to niobium and tantalum. The use of HF solutions and their mixtures with H_2SO_4 enables titanium to be separated from niobium and tantalum. Separation is observed to be particularly effective under the molar ratio $F : Ti > 6$. Tantalum is back-extracted from PSO-extracts with a much greater difficulty than niobium is. This creates prerequisites for the separation of the metals.

The composition of niobium, tantalum and titanium complexes extracted from sulphate solutions has not yet been adequately investigated.

Methods of electromigration and chemical analysis enabled to find out that titanium is extracted by PSO predominantly in the form of a complex acid $\text{H}_2\text{TiO}(\text{SO}_4)_2$. The molar ratio in the extracts $\text{SO}_4:\text{Ti}=1.40\pm 0.24$ in the case of extraction from a 0.9–1.8 M H_2SO_4 solution and 0.04–0.1 M Ti. Data obtained by infra-red spectroscopy confirm the hydrate-solvate mechanism of titanium extraction by PSO. An insignificant displacement of the band of the S=O group due to PSO (from 1030 to 1000–980 cm^{-1}) is an evidence against the coordination of the oxygen of the S=O group towards titanium. With an increase of the titanium content in the initial solution there is observable in the spectra of the extracts either a broadening or dissipation of the bands referred to titanium complexes. This points to the polymerization of the complexes being extracted and is confirmed by an increase of titanium extraction with the growth of its concentration in the aqueous solution.

The methods of saturation and dilution were employed to find out that in the case of titanium extraction from 0.2–10M H_2SO_4 solutions there are isolated into the extract the complexes with a molar ratio $\text{HA}:\text{Ti} = 2$, where HA – D2EHPA or IDPPA. On the evidence of the saturation and dilution methods, niobium and tantalum are extracted from the 8–10 M H_2SO_4 solutions in the form of complexes with a molar ratio $\text{HA}:\text{Nb}(\text{Ta}) = 3$ (Fig.3). On the basis of the infra-red spectroscopy data it was concluded that sulphate groups are absent in the composition of extracted metal complexes.

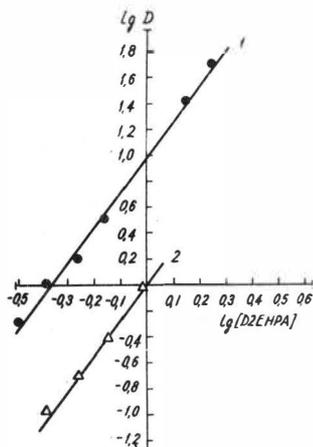


Fig.3. The effect of D2EHPA concentration on extraction of Nb(1) and Ta(2)

Alongside of metal complexes, H_2SO_4 goes over into the extract. This assumption is based on the appearance in the spectra of the blank and metal-containing extracts of absorption bands from two main frequencies ν_3 and ν_4 at 1200–1100 cm^{-1} and at 580 cm^{-1} from a high-symmetrical sulphate ion: belonging to H_2SO_4 and the absence of absorption bands typical for sulphate groups associated with metals. In the infrared spectra there are likewise observable absorption bands at 980–960 cm^{-1} due to an isolated $\text{Me} = \text{O}$ bond. Account being taken of the

chemical analysis and infra-red spectrascopy data, the composition of the complexes corresponds to the formulae TiO_2 and $\text{Nb}(\text{Ta})\text{O}_3$.

The identified regularities point to the possibility of an effective separation of niobium, tantalum and titanium from sulphate solutions by the use of P-, P-N- and S-organic extractants.

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Lanthanides mixtures separation efficiency depends to the great extent both on the structure of the extractant applied, and on an aqueous phase composition and on other parameters varying widely for each system. Among them we can name the concentration of the lanthanide salts, salting-out agents, mineral acid, the components relation in the initial RE mixture, temperature, etc. In the present work on the basis of a great amount of experimental data the effect of the above mentioned system parameters on the separation factors value (β) in different extraction systems is described. In addition, several general mechanisms are emerged and application limitations are presented relative to various parameters for different RE subgroups, different types of extractants and its mixtures.

Metal concentration. Extraction with neutral oxygen-containing extractants from weakly acid neutral solutions is widely used for RE separation [1, 2]. On increasing the lanthanide nitrates and salting-out agents (lithium, aluminium, calcium, etc.) concentration, the selectivity in relation to light elements (La-Sm) increases while in relation to heavy elements (Ho-Lu) it decreases. Typical plots of separation factors of cerium and lanthanum against the RE concentration in aqueous phase during the tributyl phosphate (TBP) extraction are shown in Fig.1.

Fig.2 presents the plots of the RE separation factors of the

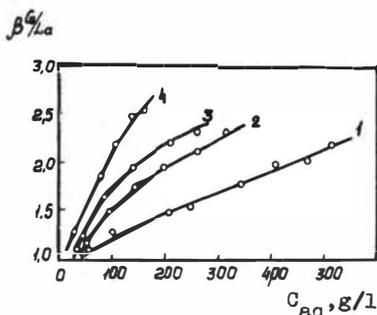


Fig.1. The plot of $\beta_{Ce/La}$ against the RE concentration. The extractant is TBP. The concentration of $Al(NO_3)_3$, M: 1 - 0; 2 - 0,67; 3 - 1,0; 4 - 1,67

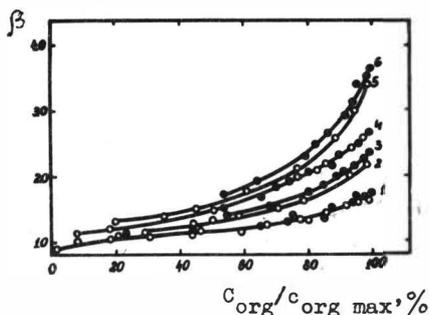


Fig.2. The plot of RE separation factors against the extractant loading degree: 1 - Nd/Pr (TBP); 2,3 - Ce/La (DAMP); (3 - with $Al(NO_3)_3$); 4 - Sm/Nd (TBP); 5,6 - Pr/La (TBP); (6 - with $Al(NO_3)_3$).

cerium subgroup versus loading of the organic phase for TBP and diisooamyl methyl phosphonate (DAMP). The higher the loading of the organic phase, the greater is β . Having the same loading the separation factor doesn't much depend on the aqueous phase composition. For neodymium-praseodymium and samarium-neodymium pairs the data for the systems with and without a salting-out agent are presented by a common curve for each pair of elements (curves 1 and 3). For cerium-lanthanum and praseodymium-lanthanum pairs the system data with a salting-out agent are presented by separate, but close curves.

During the RE nitrate extraction with neutral phosphororganic compounds (NPOC) in the form of waterless trisolvates $\text{Ln}(\text{NO}_3)_3 \cdot 3\text{S}$ the value of the separation factor is determined by the following equation:

$$\beta = \frac{K_2}{K_1} \left(\frac{\gamma_{\pm 2, \text{aq}}}{\gamma_{\pm 1, \text{aq}}} \right)^4 \frac{\gamma_{1, \text{org}}}{\gamma_{2, \text{org}}},$$

where K - extraction constants, γ - the corresponding activity coefficients. From the equation it follows that even a small difference between the activity coefficients of the lanthanide salts in aqueous phase for RE nitrate solutions and in solutions with salting-out agents may affect greatly the value of β , because the ratio

$\gamma_{\pm 2, \text{aq}} / \gamma_{\pm 1, \text{aq}}$ is a part of the equation in the fourth power.

On increasing the concentration of RE salts and salting-out agents the light lanthanide separation factors increase in the process of extraction with monocarboxylic acids of normal and branching structure, quarternary ammonium bases (nitrate and thiocyanate solutions), NPOC, sulphoxides and tertiary amines. However, the picture observed is not always the same; thus, in the phosphororganic acid systems a significant increase of metal concentration in aqueous and organic phase results in an abrupt decrease in selectivity due to the change of the formed complexes composition.

Temperature. In case with the extraction process with neutral extractants β somewhat decreases while the temperature increases. This can be attributed to the fact that on increasing the atomic number the extraction exothermicity ($-\Delta H$) increases.

The temperature increasing effect is much smaller than the opposite effect of the RE concentration increase, as shown in Table 1.

Temperature increase from 20° to 80° at the same concentration (400 g/l) results in decrease of β by about 15%, while concentration increase from 300 to 600 g/l at 60° results in β increase by 75-80%. In fact, RE concentration increase up to 500-600 g/l Ln_2O_3 (which is possible only at a high temperature) gives, in general, a significant positive effect, especially during the extraction with TIBP.

Table 1

Separation factors $\beta_{Nd/La}$ during the extraction with 100% TBP and triisobutyl phosphate (TIBP)

t° C	RE, g/l (Ln ₂ O ₃)	TBP		TIBP	
		D	Nd/La	D	Nd/La
60	300	0.43	4.1	0.45	4.9
20	400	0.41	5.4	0.40	6.4
40	400	0.39	5.3	0.39	6.2
60	400	0.39	5.0	0.38	5.8
80	400	0.38	4.7	0.38	5.5
60	500	0.32	6.4	0.33	7.4
60	600	0.29	7.2	0.30	9.0

Relative composition of the RE mixture. The effect of the relative composition of the elements mixture can be easily traced as to lanthanides binary mixtures. From Table 2 and Fig.3 it follows that the effect of the composition of the elements initial mixtures is most clearly expressed in extractant maximum loading region or close to it (at a high RE concentration in aqueous phase or in the presence of a salting-out agent).

On increasing the better extracting component share in mixture in different systems there might be possible both an increase and a decrease of the separation factors. Thus, in the studied systems there's an increase of β values for neutral extractants TBP and DAMP, and for acid (HDEHP, carboxylic acids) and basic (trialkyl benzilammonia nitrate and thiocyanate) extractants one can observe an opposite picture [3,4]. While using NPOC and trioctyl methyl

Table 2

Separation factors for binary RE mixtures

Extractant	Initial solution composition	The content of the better extracting component in mixture, %				
		1	10	50	90	99
TBP	200 g/l Ln ₂ O ₃	1.25	1.27	1.27	1.28	1.30
	300 "	1.42	1.43	1.45	1.48	1.50
	400 "	1.56	1.58	1.64	1.72	1.75
	300 g/l Ln ₂ O ₃ + +5NAL(NO ₃) ₃	1.62	1.63	1.67	1.74	1.76
TBP	400 g/l	<u>Nd/Pr</u>				
		1.63	1.62	1.66	1.71	1.74
DAMP	400 g/l Ln ₂ O ₃	<u>Ce/La</u>				
		2.12	2.14	2.20	2.31	2.37
	160 g/l Ln ₂ O ₃ + +5NAL(NO ₃) ₃	2.35	2.36	2.39	2.45	2.52

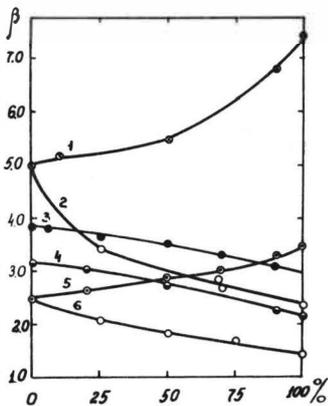


Fig. 3. The plot of the separation factors against the content of the better extracting element in the initial mixture: 1 - Nd/La, TBP; 2 - Tm/Er, HDEHP; 3 - Er/Ho, Sm/Gd, TAMAN+TAPO; 6 - La/Nd, TAMAN

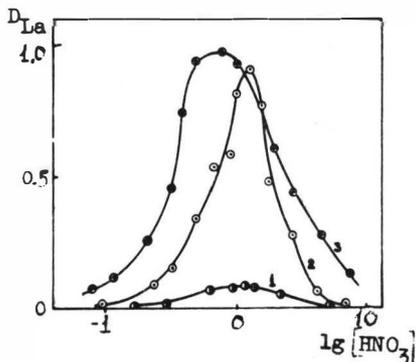


Fig. 4. The plot of the lanthanum nitrate distribution coefficients: 1 - 1 M DOMP; 2 - 1 M TOMAN; 3 - 0,5 M TOMAN+0,5 M DOMP; m-xylene

ammonia nitrate (TOMAN) mixtures the directivity of β changing for TOMAN-TBP and TOMAN-DAMP, on the one hand and TOMAN-trialkyl phosphine oxide (TAPO) where alkyl - C_7-C_9 or isoamyl, on the other hand, is opposite. A possible cause for this phenomenon lies in the fact that in mixed systems with TBP and DAMP the extraction is carried out according to anion-exchange type, and in the system with TAPO according to solvation type because TAPO has the highest extractive power in NPOC series.

Extractant mixtures. In some cases the use of extractant mixtures allows to rise not only the extractivity, but also the selectivity of the extraction systems [5-7]. On this purpose the lanthanides extraction with TOMAN and NPOC mixtures has been investigated.

Nitric acid effect on the lanthanum distribution coefficients is shown in Fig. 6. The maximums on all the curves are conditioned by the influence of the two factors. At weak acidity D_{La} increases with the increase of the same ion (NO_3^-) concentration. With the acidity increase the lanthanum distribution coefficients decrease which is conditioned by the decrease of the extractant free concentration due to the competitive extraction of HNO_3 .

Fig. 5 presents data on neodymium nitrates distribution for isomolar TOMAN and DOMP mixtures. Similar curves were obtained for lanthanum, terbium and lutecium. In the whole studied measurement interval of the organic phase composition the lanthanides distribution coefficients are higher than the additive quantities D_{Ln}

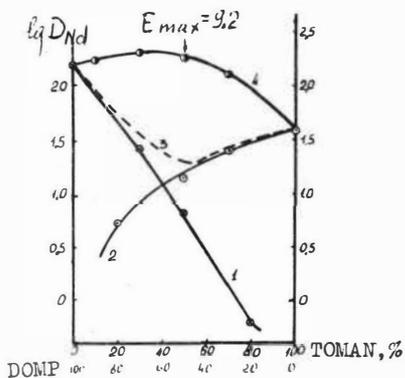


Fig. 5. Neodymium nitrate distribution coefficients: 1 - DOMP; 2 - TOMAN; 3 - additive curve; 4 - TOMAN+DOMP, the total mixture concentration (1 M) is constant; aqueous phase - 0,02 M $Nd(NO_3)_3$, 3 M $LiNO_3$, pH=3,0

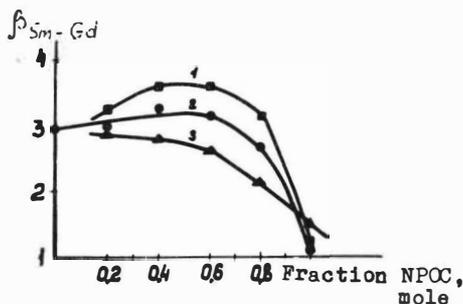


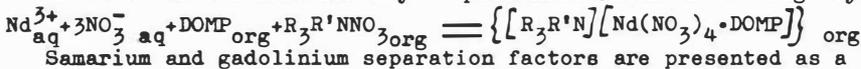
Fig. 6. The organic phase composition effect on samarium and gadolinium separation factors in the process of extraction with TOMAN and NPOC mixtures in m-xylene: 1 - DOMP; 2 - TBP; 3 - TAPO

for individual extractants, that is one can observe a synergistic effect.

Lanthanum distribution coefficients increase in the TBP < DOMP < TOMAN < TAPO series; for neodymium, terbium and lutecium one can observe another sequence: TBP < TOMAN < DOMP < TAPO. The TOMAN change of the position can be attributed to the D_{Ln} decrease with the rise of the lanthanide atomic number during the TOMAN extraction, while for NPOC one can observe an increase of this value.

Table 3 presents the maximum values of the synergistic effect during the lanthanide nitrate extraction with TOMAN and NPOC in m-xylene. The maximum synergistic effect in every system under investigation corresponds to the presented component ration in the extractant mixture.

The extraction reaction may be presented in the following way:



Samarium and gadolinium separation factors are presented as a function of a TOMAN mole fraction in mixtures with neutral phosphororganic compounds (Fig.6). Lanthanide separation factors with the

Table 3

The maximum values of synergistic effects in NPOC and TOMAN system

RE	lanthanum		neodymium		terbium		lutecium	
	E_{max}	NPOC: TOMAN						
TBP	4.8	2.5:1	6.3	2.5:1	2.8	2.5:1	2.2	2.5:1
DOMP	5.4	2.5:1	9.2	1:1	3.0	1:2.5	2.1	1:2.5
TAPO	10.5	1:1	15.9	1:1	3.4	1:2.5	-	-

Table 4

Lanthanum-140 and actinium-227 separation factor during the extraction with TBP, TOMAN and their mixtures (aqueous phase: 3M NH_4NO_3)

Extractant concentration, M		$E = D_{\text{mix}} / (D_1 + D_2)$		La/Ac
TBP	TAMAN	lanthanum	actinium	
0.8	-	-	-	1.07
-	0.8	-	-	2.36
0.6	0.2	1.06	0.87	3.02
0.4	0.4	1.09	0.80	3.28
0.2	0.6	1.19	0.76	3.55

same TOMAN content in mixture change in the DOMP+TOMAN > TBP+TOMAN > TAPO+TOMAN series.

Synergistic effect observed during RE extraction with TOMAN and TBP mixture might be used for RE separation lanthanum and actinium in particular. Lanthanum and actinium separation factor attains its maximum value while using the 25% TOMAN mixture (Table 4).

The results reported show that the extractant mixtures have been found to be potentially interesting in view of the searching of selective extraction systems for RE separation.

Referencies

1. Korpusev G.V. // Chemistry of fragment elements with long lifetime. M.: Atomizdat, 1970. 140-144.
2. Elutin A.V., Mikhailichenko A.I. // ISEC/86, Intern. Solv. Extr. Conf. Preprint. 2. 425-429.
3. Hoh Y.C., Bautista R.G. // J. Inorg. Nucl. Chem. 1979. 41, N 12. 1787-1792.
4. Mikhailichenko A.I., Pimenova R.M., Petker S.Ya. // Complex formation and extraction of actinoids and lanthanides. Leningrad: Nauka, 1974. 120-125.
5. Val'kov A.V., Kuznetsov S.A., Makarenko M.K. // Izv. Vysch. Uchebn. Zaved. Khim Technol. 1978. 21, N 4. 542-544.
6. Mikhlin E.B., Rozen A.M., Norina T.M. // Radiokhimiya. 1977. 19, N 3. 294-301.
7. Spivakov B.Ya., Zolotov Yu.A., Myasoedov B.F. // Zhurnal Neorg. Khim. 1972. 17, N 12. 3334-3340.

THE SOLVENT EXTRACTION OF RARE-EARTH AND BASE METALS BY
DIALKYL ALKYLPHOSPHONATES

7-4

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Neutral organophosphorus compounds are useful in the commercial solvent extraction of zinc, gallium, uranium, and the rare-earth metals. In this study we have synthesized a series of dialkyl alkylphosphonates, $RPO(OR')_2$, and investigated their extraction properties towards zinc(II), gallium(III), indium(III), iron(III), and aluminium(III) in chloride media; towards uranium(VI), thorium(IV), and cerium(IV) in nitrate media; and towards yttrium(III) and the lanthanides(III) in nitrate and thiocyanate media. The phosphonates used comprise a number of pure analogues of well-known commercial reagents (e.g. dibutyl butylphosphonate and dipentyl pentylphosphonate), a series of isomeric C_{16} compounds containing n-alkyl groups, a series of isomeric C_{12} compounds containing branched butyl groups, as well as some compounds that contain cycloalkyl groups.

Solubilities of extractants. The solubilities of the extractants, measured in 1,0 M sodium chloride solution at 20°C by a turbidimetric method [1], are shown in Table 1. Some trends in the solubility data that may influence the selection of extractants suitable for commercial use can be identified. Thus, as expected, the aqueous solubility decreases markedly through the homologous series of n-butyl, n-pentyl, and n-hexyl phosphonates (compounds a, b, and c in Table 1). Under certain circumstances, such as with high concentrations of extractant in the organic phase and aqueous solutions of low ionic strength, the use of the lower members of this series may become impractical on account of the high losses of reagent incurred to the aqueous phases. The incorporation of branched alkyl groups into the extractants causes increased solubility, especially when more than one branched chain is present (cf. compound a and compounds d to g). In the series of isomeric n-alkyl compounds, solubilities decrease somewhat when one of the alkyl groups contains the majority of the carbon atoms in the extractant molecule, compared to when these are more evenly distributed between the alkyl groups (cf. the C_{12} compounds a and h, and the C_{16} compounds j and n). The presence of cyclic aliphatic groups in the extractants can result in marked increases in their aqueous solubilities (cf. compounds k and l).

Table 1. Solubilities of dialkyl alkylphosphonates in 1,00 M sodium chloride at 20°C

Phosphonate	R	R'	Solubility (mg l ⁻¹)
a	n-C ₄ H ₉	n-C ₄ H ₉	629
b	n-C ₅ H ₁₁	n-C ₅ H ₁₁	316
c	n-C ₆ H ₁₃	n-C ₆ H ₁₃	82
d	i-C ₄ H ₉	n-C ₄ H ₉	760
e	s-C ₄ H ₉	n-C ₄ H ₉	767
f	t-C ₄ H ₉	n-C ₄ H ₉	736
g	s-C ₄ H ₉	s-C ₄ H ₉	1211
h	n-C ₈ H ₁₇	C ₂ H ₅	261
i	n-C ₄ H ₉	n-C ₆ H ₁₃	102
j	n-C ₆ H ₁₃	n-C ₅ H ₁₁	108
k	n-C ₈ H ₁₇	n-C ₄ H ₉	102
l	c-C ₈ H ₁₅	n-C ₄ H ₉	499
m	n-C ₁₀ H ₂₁	n-C ₃ H ₇	99
n	n-C ₁₂ H ₂₅	C ₂ H ₅	97

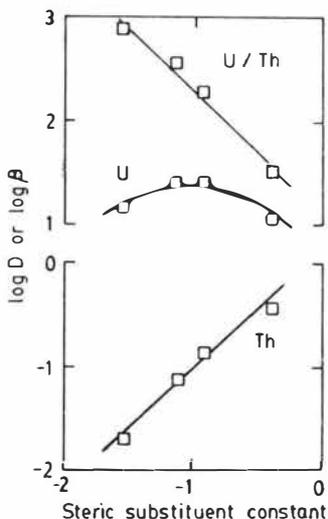
Extraction of uranium(VI), thorium(IV), and cerium(IV) from nitrate media. Slope analysis studies on the extraction of uranium(VI), thorium(IV), and cerium(IV) from sodium nitrate solutions by dialkyl alkylphosphonates(L) indicate the formation of extractable complexes of the types $UO_2(NO_3)_2L_2$, $Th(NO_3)_4L_2$, and $Ce(NO_3)_4L_2$, respectively, as found in earlier studies using tri-n-butyl phosphate [2,3]. Where only two molecules of organophosphorus ligand are incorporated into the extracted complex (uranium and cerium), the extractability of the metal is little affected by the steric complexity of the ligand, higher extractions sometimes being obtained with compounds containing branched alkyl groups, by virtue of their enhanced electron inductive effect compared with n-alkyl groups. In contrast, the extraction of thorium is significantly decreased by increasing the steric complexity of the organophosphorus ligands, resulting in much higher separation factors for uranium over thorium (β_{Th}^U) with the more sterically hindered compounds (Table 2).

Table 2. Distribution coefficients and separation factors for the extraction of uranium(VI) and thorium(IV) from 1,0 M sodium nitrate by 0,15 M dialkyl alkylphosphonates in toluene.

Phosphonate	R	R'	D _u	D _{Th}	β_{Th}^U
a	n-C ₄ H ₉	n-C ₄ H ₉	12	0,36	32
d	i-C ₄ H ₉	n-C ₄ H ₉	26	0,14	185
e	s-C ₄ H ₉	n-C ₄ H ₉	26	0,07	368
f	t-C ₄ H ₉	n-C ₄ H ₉	15	0,02	787
g	s-C ₄ H ₉	s-C ₄ H ₉	41	0,02	2149

The importance of steric factors in the extraction of thorium(IV) by dialkyl alkylphosphonates is confirmed by the linear correlations obtained between the distribution coefficients (as well as the uranium/thorium separation factors) and the Taft steric substituent constants [4] for the alkyl groups R in the isomeric series of phosphonates $RPO(n-C_4H_9O)_2$, in which R = n-butyl, isobutyl, sec-butyl or tert-butyl (Figure 1).

Fig.1. Correlation between extraction of uranium and thorium and steric constants of substituent isomeric butyl groups



Extraction of yttrium(III) and lanthanides(III) from nitrate and thiocyanate media. Previous studies [5,6] on the extraction of yttrium(III) and the lanthanides(III) from 1M sodium nitrate by solutions of dialkyl alkylphosphonates (L) in toluene showed the extracted complexes to be uniformly of the type $Ln(NO_3)_3L_3$, in which the nitrate groups were presumed to act as bidentate or monodentate ligands depending on the size of the central Ln^{3+} cation. Studies on the extraction of these metals from 2M potassium thiocyanate solutions have now shown that the extracted complexes are of the type $Ln(NCS)_3L_x$, where $x = 3, 4, \text{ or } 5$, depending upon the size of the Ln^{3+} cation (Table 3). In the 1M sodium nitrate system, extraction of the lanthanides was found to reach a maximum close to the middle of the series (at samarium or europium) and the extraction of yttrium was found to be similar to that of the heavy lanthanides erbium or thulium in all cases. In contrast, no such maxima occur in the extraction of the lanthanides from 2M potassium thiocyanate solutions, and the extraction of yttrium more closely follows that of the lighter lanthanides neodymium or samarium (Figure 2).

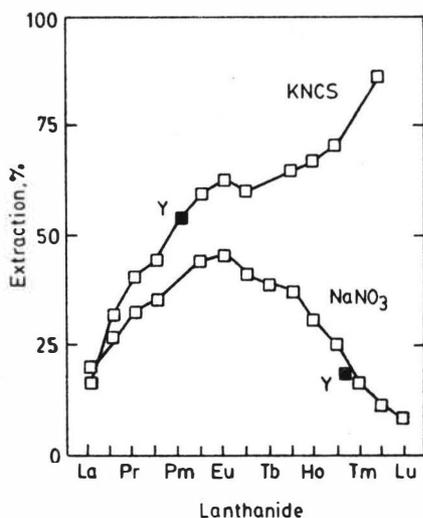


Fig.2. Extraction of rare earth metals from nitrate and thiocyanate media by di-n-butyl n-butylphosphonate

Table 3. Values of coefficient x in the complexes $\text{Ln}(\text{NCS})_3\text{L}_x$ extracted by dialkyl alkylphosphonates and tri-n-butyl phosphate

Extractant	Value of coefficient, x			
	La	Gd	Y	Yb
Tri-n butyl phosphate	4.9	4.0	4.1	3.6
Di-n-butyl n-butylphosphonate	3.9	3.6	3.6	3.0
Di-n-butyl s-butylphosphonate	4.1	3.9	3.8	3.0

References

1. Foakes H.J., Preston J.S., Whewell R.J.// *Analyt. Chim. Acta.* 1978. Vol. 97. P. 349.
2. Healy T.V., McKay H.A.C.// *Rec. Trav. Chim. Pays Bas.* 1956. Vol. 75. P. 730.
3. Siddal T.H.// *J. Inorg. Nucl. Chem.* 1960. Vol. 13. P. 151.
4. Taft R.W.// *J. Amer. Chem. Soc.* 1952. Vol. 74. P. 3120.
5. Preston J.S., du Preez R.// *S. Afr. J. Chem.* 1986. Vol. 39. P. 137.
6. Preston J.S., du Preez A.C.// *Proc. Int. Solvent Ext. Conf. ISEC '86. Munich, 1986. Vol. 2. P. 83.*

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Previously [1] we have shown that tetraphenylimidodiphosphate, $(\text{PhO})_2\text{P}(\text{O})\cdot\text{NH}\cdot\text{P}(\text{O})(\text{OPh})_2$, is a monobasic acid, HA, which forms dimeric species in benzene ($K_2 = 2 \cdot 10^3 \text{ l}\cdot\text{mol}^{-1}$). Ions of rare earth elements, M^{3+} , are extracted from mineral acid solutions according to equation (1),



if the acid concentration is smaller than 4 M. The extraction constants K_{ex1} increase with decreasing ionic radii of M^{3+} . It was concluded from results of ^1H -, ^{13}C - and ^{31}P -NMR investigations [2] and x-ray structure analysis [3] that in the complex extracted the metal ion is six coordinated via the oxygen atoms of phosphoryl groups, and is able to increase the coordination number by molecules with donor atoms (e.g. acetone).

As expected from these results, a synergism in the extraction of M^{3+} from mineral acid solution using mixtures of HA in benzene with tributylphosphate (TBP) or trioctylphosphine oxide (TOPO), respectively, has been observed.

As demonstrated in Fig. 1, the distribution ratios, D, of La^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} and Tb^{3+} rise, reach a maximum, and then decrease if the initial concentration of TBP increases. No synergism has been obtained for Im^{3+} and Lu^{3+} . TOPO behaves similar as TBP in the extraction of M^{3+} from hydrochloric acid solution. Contrary to TBP, in the case of TOPO the maxima of D are about one order of magnitude higher and appear at lower concentration. A maximum was found even for Im^{3+} .

The curves, $\lg D$ vs. $\lg c_{\text{TOPO}}$, change dramatically, if the aqueous phase contains nitric or perchloric acid (Fig. 2 and 3). At higher TOPO concentration a minimum is to notice. The minimum is deeper and afterwards, the increase has a steeper slope, if HClO_4 is used.

According to Fig. 3 we distinguish three different parts in the extraction curves: I - a first increase of the D values up to a maximum, II - a decrease, and III - a second increase after the minimum.

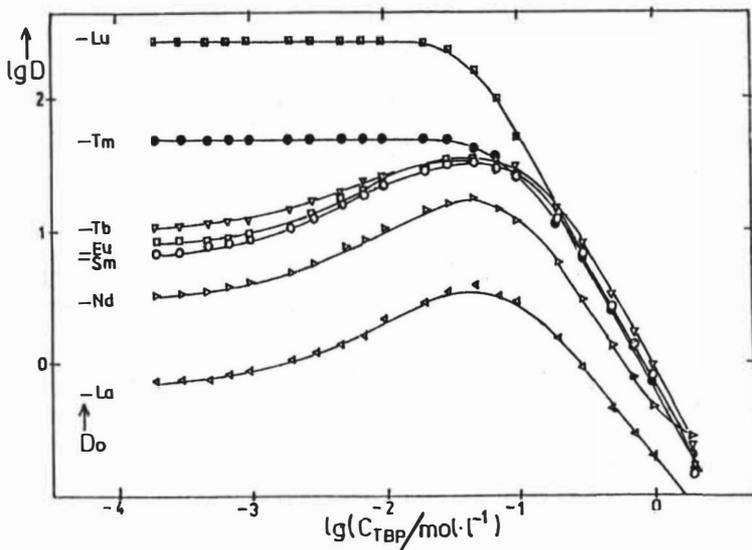


Fig. 1. Effect of TBP on the extraction of M^{3+} with 0.005 M HA in benzene from 0.1 M HCl (D_0 -distribution ratio without TBP)

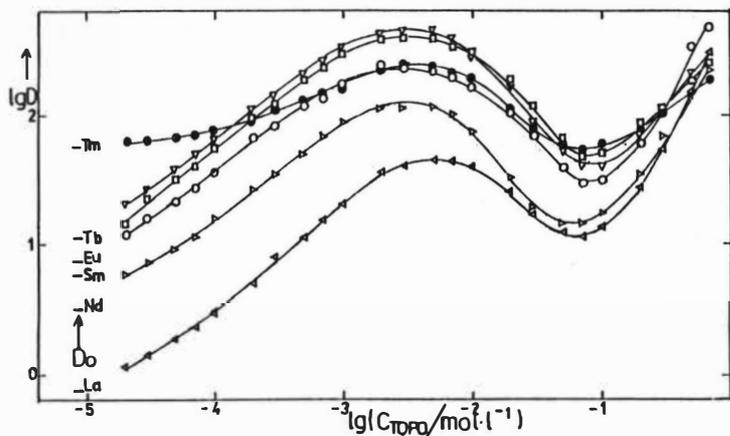


Fig. 2. Effect of TOPO on the extraction of M^{3+} with 0.005 M HA in benzene from 0.1 M HClO₄ (D_0 -distribution ratio without TOPO)

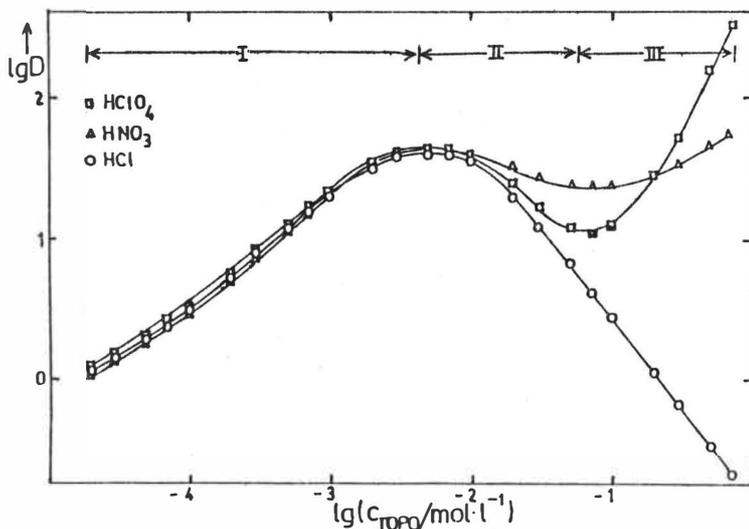
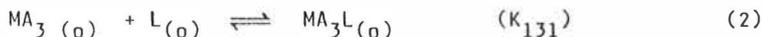
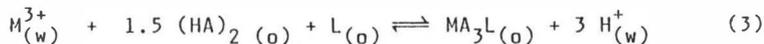


Fig. 3. Effect of TOPO on the extraction of La^{3+} with 0.005 M HA in benzene from 0.1 M HClO_4 , HNO_3 and HCl , respectively

The synergism (part I) occurs in consequence of reaction (2) in the organic phase:



(L = TBP, TOPO). So we have to write in part I besides equation (1) the extraction equation (3):

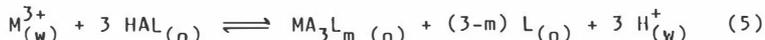


with the extraction constant $K_{\text{ex}3}$.

The decrease of D values (part II) is owing to a competition reaction of L with $(\text{HA})_2$:



By ^{31}P -NMR spectroscopy we determined the following equilibrium constants: $K_{\text{HA}\cdot\text{TOPO}} = 829(12) \text{ l}\cdot\text{mol}^{-1}$ and $K_{\text{HA}\cdot\text{TBP}} = 2.4(1) \text{ l}\cdot\text{mol}^{-1}$. The main reaction in part II is:



with the extraction constant $K_{\text{ex}4}$. The coefficient m is equal to one for most of the M^{3+} . For lutetium in both systems and Tm^{3+} in the TBP system it is lower than one. At high concentration of L beside MA_3L a complex MA_3L_2 is formed, especially by lanthanum.

The equilibrium constants K_{ex1} and K_{131} are summarized in Tab. 1. From these results it is possible to calculate K_{ex3} and K_{ex4} :

$$K_{ex3} = K_{ex1} K_{131} \quad (6)$$

$$K_{ex4} = K_{ex1} K_{131} \cdot K_{HA \cdot TOPO}^{-1.5} \quad (7)$$

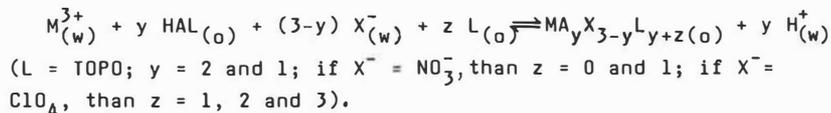
Table 1. Equilibrium constants for extraction of M^{3+} from HX solution by HA/TOPO in benzene

A: $K_{ex1} \cdot 10^{-2} \text{ mol}^{-1.5}$; B: $K_{131} \cdot 10^{-4} \text{ mol}^{-1}$

K	HX	La	Nd	Sm	Eu	Tb	Tm	Lu
A	HCl	0.080(6)	0.35(1)	0.69(1)	0.80(2)	1.1(1)	6.4(2)	33(6)
	HNO ₃	0.076	0.34(1)	0.65(1)	0.81(3)	1.4(4)	6.2(8)	
	HClO ₄	0.084(1)	0.41(4)	0.76(13)	0.85(4)	1.3(2)	7.0(4)	
B	HCl	8.5(3)	12.2(4)	12.5(14)	14.7(7)	11.6(5)	0.93(6)	0.05
	HNO ₃	7.7(3)	9.4(7)	12.4(5)	14.7(9)	11.8(9)	0.87(7)	
	HClO ₄	8.2(3)	9.7(5)	12.2(6)	14.9(7)	10.8(3)	0.84(5)	

Whereas K_{ex1} rises with increasing atomic number from lanthanum to lutetium, K_{131} has a small maximum at about europium and decreases from terbium to thulium and lutetium rapidly. The decrease is the consequence of smaller ionic radii of heavier lanthanoids, which not allowed an easy coordination of L to MA_3 .

In part III of extraction curves in Fig. 2 and 3 nitrate and perchlorate ions are coextracted:



Equationes for calculation of maxima and minima of D values are obtained.

References

- Herrmann E., Navrátil, O., Hoang ba Nang et al.//Coll. Czechoslov. Chem. Commun. 49(1984)201.
- Herrmann E., Scheller D.//Z. Anorg. Allg. Chem. 496(1983)134.
- Kulpe S., Seidel I., Herrmann E.//Z. Chem. 21(1981)333.

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Use of complexons for extraction separation of lanthanides (Me) by alkylammonium salts (Am) and tri-n-butylphosphate (TBP) increases separation coefficients of rare earth elements (REE). These extractants are associated because of hydrogen bonding (Am) and dipole-dipole interaction (Am, TBP) [1-3].

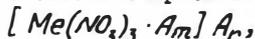
The behaviour of REE is an implicit function of association of extractant and of stability of all complexes in the organic and aqueous phase. The knowledge of the reactions equilibrium constants gives mathematical model of extraction. It should be noted there are a great number of reactions of extracted complexes with extractant in the organic phase, interaction of lanthanides with NO_3^- -ions (caused by presence of high concentration of salting-out agent) and with complexons in the aqueous phase, considerable number of components in the extraction system. All these factors do not allow (by simple analytical method) to obtain the dependence of distribution coefficients D and separation coefficients on the concentrations of reagents and on the extraction conditions.

The present study was aimed at creation of the extraction model and application programmes pack for computation of extraction equilibrium.

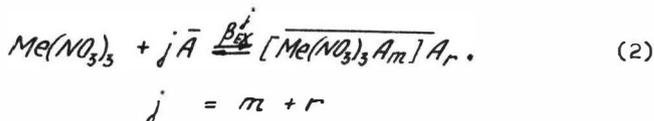
Reactions in extraction system. The association of extractant is as follows (A=TBP or Am):



In eqs.(1) β_i is association equilibrium constant. It is calculated by means of the FORTRAN-Programm KASD [4] from cryoscopic, osmometric and IR-measurements. The extraction of lanthanides from nitrate-medium becomes complicated by formation of complexes of variable chemical composition [5,6]:



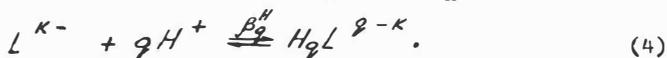
m is the number of coordinated molecules of extractant and r is the number of solvated molecules of extractant. Usually m is equal 2-3. The reactions of extraction of lanthanides are as follows:



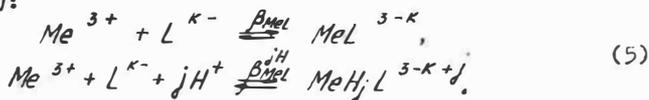
The extraction constants (β_{EX}^j) have been calculated by means of the FORTRAN-programme TASER [5] from extraction data of systems with high concentration of salting-out agent (up to 8 M LiNO₃). In this programme the activity coefficients of all species are supposed to be equal to 1. Lanthanides react with NO₃⁻-ions in the aqueous phase:



The constants $\beta_{Me}^{(p)}$ have been obtained from extraction data. There is also acid-base equilibrium of the complexon (H_kL) in the aqueous phase.



As a rule the lanthanides form normal and protonated complexes with complexons [7]:



Dissociation constants of complexons and stability constants of lanthanides with complexons have been determined from EMF-titration data of solutions with high concentration of NO₃⁻ ion (up to 8 M LiNO₃; 7 M NH₄NO₃).

All the constants required for calculation of D have been determined by independent experiments.

The extraction model. To calculate D it is necessary to find equilibrium concentrations of extracted species in organic phase and the analogous concentrations of complexes of REE in the aqueous phase.

Use of matrix writing allows to compactly record laws of mass action, conservation of mass and conservation of electric charge. The elements of last column of stoichiometric matrix A are decimal logarithms of stability constants of species formed from basic species. The rest of the columns are the stoichiometrical coefficients. The elements of vector X are decimal logarithms of concentrations of basic species, the last element of vector X being equal to 1. The elements of vector EC are decimal logarithms of concentrations of formed species.

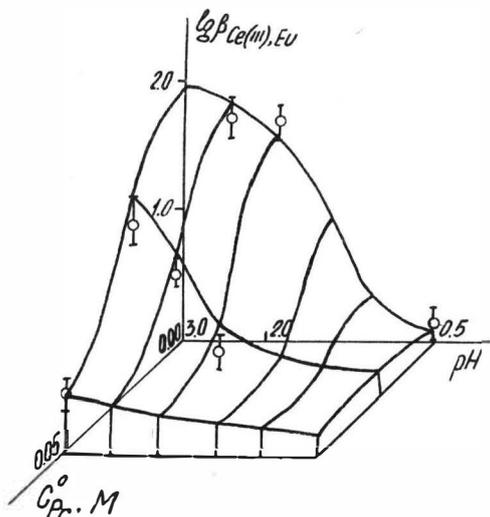
The law of mass action with law of conservation of electric charge are as follows:

$$A \times X = EC. \quad (6)$$

The law of conservation of mass is as follows:

$$A \times 10^{EC} + 10^X = C_0. \quad (7)$$

The sign "T" means the matrix is to be transposed. Record 10^X is



Dependence of separation coefficient of Ce(III), Eu on pH of aqueous phase and on initial concentration of $\text{Pr}(\text{NO}_3)_3$. Extractant: 0,2 M MDOA·HNO₃ in benzene. Aqueous phase 7 M LiNO₃. Initial concentrations of Ce(III) and Eu are equal to 0.0167 M

a vector Y. The elements of vector Y are obtained as follows:

$$Y(I) = 10^{X(I)}, \quad I = 1, 2 \dots \quad (8)$$

In eqs. (7) C_a - is the vector of analytical concentration of basic species.

The last row of eqs. (7) is not taken into account while summing up. As follows from eqs. (6) and (7):

$$A^T \times 10^{A \times X} + 10^X = C_a. \quad (9)$$

The existence and uniqueness of a solution of eqs. (9) is proved in article [8]. We used the method of Fletcher and Powell [9] for solving of eqs. (9) by means of FORTRAN-programme KARNEL. This programme allows to calculate equilibrium concentrations of all the species in extraction systems consisting of 3 complexones (EDTA, DTPA, NTA), 8 lanthanides, and one of 6 possible extractants (TOA, TBP, MDOA, TGA, TAA, TLA).

The verification of extraction model. The verification of model has been made for different combinations of lanthanides in micro- and macroconcentrations. For example the separation coefficients of mac-

roconcentration of Ce (III) and Eu in the extraction system with variable concentration of Pr and variable pH have been computed by means of programme KARNEL. The results of computing (hard lines) and experimental data (circles) have a good agreement (see Fig.).

This mathematical model and programme KARNEL has been shown to allow satisfactorily describe the influence of various factors (nature and concentration of extractant, complexon, R_{EE}, salting-out agent) on distribution of lanthanides in multicomponents extracting systems with associated extractants and complexons.

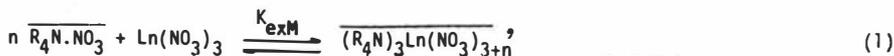
References

1. Petkovic D.M. // J. Inorg. Nucl. Chem. 1968. Vol. 30, N2. P. 603-609.
2. Burtsev I.A., Afonin M.A., Lucin J.A. // Vsesojuznaja Conferentsija po primeneniju extractsionnyh i sorbtsionnyh metodov dlja vydelenija i razdelenija actinidov i lanthanidov. Moscow, 24-26 september 1984: Tez. dokl. M.: Nauka, 1984. P. 18.
3. Komarov E.V., Komarov V.N. // Uspechi Khimii. 1974. Vol. 43, N 4. P. 632-654.
4. Projajev V.V., Afonin M.A., Kopyrin A.A., Komarov E.V. // 7 Vsesojuznaja Conferentsija po Khimii Extractsii. Moscow, 12-14 november 1984: Tez. dokl. M.: Nauka, 1984. P. 104.
5. Afonin M.A., Komarov E.V., Kopyrin A.A., Kapranchik V.P. // Ibid. P. 129.
6. Poczynailo A., Danesi R.R., Scibona G. // J. Inorg. Nucl. Chem. 1973. Vol. 35, N 6. P. 3249-3255.
7. Kostromina N.A. Complexonates of rare earth elements. M.: Nauka, 1980. P. 219.
8. Zeldovitch J. // Z. Phys. Khim. 1938. Vol. 11, N 5. P. 685-688.
9. Fletcher R., Powell M.J.D. // Computer J. 1963. Vol. 6, N 2. P. 163-168.

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High Molecular Weight Amines (HMWA) can extract rare earth elements efficiently only in the presence of extraction supporting electrolytes. It is caused by difficult complexation of lanthanoids in aqueous phase. They form nitrate adducts in acid environment which are extracted as HMWA anions. From all amines the ammonium salts are the best extractants for lanthanoids from nitrate solution. The formation of the addition product can be described by the chemical reaction:

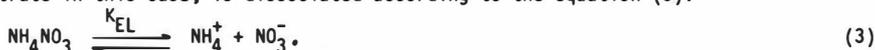


where $Ln(NO_3)_3$ denotes all species that can react with $\overline{R_4N \cdot NO_3}$ to extracted complex.

Undissociated $Ln(NO_3)_3$ is in equilibrium with nitrate anions in aqueous phase:

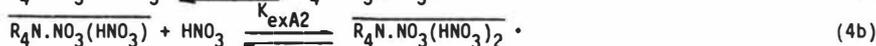
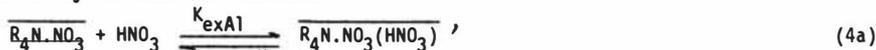


The supporting electrolyte increases the concentration of NO_3^- ions in aqueous phase and shifts the equilibrium (2) to the right. The supporting electrolyte, ammonium nitrate in this case, is dissociated according to the equation (3):



The value of the extraction constant K_{exM} and of the stoichiometric coefficient n depends on the atomic number of the lanthanoid. The value of K_{exM} monotonously decreases with the atomic number if a quaternary ammonium nitrate or a tri-*n*-octylammonium nitrate are the extractants⁽¹⁾. The stoichiometric coefficient depends on coordination number of the element and is higher for lighter lanthanoids⁽²⁾.

HMWA are excellent extraction agents for inorganic acids. Consequently, it is necessary to take into account the coextraction of HNO_3 if RE elements are extracted from acid environment. Nitric acid forms addition products with quaternary ammonium nitrate by consecutive reactions



Undissociated form of HNO_3 is in equilibrium with nitrate ions:



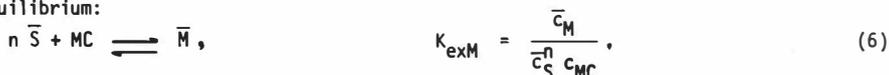
The supporting electrolyte enhances HNO_3 extraction as well, because it shifts equilibrium (5) to the left side.

The aggregation of amine salts in the organic phase was taken into account since we are dealing with the system with a high dipole moment of the strong basis and a relatively low permittivity of the solvent.

Three elements of rare earths (lanthanum, neodymium and gadolinium) were selected for the extraction according to (1). Coextraction of HNO_3 described simultaneously by reactions (4a) and (4b), was investigated in the system with lanthanum. The great deal of equilibrium measurements was performed with tri-alkylmethylammonium nitrate in xy-

lene, prepared by converting Aliquat 336 with HNO_3 . The nitrate of tri-n-octylamine was used in additional experiments. Two levels of total concentration of extractant were used in experiments: 0.2M or 0.05M. The lanthanoid nitrate concentration in the aqueous phase varied from 0.001M up to the solubility limit. Ammonium nitrate was added to total nitrate concentration 4M or 8M. The acidity of the aqueous phase was adjusted to pH=2 by nitric acid. In the investigation of HNO_3 coextraction, the pH value was set to 1.9 or 0.9. The extraction of HNO_3 alone was studied in the concentration range 0.001M to 2M at nitrate concentration 4M and 8M. The equilibrium concentrations of RE elements in both phases were determined complexometrically after a stripping of the organic phase with diluted HNO_3 .

The extraction constant K_{exM} of the extraction of the RE elements by (1) defines equilibrium:



The concentration of the undissociated nitrate of RE elements c_{MC} in eqn. (6), can be expressed by means of dissociation constant K_M and nitrate anion concentration c_N :

$$c_{\text{MC}} = K_M c_N^3 c_M / (1 + K_M c_N^3). \quad (7)$$

The extraction constants for equations (4a) and (4b) are defined as:

$$\bar{S} + \text{AC} \xrightleftharpoons{K_{\text{exA1}}} \bar{A1}, \quad K_{\text{exA1}} = \bar{c}_{A1} / (\bar{c}_S c_{AC}), \quad (8)$$

$$\bar{A1} + \text{AC} \xrightleftharpoons{K_{\text{exA2}}} \bar{A2}, \quad K_{\text{exA2}} = (\bar{c}_A - \bar{c}_{A1}) / (2\bar{c}_{A1} c_{AC}). \quad (9)$$

The equilibrium concentration of the undissociated complex c_{AC} in (8) and (9) is:

$$c_{AC} = c_A c_N / (K_A + c_N). \quad (10)$$

Concentration of nitrate anion c_N in (7) and (10) can be determined on the basis of analytical concentrations of acid c_A and lanthanoid c_M by solving eqn. (11) and (12)

$$c_N = \frac{-K_A - K_{EL} + \sqrt{(K_A + K_{EL})^2 + 4(c_A K_A + c_{ELT} K_{EL} - K_A K_{EL} - p)}}{2}, \quad (11)$$

$$p = ((1 - c_{ELT} K_{EL} K_A K_M - c_A K_{EL} K_A K_M) c_N^3 + (K_A + K_{EL} - 3c_A) c_N^2 + (K_{EL} K_A - c_{ELT} K_{EL} - K_A c_A - 3c_M K_{EL} - 3c_M K_A) c_N - K_{EL} K_A (c_{ELT} + c_A + 3c_M)) / (K_M c_N^4). \quad (12)$$

obtained from material balances of nitrate, acid and lanthanoid in aqueous phase.

Equilibrium concentration of the extractant \bar{c}_S in (6) and (8) is the concentration of the amine salt in the form which really participates in reaction, i.e. monomeric form. Because of lack of direct information about non-ideal behaviour of the organic phase, the extent of the aggregation which blocks extractant for the lanthanoid extraction was described by the so called series model of polymerization⁽³⁾:

$$\bar{c}_S = \bar{c}_{SF} (1 - K_P \bar{c}_S)^2, \quad (13)$$

where \bar{c}_S is concentration of the extractant in monomeric form.

Concentration of the free amine \bar{c}_{SF} (including monomer and polymer as well) is related to the total amine concentration in system, \bar{c}_{ST} , by mass balance:

$$\bar{c}_{SF} = \bar{c}_{ST} - n \bar{c}_M - (\bar{c}_A + \bar{c}_{A1}) / 2, \quad (14)$$

where the last term accounts for the amount of extractant bound with HNO_3 .

Equations (6) to (14) describe extraction equilibria in the system containing RE

element and nitric acid. The general mathematical model reduces to the description of the extraction of nitric acid alone and an RE element alone for special cases.

The experimental data were fitted by the proposed model by means of a nonlinear programming system DEMING⁽⁴⁾. This system used maximum likelihood method of parameters estimation in implicate models and takes in account that all variables are measured with errors. The parameters of the model, stoichiometric coefficient n , extraction constants K_{exA1} , K_{exA2} and K_{exM} were estimated from the dependences of analytical concentrations of La, Nd and Gd (\bar{c}_M, c_M) and nitric acid (\bar{c}_A, c_A) in both phases, as well as dissociation constants of the nitric acid K_{A^*} , of the supporting electrolyte K_{EL} and of the rare earth nitrates $1/K_M$. The calculation indicated that parameters of the model are strongly concentration dependent, which can be expected with regard to the non-ideality of both phases. The primary salt effect (salting-out of amines) varies with a change of total supporting electrolyte concentration (from 4M to 8M). That is why the estimated values of parameters for each experimental data set are varied only within narrow range of experimental conditions.

Measured and calculated data are plotted in Figure 1-3. A typical set of estimated constants, related to data in Figure 1, is given in Table 1. The stoichiometric coefficient 3 was found for La and Nd extraction, while the value 2 for Gd extraction. It follows from the values of polymeration constants K_p that the aggregation of the amine nitrate has an important effect in the concentration region (about 5 % wt. of the amine) used in practice. Isotherms of the extraction of HNO_3 alone in Figure 2 show that their shape is changing in the presence of the supporting electrolyte. The isotherm is S-shaped in the system without NH_4NO_3 , which indicates a low value of the extraction constant of the first HNO_3 addition step and higher value of the second. On the other hand, the figure indicates that the extraction constant of the first step is high and that of the second is negligible if NH_4NO_3 is present in aqueous phase. Simultaneous extraction HNO_3 and RE elements is illustrated in Figure 3. Estimated parameters from the coextraction experiments indicate two opposite roles of HNO_3 . Nitric acid suppresses polymeration in the organic phase, thus the fraction of monomer in free extractant is increased, but simultaneously coextraction of HNO_3 has a negative influence upon extent of RE element extraction, as amine nitrate is bound by HNO_3 . The optimum acidity of aqueous phase was found around $pH = 2.5$.

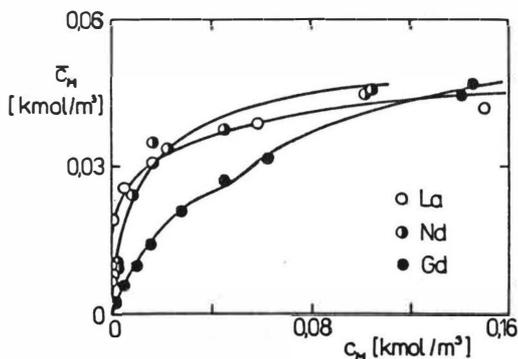


Fig. 1.
Extraction of RE elements by
0.18M nitrate of Aliquat 336
in 8M NH_4NO_3

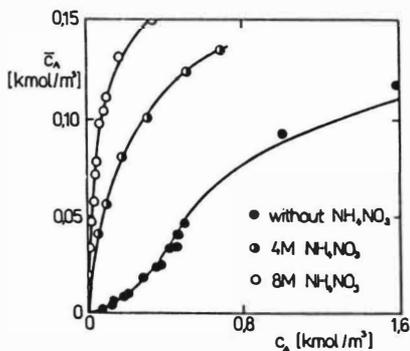


Fig. 2. Extraction of HNO_3 by 0.18M nitrate of Aliquat 336

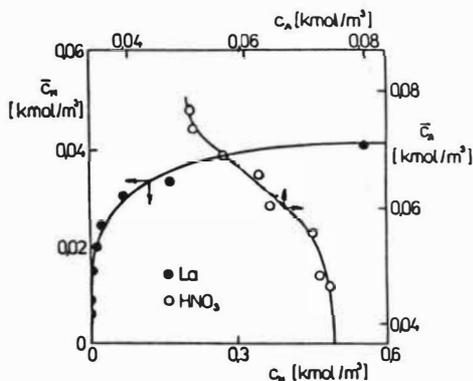


Fig. 3. Extraction of lanthanum by 0.18M nitrate of Aliquat 336

Table 1. Estimated parameters of the model of RE elements extraction

Element RE	Extraction constants $K_{ex} \cdot 10^3$ (m^3/kmol) ³	Stoich. coeff. n	Dissociation constants		Polymeration constants K_p (m^3/kmol)	Total nitrates (kmol/m^3)
			K_{EL} (kmol/m^3)	$1/K_M$ (kmol/m^3) ³		
La	2.4	3	0.44	1.6	15.	4.
La	297.0	3	1.16	1 000.0	15.	8.
Nd	151.9	3	0.04	6.6	15.	8.
Gd	0.1	2	0.44	7.1	15.	8.

The proposed model is suitable for the RE elements and HNO_3 extraction by tri-n-octylammonium nitrate in the presence of LiNO_3 as well. The stoichiometric coefficient $n=4$ and two steps addition of HNO_3 was found in this case.

Symbols used

\bar{c}, c - concentration in org. and aqueous phase, resp. K - dissociation constant.
 K_{ex} - extraction constant. n - stoichiometric coefficient.

Subscripts

A, A1, A2 - acid analytical, first step, second step (H^+ or HNO_3 in org.).
 AC - extractable complex of acid (HNO_3 aq.).
 EL - supporting electrolyte (NH_4NO_3 aq.).
 M - lanthanoid analytical (Ln^{3+} aq. or Ln in org.).
 MC - extractable complex of lanthanoid ($\text{Ln}(\text{NO}_3)_3$ aq.).
 P - polymeration.
 S, SF - amine monomer, free (quaternary ammonium nitrate).
 T - total value.

References

- Marcus Y., Abrahamer I. // Inorg. Nucl. Chem. 22. 141 (1961).
- Huang Chun-Hui, Jin Tian-zhou et al. // ISEC'86. II-215. Munchen, 1986.
- Whewell R.J., Hughes M.A. // Hydrometallurgy. 4. 109 (1979).
- Bard Y. Nonlinear Parameter Estimation in Engineering and Science. N.Y.: John Wiley & Sons, 1977.

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Although 2-ethylphosphonic acid mono-2-ethylhexyl ester(HEH/EHP,HL) is an excellent extractant for the extraction of rare earths[1], the synergic extraction of rare earth ions by HEH/EHP and 1-phenyl-3-methyl-4-benzol-pyrazolone-5(PMBP, HA) from aqueous mineral acid is not well understood. The synergic extraction of rare earth ions(III) including La, Nd, Gd, Dy, Er, Yb, Lu and Y by HEH/EHP and PMBP in benzene has therefore investigated in detail.

The species of synergic extraction have been determined by slope analysis method. The equilibrium constants and the thermodynamic functions of the synergic reactions have been calculated. The studies of IR and NMR spectra were carried out for the synergic extracted complexes.

Extraction of rare earths(III) with HEH/EHP and PMBP alone

The extraction mechanism of rare earths from HNO₃ solution by HEH/EHP has been studied[2], and the extraction reaction is as follows:

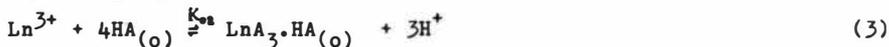


and the equilibrium constant K_{10} can be expressed as

$$K_{10} = \frac{[\text{Ln}(\text{HL}_2)_3]_{(o)} [\text{H}^+]^3}{[\text{Ln}^{3+}] [(\text{HL})_{2(o)}]^3} = \frac{D_1 Y [\text{H}^+]^3}{[(\text{HL})_{2(o)}]^3}, \quad (2)$$

where $Y = 1 + \sum_1^n \beta_n [\text{NO}_3^-]^n$, β represents the overall stability constant of rare earths with nitrate anion ions.

The extraction reaction of rare earths by PMBP has been reported to be much more[3-5]. However, the extraction reaction of rare earths by PMBP under present experimental conditions has been represented by the following equation, viz.



and the equilibrium constant K_{02} can be expressed as

$$K_{02} = \frac{[\text{LnA}_3 \cdot \text{HA}]_{(o)} [\text{H}^+]^3}{[\text{Ln}^{3+}] [\text{HA}]_{(o)}^4} = \frac{D_2 [\text{H}^+]^3}{[\text{HA}]_{(o)}^4}, \quad (4)$$

where D_2 stand for the distribution ratio of rare earth ions with PMBP.

Synergic extraction of rare earths with HEH/EHP and PMBP

As seen from Fig.1 and Fig.2, the synergic effect of rare earths in HEH/EHP-PMBP system has been shown. It has been found that the species of the synergic extraction alone with the different rare earth(III). The mole ratio of HEH/EHP and PMBP is approximately 1:2 for the light rare earths; and 2:1 for the heavy rare earths approximately.

* The Project Supported by National Natural Science Foundation of China.

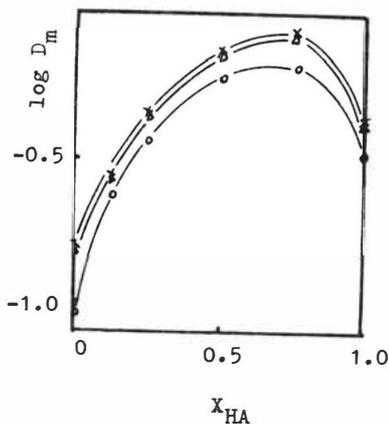


Fig. 1. Plots of $\text{Log} D_m$ vs the mole fraction of X_{HA} constant $C_{tot.} = 0.15M$
 o- $\text{Nd}_2(\text{SO}_4)_3$, Δ - $\text{Nd}(\text{NO}_3)_3$, x- NdCl_3

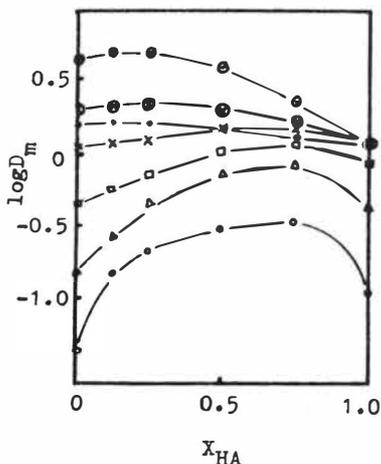
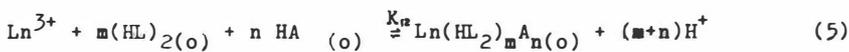


Fig. 2. Plots of $\text{Log} D_m$ vs the mole fraction of X_{HA} constant $C_{tot.} = 0.15M$
 o-La, Δ -Nd, x-Dy
 •-Y, •-Er, •-Yb

Mechanism of the synergic extraction of rare earths(III) with HEH/EHP-PMBP

The synergic extraction reaction of rare earths with HEH/EHP-PMBP from nitrate solution can be assumed as follows:

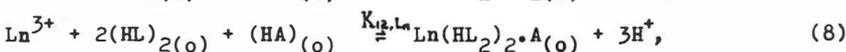
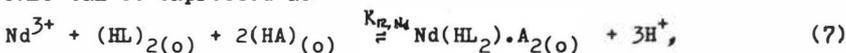


and the equilibrium constant K_{12} can be expressed as

$$K_{12} = \frac{[\text{Ln}(\text{HL}_2)_m \text{A}_n]_{(\text{o})} [\text{H}^+]^{(m+n)}}{[\text{Ln}^{3+}]_{(\text{o})} [(\text{HL})_2]_{(\text{o})}^m [\text{HA}]_{(\text{o})}^n} = \frac{D_{12} Y [\text{H}^+]^{(m+n)}}{[(\text{HL})_2]_{(\text{o})}^m [\text{HA}]_{(\text{o})}^n}, \quad (6)$$

where D_{12} represents the distribution ratio of the synergic extraction of rare earths with HEH/EHP and PMBP. Then the synergic extracted species has been determined by the method of slope analysis. Results shown in Fig. 3 and Fig. 4 suggest that the coefficients of the synergic reaction is $m=1, n=2$ for Nd^{3+} and $m=2, n=1$ for Yb^{3+} and Lu^{3+} respectively. The value of $(m+n)$ can be confirmed to be 3 in Fig. 5.

Accordingly, the synergic reaction of rare earths(III) with HEH/EHP-PMBP can be expressed as



where $\text{Ln} = \text{Yb}^{3+}, \text{Lu}^{3+}$. The equilibrium constant K_{12} can be represented by the Equation (9), (10) viz.

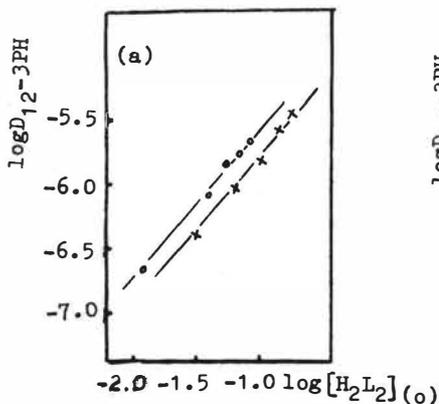


Fig. 3. (a). Relationship of $\text{Log}D_{12}$, Nd to $\text{Log}[H_2L_2]_{(o)}$ at constant $[HA]_{(o)}=0.05M$,
o- PH=2.53, x- PH=2.98

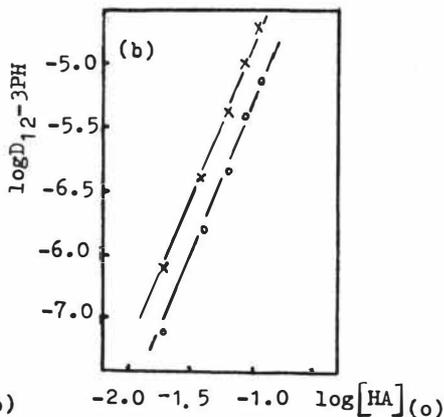


Fig. 3. (b). Relationship of $\text{Log}D_{12}$, Nd to $\text{Log}[HA]_{(o)}$ at constant $[H_2L_2]_{(o)}$
o-o-0.037M, x-0.113M

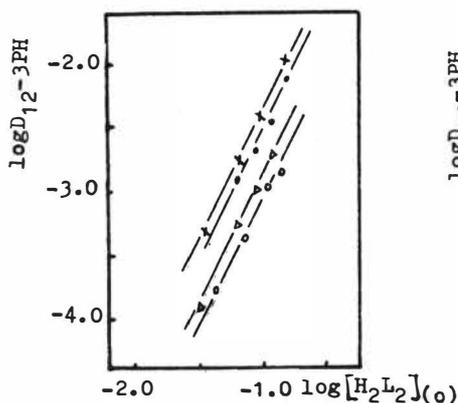


Fig. 4. (a). Relationship of $\text{Log}D_{12}$ to $\text{Log}[H_2L_2]_{(o)}$
to $\text{Log}[H_2L_2]_{(o)}$
X-Yb PH=0.60, O-Yb PH=2.64
•-Lu (HA)=0.05M, Δ-Lu (HA)=0.025M

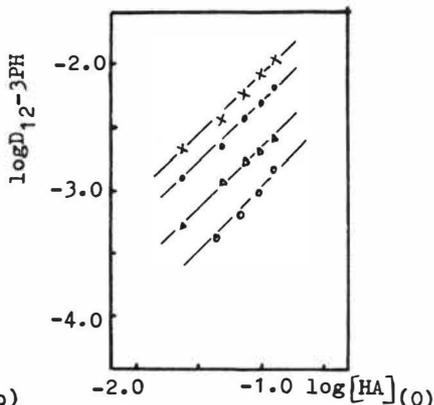


Fig. 4. (b). Relationship of $\text{Log}D_{12}$ to $\text{Log} HA_{(o)}$
 $\text{Log}D_{12}$ to $\text{Log} HA_{(o)}$
X-Yb PH=0.60, O-Yb PH=2.64
•-Lu $(H_2L_2)=0.113M$,
Δ-Lu $(H_2L_2)=0.075M$

$$K_{12, Nd} = \frac{[Nd(HL_2)_2 \cdot A_2]_{(o)} [H^+]^3}{[Nd^{3+}] [(HL)_2]_{(o)}^2 [(HA)]_{(o)}^2} = \frac{D_{12} \gamma [H^+]^3}{[(HL)_2]_{(o)} [(HA)]_{(o)}^2}, \quad (9)$$

$$K_{12, Ln} = \frac{[Ln(HL_2)_2 \cdot A]_{(o)} [H^+]^3}{[Ln^{3+}] [(HL)_2]_{(o)}^2 [(HA)]_{(o)}} = \frac{D_{12} \gamma [H^+]^3}{[(HL)_2]_{(o)}^2 [(HA)]_{(o)}} \quad (10)$$

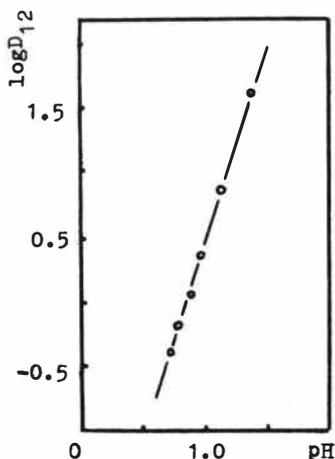


Fig. 5. Relationship of $\text{Log}D_{12}$ to PH, constant $\text{Yb}(\text{NO}_3)_3 = 0.015\text{M}$, $(\text{H}_2\text{L}_2)_{(o)} = 0.15\text{M}$, $(\text{HA})_{(o)} = 0.05\text{M}$

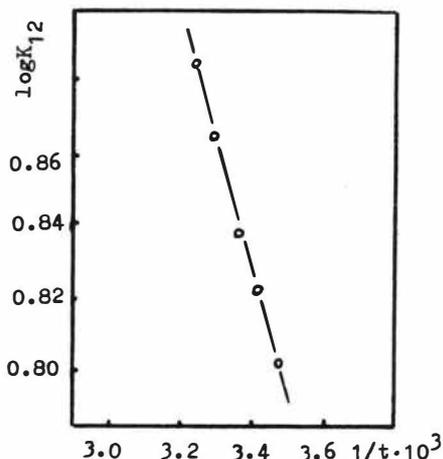


Fig. 6. Relationship of $\text{Log}K_{12}$ to $1/T$, constant $\text{Yb}(\text{NO}_3)_3 = 0.015\text{M}$, $(\text{H}_2\text{L}_2)_{(o)} = 0.15\text{M}$, $(\text{HA})_{(o)} = 0.05\text{M}$

Calculation of the equilibrium constants and thermodynamic functions

Under the experimental conditions, according to $\beta_n [6]$, the equilibrium constants of the synergic reactions can be calculated to be $\text{Log}K_{12, \text{Nd}} = -0.707$, $\text{Log}K_{12, \text{Yb}} = 1.041$ and $\text{Log}K_{12, \text{Lu}} = 0.874$ respectively. The thermodynamic functions of the synergic extraction reactions were measured to be $\Delta H_{12} = 6.133 \text{KJ} \cdot \text{mol}^{-1}$, $\Delta G^0 = -4.832 \text{KJ} \cdot \text{mol}^{-1}$ and $\Delta S^0 = 36.77 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ in terms of the slope in Fig. 6 at 25°C .

IR and NMR spectra of the synergic extracted complexes

Results obtained from the IR and NMR spectra of the synergic extracted complexes have been shown that ligand both PMBP and HEH/EHP are the solvating molecular exist in the synergic extracted complexes. This is in good agreement with the former results.

References

1. Li Deqian et al.//ISEC'80. Liege, Belgium, 1980. No. 80-202.
2. Li Deqian Zhang Jie and Xu Min//Chinese Journal of Applied Chemistry. 1985. Vol.2, N 2. P.17.
3. Roy A., Nag K.//J. Inorg. Nucl. Chem. 1978. Vol.40. P331.
4. Liu Jianmin, Yang Rudong, Ma Tairu.//Chemical Journal of Chinese Universities. 1980. Vol.1. P.23.
5. Chen Tian et al.//KeXue TongBao. 1983. Vol.28. P.1237.
6. Peppard D.F. et al.//J. Inorg. Nucl. Chem. 1962. Vol.24. P.881.

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The extraction of Rare Earth(SE) nitrates of the elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Tm, Lu and Y was experimentally investigated by using 50% tri-n-butyl phosphate(TBP) as extractant and a mixture of n-alkanes(Parex Paraffin) or of aromatic hydrocarbons each in a boiling range of 453 to 493 K.

Varying in a wide range the concentration of the Rare Earth nitrates in the aqueous phase from 0 to 2.5 moles/l, the salting concentration from 0 to 1 mole/l magnesium nitrate, and the concentration of the nitric acid from 0 to 3 moles/l the distribution ratios (D_1) were determined. The separation factors and quasi-equilibrium constants (\bar{K}_1) of the Rare Earths are calculated.

Based on the experimentally determined and balanced distribution data for the systems consisting each of a macro-component and of the other SE as micro-component the mathematical modelling of the distribution ratios and separation factors was obtained (see figure 1).

The distribution coefficients, separation factors, and quasi-equilibrium constants of the corresponding macro-component were then expressed as power function of the aqueous and of the organic SE total concentration.

From this the distribution ratios and separation factors in any desired mixtures can be calculated combining the equations for the macro-components according to their mole fractions. The obtained precision is good.

The mathematical presentation of the system expanded by acid and magnesium nitrate was obtained in the same way founded on the three-dimensional distribution isothermes of the macro-components and of the nitric acid at constant magnesium concentration. The salting concentration was either 0.5 or 1 moles/l (see figure 2).

The distribution ratios and the separation factors were calculated as a function of the concentrations of the nitrate and of the free extractant for some selected Rare Earths. The equations were linear-

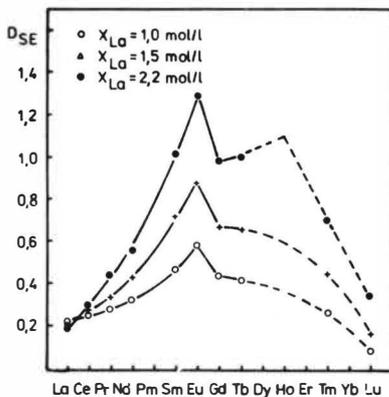


Fig.1. Distribution coefficients of SE at different aqueous equilibrium concentrations of Lanthanum in diluent Parex Paraffin

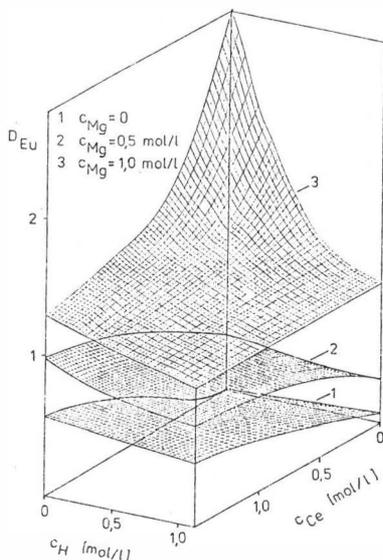


Fig.2. D_{Eu} in the system $Ce(NO_3)_3$ - HNO_3 - $Eu(NO_3)_3$ (0.02 M)- $Mg(NO_3)_2$ -50% TBP in Parex Paraffin

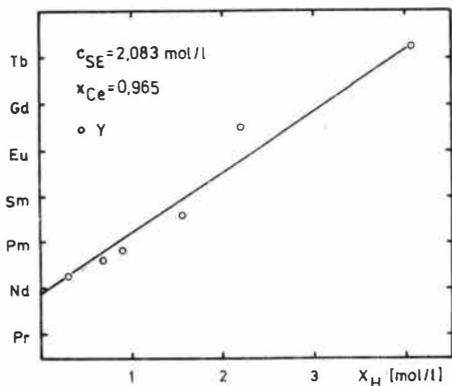


Fig.3. Position of Yttrium as a function of nitric acid concentration and Cerium as macro-component

ly correlated to the mole fractions for the calculation of mixtures consisting of several SE. The obtained precision is sufficient. As expected the presentation of Yttrium in the equation systems is complicated since the position of Yttrium in the extraction sequence is more significantly altered either by the equilibrium concentration of the Rare Earths as by the nitric acid concentration, too (Fig.3).

^{31}P , ^{45}Sc NMR COMPARISON OF MECHANISMS OF RARE METALS EXTRACTION BY SOLVENT EXTRACTANTS AND ONES INTRODUCED IN TVEX POROUS MATRIX

7-10

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The materials of new type known in the USSR as solid extractants (TVEX) [1] and as Levextrel [2] abroad are of high interest nowadays. These materials represent porous polymer matrix with extractant introduced during its synthesis. It was interesting to study TVEX matrix influence on the rare metals extraction.

Figure 1 illustrates the main porous characteristics of the TVEX styrene-divinylbenzene (SDVB) matrix according to data of mercury porosimetry and nitrogen adsorption. The data received show that the average pore radius of the TVEX now widely used (50-60% TBP and 20-25% DVB) equals 150 Å.

The linewidth in the ^{31}P NMR spectra of TVEX-TBP is 1,5-2,0 times exceed the linewidth in spectra of liquid TBP. This fact testifies that the extractant exists as liquid in the polymer matrix.

The constant phosphorum emission intensity along the diameter of TVEX bead's cross section show the uniform distribution of extractant in the porous matrix. This probab-

ly distinguishes TVEX from the SDVB impregnate, which is characterized by TBP concentration lowering to the centre of the bead.

IR- (the absence of functional groups' vibration shifts) and ^{31}P NMR (the absence of chemical shifts relatively liquid TBP) data and the value of the extractant's adsorption heat on the matrix, equaled $45 \pm 0,1$ kJ/mol reveal that TBP is confined in the TVEX matrix by the physical adsorption. The dependence of equilibrium extractant's distribution between aqueous phase and TVEX matrix has typical S-form. This fact shows that the part of TBP has created the polymolecular adsorbed layer on the matrix surface.

The study of exchange of free and coordinated to the different metal ions TBP results the fact that the whole extractant in TVEX matrix is able to create the solvate bonds with the extracted component.

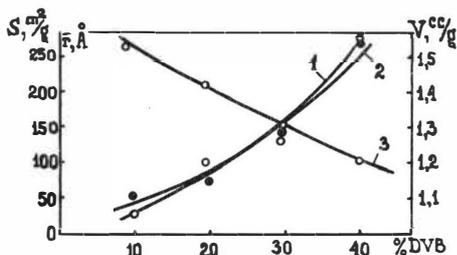


Fig.1. The dependence of the surface area (1), pore volume (2) and average pore radius (3) for TVEX-TBP 60% to the bead's centre

Thus, the extractant in the TVEX matrix (50% TBP and 25% DVB) exists as liquid in pores with average pore radius 150 Å. The extractant is uniformly distributed in the whole bead's volume, confined by the physical adsorption and accessible for the reaction with the removal component. Hence, the physico-chemical properties of extractants introduced in TVEX matrix have not been changed and the main mechanisms of solvent extraction remain for TVEX.

Our investigations show the absence of differences between the extraction of Zr and Hf [3] (Fig.2), La and Ce [4] by solvent extraction and by TVEX on their base.

However, it was determined that the extraction capacity of TBP in TVEX matrix is higher as compared with liquid TBP under the Sc extraction from hydrochloric solutions (Fig.2).

We have investigated the mechanisms of Zr, Hf and Sc extraction by liquid TBP and by TVEX-TBP using the NMR method in order to make clear the reasons of the differences between solvent and TVEX extraction.

One can observe the signals of free and coordinated with metals TBP

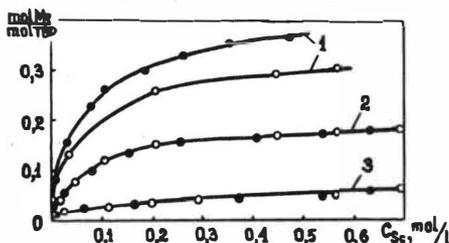
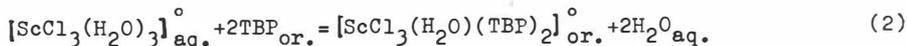
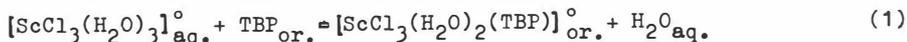


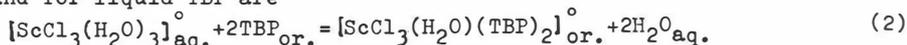
Fig. 2. Extraction isotherme of Sc (1) from 8M HCl, Zr (2) and Hf (3) from 6M HNO₃ by liquid TBP (o) and by TVEX-TBP (•)

in the NMR spectra of Zr, Hf and Sc extracts (Fig.3a). The average solvate number (ASN) of Zr, Hf and Sc on TBP have been calculated according to the relation between TBP signals in every isotherme point. The value of ASN for Zr and Hf equals 2,0±0,1 both for liquid TBP and TVEX-TBP. This fact testifies that Zr and Hf have been extracted as disolvates by liquid TBP and by TVEX-TBP.

ASN value for Sc extract is within the limit of 2,7-3,5 for liquid TBP and within the limit of 1,3-1,7 for TVEX-TBP. These facts reflect the different mechanisms of Sc extraction by liquid TBP and by TVEX-TBP. According to ⁴⁵Sc NMR spectra (Fig.4) Sc has been extracted by TVEX-TBP as two complexes and by liquid TBP as four ones. According to [5] Sc chloroaquacomplexes' mixture is in hydrochloric solutions. Therefore extraction equilibriums for TVEX are



and for liquid TBP are



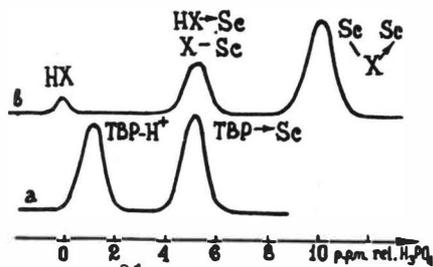


Fig. 3. ^{31}P NMR (81,0 MHz) spectra of TVEX-TBP (a) and D2EHPA in CCl_4 (b) after Sc extraction from 8M HCl

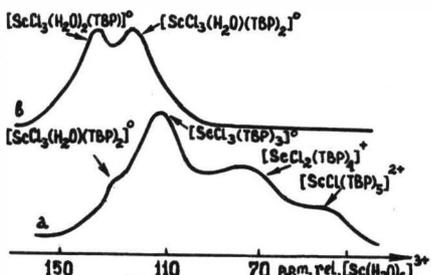
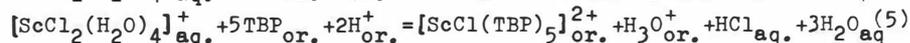


Fig. 4. ^{45}Sc NMR (48,6 MHz) spectra of liquid TBP (a) and TVEX-TBP (b) after Sc extraction from 8M HCl



The differences between mechanisms of Sc extraction cause apparently the higher capacity of TBP in TVEX. One may note that while using TVEX there are no complexes in organic phase, which contain more than two TBP molecules in coordinated sphere. The creation of such complexes in porous TVEX matrix is somewhat impede because the average pore radius equals 150 Å, as mentioned above.

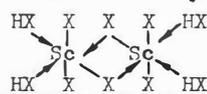
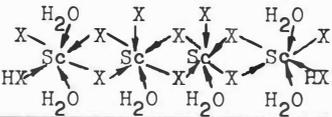
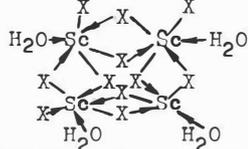
Thus, the TVEX matrix is not only inert carrier but it can change the mechanism of extraction of aimed component in some cases.

To compare the influence of the inert diluent and TVEX matrix on the extraction mechanisms is of great interest. For this purpose the composition and structure of Sc complexes extracted by pure D2EHPA (HX) 0,3 M HX solution in CCl_4 and TVEX-48% HX have been studied by ^{31}P and ^{45}Sc NMR method.

One broad signal has been observed in ^{45}Sc NMR spectra of all extracts. Its position (3 p.p.m. relatively $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$) shows that there are no Sc complexes with Cl-ions in the first coordinate sphere. There are 3 signals in ^{31}P NMR spectra of extracts received: free HX signal, signal of HX combined with Sc by one link (HXmon), signal of HX reacted with Sc by two links (HXbid). Hence, it is possible to use ^{31}P NMR method to determine the ASN of HX and the relation between bidentate and monodentate HX molecules in polymer complexes created in extracts. Taking into account the absence of Cl-ions in the extraction complexes the data obtained allow to determine the composition and the structure of the compounds removed (Table 1).

Table 1 shows that the mechanism of Sc extraction has been changed under the influence both of HX dilution and its introduction in TVEX matrix. There are different reasons evoked this fact for the examined

Table 1. The ASN value and most probable structure of Sc extracts

Extract	M HCl	HX/Sc	ASN	HXbid HXmon	Structure of the extract
Pure HX	1	17,68	5,90	0:1	$[\text{ScX}_3(\text{HX})_3]^{\circ}$
	8	10,93	5,53	1:6	the mixture of $[\text{ScX}_3(\text{HX})_3]^{\circ}$ and 
0,3M HX so- lution in CCl ₄	1	3,83	3,15	1:1	
	8	2,96	2,96	2:1	
TVEX-HX	1	3,95	1,17	0:1	$[\text{Sc}(\text{H}_2\text{O})_5\text{X}]^{2+}$
	8	5,50	2,68	1:30	$[\text{Sc}(\text{H}_2\text{O})_3\text{X}_3]^{\circ}$

cases. The CCl_4 dilution of HX involve the dielectric constant lowering and association of polar complexes with the polymer structure. The creation of forms such as $[\text{ScX}_3(\text{HX})_3]^{\circ}$ and the polymer complexes (Table 1) is somewhat difficult in TVEX matrix. This fact determines the Sc extraction as $[\text{Sc}(\text{H}_2\text{O})_3\text{X}_3]^{\circ}$ and $[\text{Sc}(\text{H}_2\text{O})_5\text{X}]^{2+}$ by TVEX.

Thus, the investigations carried out show that the presence of polymer matrix may change the extraction mechanism in some cases. We may observe the influence of polymer matrix for the metals which simultaneously are extracted in a few forms.

References

1. Kuzovov Yu. I., Korovin V. Yu., Kodubenko L. K. // Tr. Mosc. him.-tehnol. in-ta. 1977. Vol. 97. P. 43-47.
2. R. Kroebel, A. Mayer // Proc. Int. Solvent Extraction Conference (Lyon), 1974. N 56. Vol. 3. P. 2095-2107.
3. Korovin V. Yu., Savel'eva V. I., Kuzovov Yu. I. // Tr. Mosc. him.-tehnol. in-ta. 1982. Vol. 125. P. 55-58.
4. Yagodin G. A., Savel'eva V. I., Kireeva G. N. et al. // Izvestiya vuzov, himiya i him. tehnologiya. 1984. Vol. 27, N 10. P. 1179-1184.
5. Kirakosyan G. A., Tarasov V. P. // Koordinatsionnaya himiya. 1982. Vol. 2. P. 261-267.

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It is well known that pertechnetetic acid and pertechnetates of different metals are extracted by tributylphosphate (TBP), either diluted or not (1-4). The object of this work is to show that it is possible to predict distribution coefficients of technetium from rather complex solutions, using a modern interpretation of salting-out effects which has been exposed in details elsewhere (5-6). According to this theory, the activity coefficient of any species in the aqueous phase may be expressed by the ratio between a function of the water activity in the system characteristic of the species and the total concentration of species in the aqueous phase :

$$y_i \approx \frac{f_i(a_w)}{\sigma}$$

On the other hand, the activity coefficient of any species in the organic phase depends only on the water activity in the system :

$$\bar{y}_i = \bar{f}_i(a_w)$$

As a consequence, any reaction in aqueous solution as well as any distribution equilibrium may be characterized by a function of the water activity, related to the concentration equilibrium constant for any specific medium defined by the values of a_w and σ :

$$Kc = G(a_w) \cdot \sigma^\lambda$$

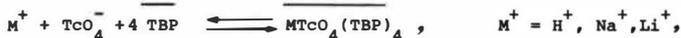
General experimental conditions were : temperature 22 °C, technetium concentration 1.5×10^{-5} M, TBP 30 % v/v in dodecane, water activity between .6 and 1, which means a maximum concentration of nearly 6 M for 1:1 electrolytes and 3.5 M for 1:2 salts. HCl, NaCl, LiCl, CaCl₂ and MgCl₂ were used as salting-out agents. Extraction of hydrochloric acid was taken into account. Other salts did not extract. ^{99m}Tc was used as a γ -tracer to measure the distribution coefficients.

We first checked the mechanism of extraction. Experiments at constant a_w , σ and concentration of technetium but varying TBP/dodecane ratio in the organic layer showed that the extracted species contained four TBP molecules in the case of extraction from 1:1 electrolytes and three TBP when the extraction was performed from alkaline-earth chloride solutions.

Experiments realised at constant a_w , σ and TBP concentration showed that during extraction from HCl, NaCl and LiCl solutions the distribution coefficient was independent of the amount of technetium in the system, whereas

with CaCl_2 or MgCl_2 as salting-out agents D was linearly related to the concentration of technetium in the aqueous phase.

On this basis the following distribution equilibria are proposed :



$$G_{\text{ext}}^M = \frac{D \cdot \sigma^2}{(M)(\text{TBP})^4},$$



$$G_{\text{ext}}^{\text{Ca}} = \frac{D \cdot \sigma^3}{(M)(\text{Cl})(\text{TBP})^3}.$$

We further extracted technetium from series of solutions of each salting-out agent at varying concentration and from ternary chloride solutions. The results of the distribution experiments involving HCl , LiCl and MgCl could be explained taking in account only one interference reaction in the aqueous phase : the formation of pertechnetic acid. The water activity functions corresponding to the three distribution equilibria and the formation of HTcO_4 were determined. When sodium or calcium chloride was involved, results could only be explained assuming the formation of the weak complexes NaTcO_4 and CaTcO_4^+ in the aqueous layer. Corresponding water activity functions are reported.

Confirmation of these results was obtained by measuring distribution coefficients of technetium between aqueous layers containing at least three salting-out agents and 30 % TBP in dodecane and comparing the results with calculated values by means of the following expression based on the previously determined water activity functions :

$$\left(G_{\text{ext}}^{\text{H}} [\text{H}] + G_{\text{ext}}^{\text{Na}} [\text{Na}] + G_{\text{ext}}^{\text{Li}} [\text{Li}] \right) \cdot \frac{(\overline{\text{TBP}})^4}{\sigma^2} + \left(G_{\text{ext}}^{\text{Mg}} [\text{Mg}] + G_{\text{ext}}^{\text{Ca}} [\text{Ca}] \right) \frac{[\text{Cl}][\text{TBP}]}{\sigma^3}.$$

$D =$

$$1 + G_{\text{H}} \frac{[\text{H}]}{\sigma} + G_{\text{Na}} \frac{[\text{Na}]}{\sigma} + G_{\text{Ca}} \frac{[\text{Ca}]}{\sigma}$$

Fitness within 8 % between calculated and experimental values was obtained for the distribution coefficients that varied in a range from .1 to 200. Further experiments on extraction of technetium with tetraphenylarsonium chloride confirmed the present results on the stability of the complexes NaTcO_4 and CaTcO_4^+ in concentrated aqueous solutions.

References

1. BOYD G.E., LARSON Q.V. // J. Phys. Chem. 1960. 64. 988.
2. PRUETT D.J. // Radiochimica Acta, 1981. 28. 153.
3. PRUETT D.J. // Radiochimica Acta, 1981. 29, 107.
4. PRUETT D.J. // Radiochimica Acta, 1983. 34. 203.
5. VDOVENKO V.M., RYAZANOV M.A. // Zh. Fiz. Khim. 1968, 42. 1936.
6. PITSCH H., POITRENAUD C. // ISSEC'86, Munchen, FRG.

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Crown compounds have been used in our laboratory for the radiochemical separations of some fission products from irradiated uranium samples .From picrate media Cs, Sr and Ba could be separated selectively using liquid-liquid and extraction chromatographic techniques [1,2] .From HCl and NaOH media iodine I and Tc are separated selectively as $H^+DB18C6I_2Cl^-$ and $Na^+DB18C6 TcO_4^-$ [3,4] .Efficient separation for Tc could be achieved from H_2SO_4 solutions as H^+ crown $TcO_4^- H_2SO_4$ [5] ,where n depends on the initial H_2SO_4 concentration in the aqueous phase .

Basic solutions proved to be good media for the selective separation of Tc from irradiated uranium samples .In this work the distribution coefficients (D) of TcO_4^- ions are determined in the presence of several Uni-and bivalent metal hydroxides using various crown compounds dissolved in 1,2-dichloroethane (DCE). Hydroxide solutions of Li, Na, K, Mg, Ca, Sr and Ba are freshly prepared and standardized by acid-base potentiometric titration .The hydroxides of Rb and Cs are prepared by passing chloride solutions on a strong anion exchange resin . $NH_4^+^{99}TcO_4^-$ is converted to $H^+^{99}TcO_4^-$ by passing on a strong cation exchange resin and determined potentiometrically . The activity of ^{99}Tc was assayed using liquid scintillation counting technique .

The extraction equilibria may be represented by the following relation :



z may equal to 1 or zero. The values of l,m and n depend on the crown cavity size ,substitutions, organic solvent , charge density of the cation and on the relative concentrations of metal : crown [4,6] . At lower concentrations of the univalent metal hydroxides (0.004M) ,Fig.1 shows the relation of log D vs ionic diameter (I.D). Generally the extraction increases with the cationic size reaching a maximum with $Na^+(I.D=1.90^{\circ}A)-12C4$ and $K^+(I.D=2.66^{\circ}A)$ -other crowns .

The maximum at K^+ has already been proved due mainly to the matching of sizes, however 12C4 and 15C5 are smaller than Na^+ and K^+ respectively .The ratio of diameters Na^+ : 12C4 and K^+ : 15C5 are equal to 1.41 and 1.36 respectively . A sandwiched structures for 12C4 has been reported [6] .

The extraction of 0.004M $H^+TcO_4^-$ by the various crowns has also been studied .The order of D values are found to be DB24C8 (0.201)- DCH18C6 (0.188) > 18C6 (0.021)-12C4 (0.021) > 15C5 (0.011) > DB18C6 (0.0042) .

The relation between log D vs I.D was reconsidered at higher concentrations of the cations (Fig.2) .Two main features can be extracted from this figure : first ,is the sharp increase of D values ; second is the change in the sequence of extraction by the various crowns. This may be attributed to the change in the stoichiometry of the extracted species, formation of different types of associated ion pairs (loos ,tight or crown separated ion pairs), inclusion of more than one small cation into the bigger cavities .It should be mentioned that during Cs extraction systems precipitate formation was observed with 12C4, 18C6, DB24C6 and DB18C6 .

As expected bivalent cations give lower D values because of their higher charge densities and subsequently higher hydration energies (Fig.3 and 4) .

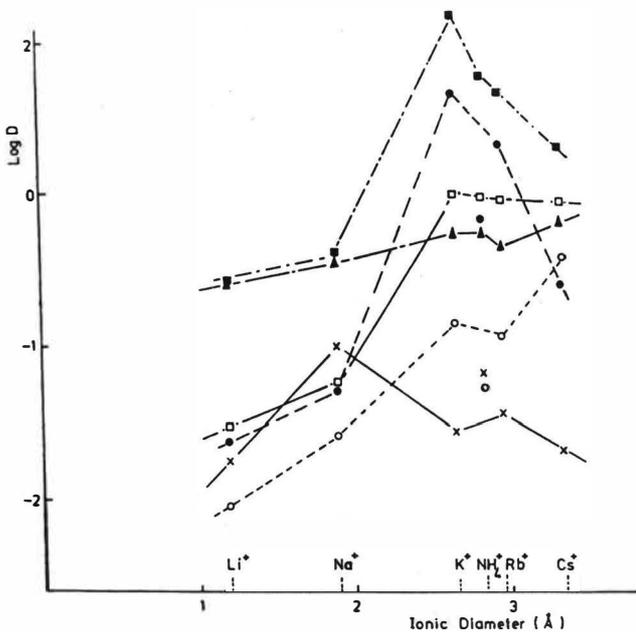


Fig. 1. Plot of $\log D$ of TcO_4^- vs I-D. crown-1,2 DCE/0.004M MeOH.
 x 12C4, ● 15C5, ■ DCH 18C6, ▲ DB 24C8, □ 18C6, ○ DB 18C6.
 DB 24C8, DB 18C6- Cs^+ precipitate formation.

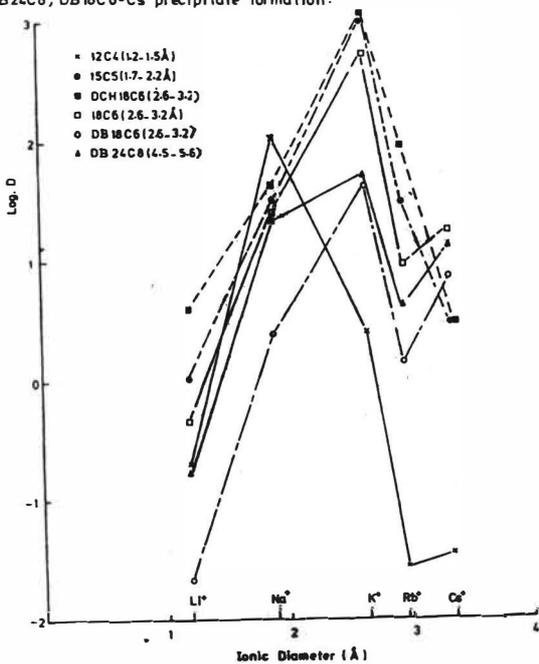


Fig. 2. Plot of $\log D$ of TcO_4^- vs I-D. crown-1,2 DCE/4M MeOH, 0.181M RbOH,
 0.181M CsOH. 12C4, 18C6, DB 18C6, DB 24C8- Cs^+ precipitate formation.

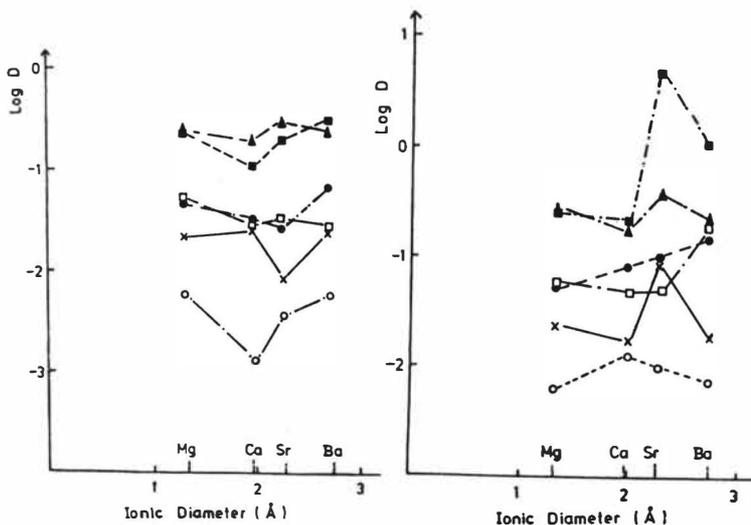


Fig. 3. Plot of log D vs I.D. x 12C4, ● 15C5, ■ DCH18C6, □ 18C6, ○ DB18C6, ▲ DB24C8-1,2DCE/0.004M MeOH.

Fig. 4. Plot of log D vs I.D. x 12C4, ● 15C5, ■ DCH18C6, □ 18C6, ○ DB18C6, ▲ DB24C8-1,2DCE/0.004M Mg(OH)₂, 0.04M Ca(OH)₂, 0.154M Sr(OH)₂, 0.10M Ba(OH)₂.

Slope analysis experiments showed the formation of 1:1 (cation: crown) complexes for Cs and Sr with DB18C6, DCH18C6 and DB24C8, and 2:3 complexes with 12C4. Previous studies [4] revealed that extraction of TcO_4^- increases steadily with the polarity of the organic solvent and with the presence of methanol in the aqueous phase. These conditions might be utilized for the better extraction of Cs and Sr as pertechnetate. The simultaneous separation of Cs, Sr and Tc fission products is of special importance in nuclear technology.

References

1. Jalhoom M.G., Mani I.A., Al-Juburi J.A. // *Radiochimica Acta*, 1985, Vol. 38, P.215.
2. Jalhoom M.G., Mani I.A., Hassan J.A. // *Radiochimica Acta*, 1985, Vol. 38, P.219, .
3. Jalhoom M.G. // *Radiochimica Acta*, 1986, Vol. 40, P.203.
4. Jalhoom M.G. // *J. Radioanal. Nucl. Chem. Letters*, 1986, Vol.104, p.131.
5. Jalhoom M.G. // *Radiochimica Acta*, 1986, Vol. 39, P.195, .
6. Izatt R.M., Christensen J.J. *Progress In Macrocyclic Chemistry*, Vol.2, Wiley-Interscience Publication, 1981,
7. Hiraoka M. *Crown Compounds, Their Characteristics and Applications*, Elsevier, 1982.

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The use of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH/EHP,) as an extractant for thorium(IV) from sulphuric acid solution has been demonstrated by our earlier reports[1]; the present author has previously investigated the extraction mechanism of cerium (IV)[2] and erbium(III)[3] from sulphuric acid solutions by HEH/EHP and it was the purpose of this study to determine the extraction mechanism of thorium(IV) in the sulphate by HEH/EHP.

The partition equilibria of Th(IV) between H_2SO_4 and HEH/EHP in octane were investigated. The extraction mechanism of Th(IV) at different acidities has been discussed with the methods of slope, saturation, IR and NMR. The equilibrium constants and the thermodynamic functions of the extraction reaction have also been calculated.

Extraction equilibrium

The extraction of Th(IV) from its solution(0.0043M) in sulphuric

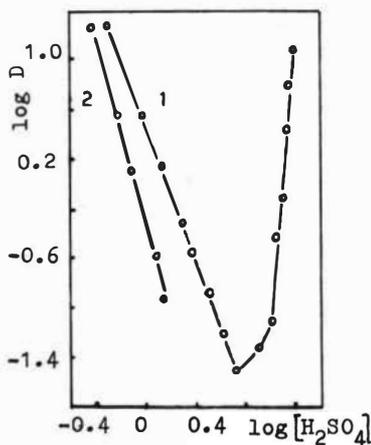
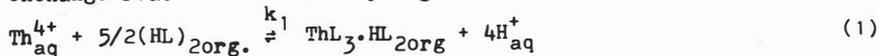


Fig.1. Effect of acidity of equilibrium aqueous phase on Th(IV) extraction by HEH/EHP (1) $\log [H_2SO_4]_{aq}$, (2) $\log [H^+]_{aq}$

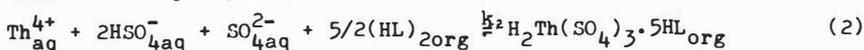
tation of free HEH/EHP. The slopes of the plot of Fig.2(a) are 2.5 at low aqueous acidity. For high aqueous acidity the data of Fig.2(b) also determine a straight line having a slope of 2.5. Thus, the extraction mechanism of Th(IV) in the sulphate system by HEH/EHP could be written

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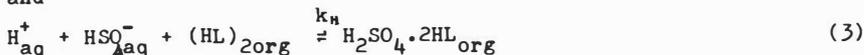
as follows: at low aqueous acidity, Th(IV) is extracted by a cation-exchange reaction in which hydrogen ion is displaced:



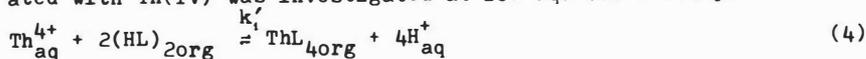
and at high aqueous acidity by a solvation reaction similar to that with neutral phosphorus extractants:



and



The extraction mechanism for the case that the organic phase is saturated with Th(IV) was investigated at low aqueous acidity:



The equilibrium constant for the reaction of Equation (1) is

$$\text{Log}K_1 = \text{Log}D + \text{Log}\left(1 + \sum_1^j \beta_j [\text{SO}_4^{2-}]_{\text{aq}}^j\right) + 4\text{Log}[\text{H}^+]_{\text{aq}} - 5/2(\text{HL})_{2\text{org}} \quad (5)$$

The calculated equilibrium constant $\text{Log}K_1$ is 4.07 ± 0.02 .

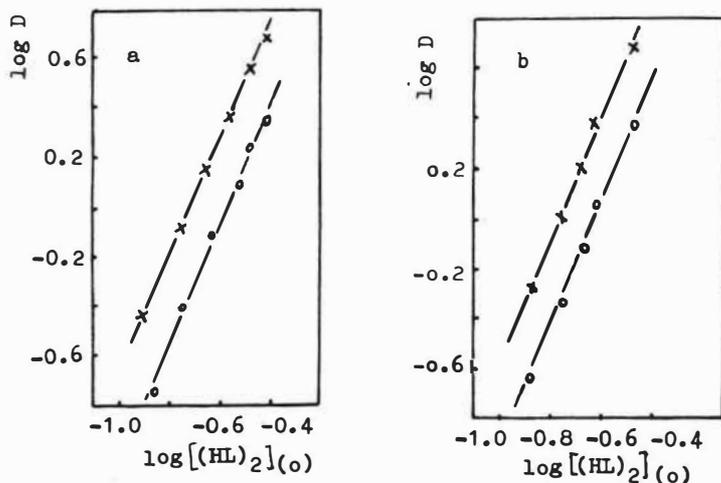


Fig.2. Effect of HEH/EHP concentration on Th(IV) extraction

(a) $\text{Log}D - \text{Log}[(\text{HL})_2]_{\text{org}}$: x- 1.6N H_2SO_4 o- 2.2N H_2SO_4

(b) $\text{Log}D - \text{Log}[(\text{HL})_2]_{\text{org}}$: x- 13.1N H_2SO_4 o- 12.1N H_2SO_4

Dependence on temperature

The extraction of Th(IV) from its solutions (0.0043M) in 1.3 and 1.6N H_2SO_4 by 0.50F HEH/EHP in octane at temperatures (15–35°C) is shown in Fig.3. From this the value of enthalpy change (ΔH) in Equa-

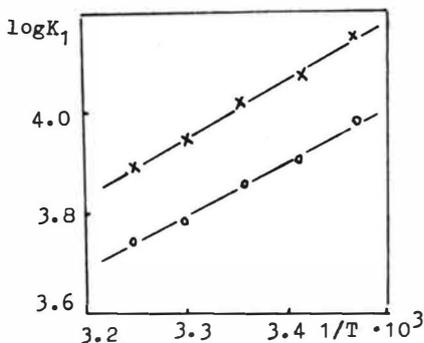


Fig.3. $\log K_1$ of extraction of Th(IV) by(HEH/EHP at different temperatures x- 1.6N H_2SO_4 , o- 1.3N H_2SO_4

tion(1) was estimated to be approximately $-20KJ.mol^{-1}$ ($-19.7KJ.mol^{-1}$ in 1.3N H_2SO_4 and $-20.7KJ.mol^{-1}$ in 1.6N H_2SO_4). This value is less than for the thorium(IV) extraction by HDEHP[4], but it is in the similitudes of the cerium(IV) extraction [2]. The value of the corresponding free energy(ΔG°) and entropy change (ΔS°) can be calculated as approximately $-22.2KJ.mol^{-1}$ and $7.5J.mol^{-1}.K^{-1}$ respectively.

IR and NMR spectra

The IR and NMR spectra were carried out for the extracted complex of thorium(IV) with HEH/EHP. The data of the IR and NMR are in good agreement with the obtained extraction mechanism of thorium(IV) by HEH/EHP.

References

1. Li Deqian, Wan Xiong, Lin Daozhi et al.//ISEC'80, Liege, Belgium. 1980. No 80-202.
2. Li Deqian, Wang Zhonghuai, Zeng Guangfu et al.//Journal of The Chinese Rare Earth Society. 1984. Vol. 2, No 2. P.9.
3. Li Deqian, Wang Zhonghuai, Chen Zhifu et al.//ISEC'86, München. Fed. Rep. of Germany. 1986. Vol. 11. P.231.
4. Sato T.//J. Inorg. Nucl. Chem. 1965. Vol. 27. P.1395.

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Organic reagent of different classes have been used for zirconium extraction. But zirconium extraction with extractant mixture has not been studied so far. It has been reported that zirconium extraction with mixtures of tributylphosphat (TBP) and di-2-ethylhexylphosphoric acid (D2EHPA) leads to a sharp increase in the distribution coefficients of metal [1].

The present paper reports the results of zirconium extraction with extractants mixtures and comparison of extraction with individual extractants. Extractants used were mixtures of neutral (TBP) and acid (D2EHPA) reagent, mixtures of synthetic fatty (SFA), higher carboxylic (HCA) and higher isomeric (HIA-2) acids with TBP and D2EHPA and trialkylamin (TAA).

Zirconium content in the aqueous phase has been determined spectrophotometrically using Arsenazo III and on the organic phase X-ray fluorescently measuring zirconium radiation in solid extracts at X-ray spectrometer PW-I410/20 Philips Firm.

It has been investigated the effect of aqueous phase acidity, the concentration of reagents and metal, the temperature on the distribution coefficients of zirconium in the systems studied.

The addition of TBP to SFA and HCA allows to extract zirconium from a more acid medium (Fig.1). At pH 1,0 quantity extraction of metal into the organic phase is observed.

The increase in zirconium concentration from $1 \cdot 10^{-4}$ to $2 \cdot 10^{-2}$ at constant value of acidity of the aqueous phase does not change the extent of extraction and the distribution coefficients of the metal.

Temperature change from 283 to 313K for SFA-TBP mixtures and from 333 to 363 for HCA-TBP mixtures increases the distribution coefficients of zirconium from 85 to 140 and from 94 to 165 correspondingly.

Adding D2EHPA to SFA, HCA and

HIA-2 leads to zirconium extraction from acid media (Fig.2), the distribution coefficients being $\sim 10^3$. High values of zirconium distribution coefficient are also attained in extraction from acid media (Fig.2, curve 4) with mixtures of TBP-D2EHPA.

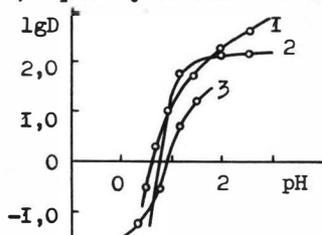


Fig.1. Dependence of distribution coefficients of zirconium on the pH of the aqueous phase. Curve 1- 10 vol% TBP in SFA; Curve 2- 10 vol.% TBP in HCA; Curve 3- SFA

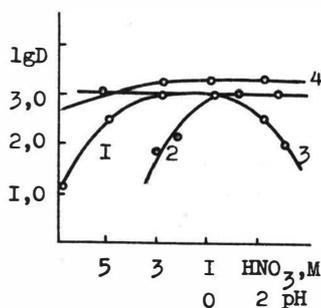


Fig. 2. Dependence of distribution coefficient of zirconium on the pH of the aqueous phase. Curve 1-D2EHPA-SFA; Curve 2-D2EHPA-HCA; Curve 3-D2EHPA-HIA-2; Curve 4-D2EHPA-TBP

Adding TAA to SFA, HCA, TBP does not change the extent of extraction and the distribution coefficient of zirconium compared to individual extractants.

Changing concentration of D2EHPA in SFA and HCA from 5 to 15 volume per cent causes changes in the extent of zirconium extraction from 85 to 99 %. Further increase in reagent concentration does not change extraction.

When zirconium concentration changes from $2 \cdot 10^{-4}$ to $3 \cdot 10^{-2}$ mol/l the distribution coefficients remain almost constant.

Separating phases in the case of HIA-2-D2EHPA mixtures is less distinct compared to SFA and HCA mixtures, mixtures SFA-D2EHPA being more suitable technologically.

Optimal condition for zirconium extraction with extractants mixtures are given in Table I.

Table I. The optimal condition zirconium extraction ($[Zr] - 3 \cdot 10^{-2}$ mol/l)

Extractant	Extraction conditions		
	C_{HNO_3}, M, pH	T, K	τ, min
HCA	$pH > 1,5$	333-363	3
SFA-TBP	$pH > 1,0$	293-303	5
HCA-TBP	$pH > 1,0$	333-353	5
SFA-D2EHPA	$HNO_3 I-8 M$	283-313	3
HCA-D2EHPA	$HNO_3 I-8 M$	333-363	3
HIA-2-D2EHPA	$HNO_3 I-5 M$	333-353	5

The behaviour of accessory elements (iron, aluminium, titanium, magnesium scandium and rare earth) have been investigated. The separation coefficients Zr/Me have been determined.

Different extraction system have been compared and more perspective ones have been chosen proceeding from selectivity extraction.

A number of physico-chemical methods have been employed to investigate the composition of mixed zirconium complexes and to explain synergism observed in certain systems.

Back extraction of zirconium has been studied and regeneration conditions of mixtures used have been established as well as the effect of concentration and reagent nature on the process metal re-extraction.

Reference

I. Nikolaev A. I. et al. // Khim., Khim. Tekhnol. i Metallurgiya redkih elementov. Apatiti. 1982. S. 89-93.

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In our previous paper [1-3] the extraction and separation of niobium(V), zirconium(IV) and hafnium(IV) with 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) were described. We now report the extraction of niobium(V) with 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY). This extraction has the advantage over the extraction with HX [1] because it is feasible from solutions without the presence of large amounts of chloride or thiocyanate ions. Niobium(V) can be quantitatively extracted with HY dissolved in chloroform from aqueous hydrochloric or sulphuric solution in the range 0.8-2.0 M hydrogen ion concentration (Fig.1.) if chloride concentration is less than 3M (Table 1.). With increase in chloride ion concentration in the range 3-6 M the percentage of extracted niobium gradually decreases, but with increase in chloride concentration above 6M the percentage of extracted niobium increases again and at a chloride ion concentration higher than 8M niobium(V) is quantitatively extracted from hydrochloric acid solutions. From sulphuric acid solution and at a chloride ion concentration higher than 8M maximum niobium extraction is about 83%. The absorption maximum of the extracted complexes depends on chloride concentration and lies between 310 and 350 nm (Fig.2.). With an increase in chloride concentration it is shifted towards higher wavelengths. In the range of chloride concentrations less than 3M the absorption maximum of the extracted complex is in the range 310-320 nm. With a chloride concentration between 3 and 5M the absorbance at 310-320 nm gradually decreases and, simultaneously, another absorption maximum appears at 350 nm. At a chloride concentration higher than 6M the absorption maximum of the organic phase is at 350 nm. At this wavelength there is no shift of either the absorption maximum or the absorbance values with increase in chloride concentration. The absorbance of the organic phase obtained at excess of chloride in the aqueous phase is stable for about 30 minutes. With prolonged standing the absorption maximum appears at 310-320 nm and the absorbance values at 310-320 nm increase with time. After 120 minutes, the maximum at 350 nm is still visible and after one day, the spectrum shows a maximum at 320 nm only (Fig.3.). These results suggest that niobium(V) can be extracted with HY in the form of two different complexes depending on the chloride ion concentration in the aqueous phase.

Table 1. The dependence of niobium extraction on chloride ion concentration

Conc. LiCl (M)	%E	
	HCl	H ₂ SO ₄
-	99.6	99.5
0.5	99.7	99.7
1.0	99.6	99.5
1.5	99.6	99.6
2.0	99.7	99.6
2.5	99.7	99.7
3.0	99.2	99.4
4.0	98.0	95.3
5.0	95.2	89.0
6.0	92.8	73.2
7.0	95.3	78.3
8.0	99.2	79.5
9.0	99.6	82.3
10.0	99.7	83.2

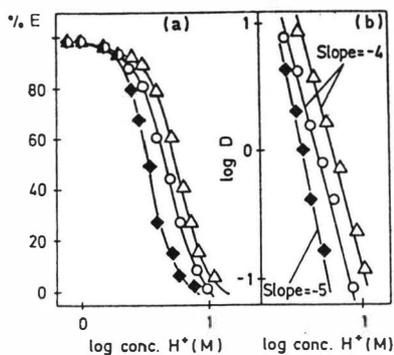
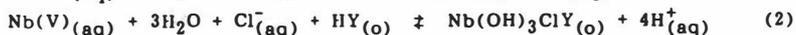


Fig. 1. The dependence of the percentage of extraction (a) and the distribution ratio (b) of niobium on initial hydrogen ion concentration: O, Δ, 10 M Cl⁻; ◆, without addition of Cl⁻

The compositions of the extracted niobium(V) complexes have been studied by radiometric and spectrophotometric methods. Distribution studies (Fig. 4.) show that at a low chloride concentration or without the presence of chloride in the aqueous phase niobium(V) can be extracted as a complex with two HY molecules bonded to a single niobium atom and at a high chloride concentration as a mixed chloro-HY complex with one HY molecule bonded to a single niobium atom. The ratio of niobium to HY was

also determined on the basis of the dependence of niobium extraction on its initial concentration in the aqueous phase and spectrophotometrically by Job's method. The results also indicate that niobium can be extracted as a complex with two HY molecules bonded to a single niobium atom or as a mixed chloro complex with one HY molecule bonded to a single niobium atom. It was not possible to determine the ratio of niobium to chloride in the mixed chloro-HY complex, but the ratio was determined at extraction of niobium with HX as a mixed chloro-HX complex [1]. Comparison of these results and the results described here shows the compositions of the mixed Nb-Cl-HX and Nb-Cl-HY complexes to be identical. On the basis of all the results obtained we suggest that complexes having the stoichiometries Nb(OH)₃Y₂ and Nb(OH)₃ClY can be quantitatively extracted. The formation of these complexes may be shown as:



The formation of the complex at low chloride concentration or without chloride in the aqueous phase shown in eqn. (1) is fundamentally different from extraction of niobium with HX. With HX niobium is quantitatively ex-

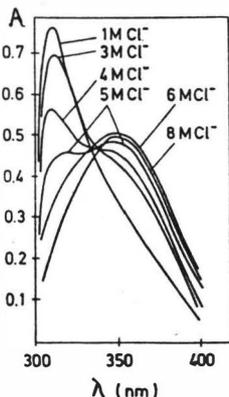
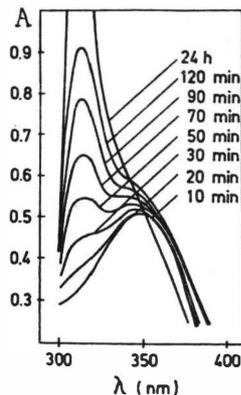


Fig. 2. The dependence of the absorption spectra of the organic phase on chloride ion concentration

Fig. 3. The dependence of the absorption spectrum of the organic phase on time of standing



tracted only as mixed ligand complex [1]. Based on the absorption spectra of the extracted complexes (Fig.2.) it is also suggested that the mixed ligand complex produced from a high chloride concentration in the aqueous phase shown in eqn. (2) with maximum absorption at 350 nm by prolonged standing reacts with the excess of undissociated HY molecules [4,5] in the organic phase giving more stable $Nb(OH)_3Y_2$ with maximum absorption at 310-320 nm:

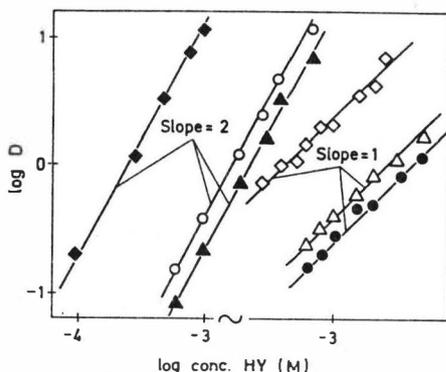


Fig. 4. The dependence of the distribution ratio of niobium(V) on initial HY concentration; \blacklozenge , \circ , \blacktriangle , without addition of Cl^- ; \diamond , \triangle , \bullet , 10 M Cl^-

The extracted niobium(V) in the presence of an excess of chloride or without the presence of chloride can be quantitatively stripped with 10M HCl or 5M H_2SO_4 . At optimum extracting conditions only citrate, tartrate, fluoride and oxalate minimize niobium extraction. These anions mask niobium(V) but do not interfere if present in moderate quantities. Citrate and tartrate may not exceed a 100-fold amount and fluoride and oxalate a 10-fold amount with respect to niobium(V).

The different behaviour of niobium(V), zirconium(IV) and hafnium(IV) in extraction with HY can be exploited for their separation. From 1-2 M HCl solutions niobium is quantitatively extracted (Fig.1.), while zirconium and hafnium remain in the aqueous phase [6]. The separation of zirconium and niobium is of large practical importance because of the radiochemical equilibrium $^{95}Zr/^{95}Nb$. The separation of zirconium and niobium was tested using $^{95}Zr/^{95}Nb$ and that of hafnium and niobium using a mixture of ^{181}Hf and ^{95}Nb .

References

1. Tamhina B., Gojmerac Ivšić A., // Solvent Extr. Ion Exch. 1987. Vol. 5. In press.
2. Vojković V., Tamhina B. // Solvent Extr. Ion Exch. 1987. Vol. 5. P.245.
3. Vojković V., Tamhina B. // Solvent Extr. Ion Exch. 1986. Vol. 4. P.27.
4. Tamhina B., Jakopčić K., Zorko F., Herak M.J. // J.Inorg.Nucl.Chem. 1974. Vol. 36. P.1855.
5. Jakopčić K., Tamhina B., Zorko F., Herak M.J. // J.Inorg.Nucl.Chem. 1977. Vol. 39. P.1201.
6. Tamhina B., Vojković V. // Unpublished data.

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For the purpose of extractational derivation of niobium and tantalum compounds use is exclusively made of fluoride, predominantly sulphate-fluoride systems. These elements give rise in an aqueous solution to stable, well-soluble fluoride complexes which differ significantly with respect to chemical properties. Fluoride solutions are likewise favourable for the purpose of extractational separation of tantalum and niobium from accompanying impurities. Sulphuric acid affects the equilibrium of different complex fluorides in the solutions and increases the selectivity of metal separation.

A great many organic substances have been studied as extraction reagents for separation of niobium and tantalum from fluoride solutions. As regards technological purposes, there has been demonstrated the possibility of using more than 60 extractants: amines and other nitrogen-containing reagents, phosphorus- and sulphur-containing reagents, ketones, aldehydes, alcohols, ethers, etc.

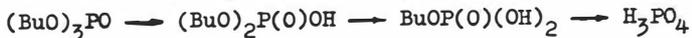
In practice the choice of potential extractants is restricted on account of numerous and conflicting requirements being put to a commercial extractant. The choice of an extraction reagent is determined by the aggregate of its characteristics - stability, solubility, fire-hazardous properties, toxicity, cost, availability, etc. The problem pursued in the search for optimal extractants for niobium and tantalum is to bring together the complex of requirements to organic solvents and those put to the end product obtainable in extraction and the specifics of processed technological solutions.

In the present work we have investigated a comparative selectivity of seven extractants for the separation and purification of niobium and tantalum: tributylphosphate (TBP), phosphoric acid hexabutyltriamide (PAHBTAA), trialkylphosphineoxide (TAPO), petroleum sulphoxides (PSO), cyclohexanon (CHN), methylisobutylketone (MIBK) and trialkylamine (TAA). All these extractants are either promising or available commercial reagents belonging to neutral oxygen-containing solvents, except for TAA which is an ion-exchange extractant. We made use of extractants of "commercial" grade.

The employed extractants are the ones particularly well explored by us for the purpose of separation of tantalum and niobium from fluoride media. Highly interesting is the study of their stability.

A particularly widespread extractant of niobium and tantalum proves to be TBP. The collapse of TBP upon contact with acid solutions is co-

commonly associated with a progressive hydrolysis in the series:

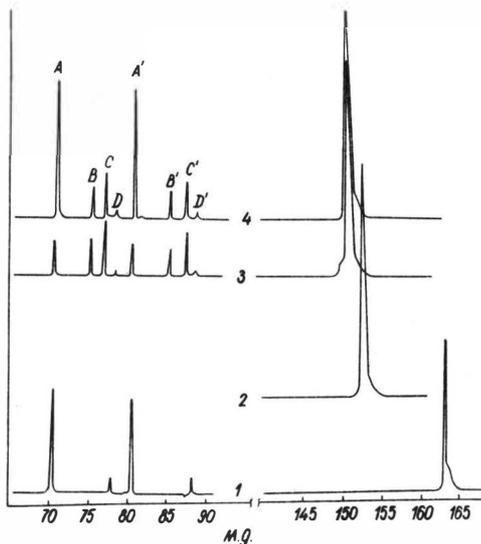


Making use of NMR spectral data at the nuclei ^{31}P and ^{19}F , chemical analysis and potentiometric titration, we have studied the process of TBP collapse upon contact with fluoride-sulphate solutions under conditions of niobium and tantalum extraction. We have discovered the formation of all TBP hydrolysis products of the aforementioned series and of the fluorination products of TBP, phosphoric acid and acid esters of butylphosphoric acids (Fig.1,2).

The concentration of products of TBP collapse was found to be increasing with time. It is related not so much to the number of cycles in the use of the extractant as to the time of contact between TBP and the fluoride-sulphate solutions. Thus, on the evidence of laboratory data, for 170 cycles of an accelerated extraction-stripping of tantalum from process solutions the organic phase contained 0.1M of dibutylphosphoric acid (DBPA) - one of the principal products of TBP collapse. In a real process under a smaller number of extraction-stripping cycles the return extractant contains 0.3-1.0M DBPA.

Accumulation of TBP collapse products leads to a higher viscosity of the organic phases, a deterioration of the hydrodynamic characteristics of the process, and contributes to the formation of precipitates and crud at the interfase principally due to the formation of iron butylphosphates. Phosphoric acid under stripping goes over into the aqueous phase and contaminates niobium and tantalum compounds with phosphorus. The phosphorus content in niobium and tantalum oxides increases dozens of times in the use of a return extractant.

Fig.1. NMR spectra for ^{19}F : aqueous solution of HF and H_3PO_4 (1); $(\text{BuO})_3\text{PO}$ -extracts from the solution (M): 5.0 HF, 6.0 H_2SO_4 , 1.3 H_3PO_4 (2,4); from the solution (M): 5.0 HF, 6.0 H_2SO_4 (3). Extracts: freshly-prepared (2) and the ones matured in contact with an acid aqueous solution for 30 days (3, 4); AA' - $\text{H}_2\text{PO}_3\text{F}$, BB' - $(\text{BuO})_2\text{POF}$, CC' - BuOPOF_2 , DD' - HPO_2F , E - HF



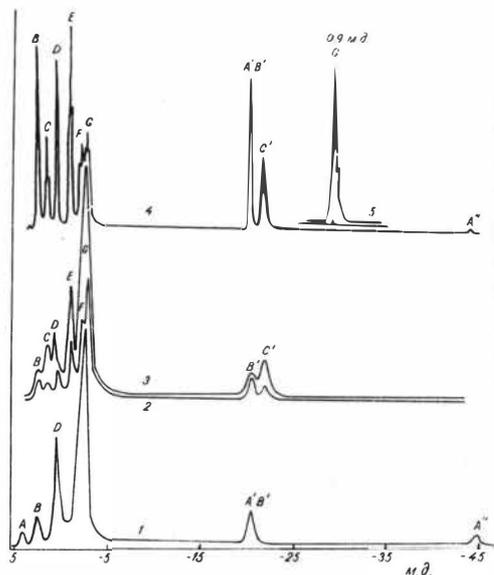
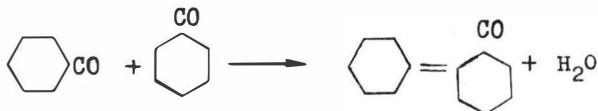


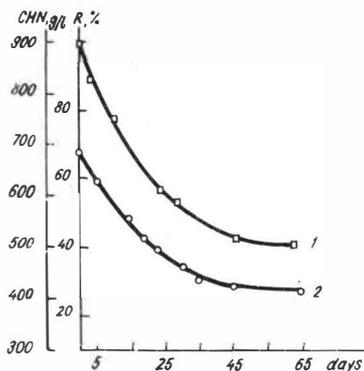
Fig.2. NMR spectra for ^{31}P :
 $(\text{BuO})_3\text{PO}$ (5); $(\text{BuO})_3\text{PO}$ -extracts from the solution (M): 5.0 HF, 6.0 H_2SO_4 (2,3); from the solution (M): 5.0 HF, 6.0 H_2SO_4 , 1.3 H_3PO_4 (1,4). Extracts: freshly-prepared (1) and ones matured in contact with an acid solution for 20 days (2) and 30 days (3,4); AA'A'' - HPO_2F_2 , BB' - $\text{H}_2\text{PO}_3\text{F}$, CC' - $(\text{BuO})\text{POF}(\text{OH})$, D - H_3PO_4 , E - $\text{BuOPO}(\text{OH})_2$, F - $(\text{BuO})_2\text{PO}(\text{OH})$, J - $(\text{BuO})_3\text{PO}$

Under conditions of niobium and tantalum extraction CHN is subject to a condensation reaction. Using the method of gas-liquid chromatography it was shown that cyclohexylidencyclohexanon is formed:



The rate of formation of the condensation product increases with the rising acidity of the aqueous solution. Accumulation of this product is accompanied by a decline of the extractational properties of the organic solution and a higher viscosity of the extract (Fig.3).

The extractational properties of PSO under comparable conditions were observed to be changing less perceptibly.



The extract left to stand for 250 days was found to increase in viscosity more than two times for a sample of low-viscosity PSO. Simultaneously the ratio of phase volumes $V_0 : V_{\text{aq}}$ was observed to increase with time.

Fig.3. Variation of the CHN content in the extractant and of Nb separation in time
 CHN concentration, g/l (1); separation of Nb, % (2)

A higher stability, compared to TBP was observed in TAPO. This is associated with a lower reaction capacity of P-C bonds in TAPO in contrast to P-N-C bonds in PAHBTA and P-O-C bonds in TBP. Under contact conditions, similar to those of TBP, no TAPO hydrolysis and fluorination products were observed in NMR spectra of the TAPO extracts.

High stability of triisobutylphosphate(TIBP) and triisoamilphosphate (TIAP) was observed under niobium and tantalum extraction from fluoride-sulphate solution. With respect to stability TIBP and TIAP occupy an intermediate position between TAPO and TBP, whilst their extractional capacity is at the TBP level. This enables us to recommend TIBP and TIAP as more suitable extractants, as compared to TBP.

Comparison of extractant selectivity was made with respect to niobium and tantalum separation from a process solution containing (M): 5 H₂SO₄, 0.96 Ti, 0.13 Nb, 0.05 Ta. A successive extraction of tantalum and niobium was made after hydrofluoric acid had been introduced in the solution. Optimal conditions of tantalum and niobium extraction must be different for different extractants. However, the results obtained permit the extractional efficiency of the reagents used to be evaluated. A decline of extractional properties for neutral oxygen-containing extractants is observed in the series: TAPO > PAHBTA > PSO > TBP > CHN > MIBK. The extractional efficiency of TAA is observed to be close under the investigated conditions to TAPO, PAHBTA, PSO.

It could be expected that the purity of the isolated specimens of niobium and tantalum oxides would increase in accordance with the aforementioned series of extractants, i.e. the weaker the extractional properties, the greater should be the selectivity of the extractant. This has found confirmation with respect to the extraction of the main impurity elements - niobium in the case of tantalum extraction and titanium in the case of niobium extraction. However, with respect to other impurities this regularity fails to be rigorously observed. A particularly low content of the majority of impurities is observed to take place in the specimens of niobium and tantalum oxides separated from MIBK-extracts.

The isolation of tantalum and niobium by all the extractants is accompanied by significant purification from impurities. An additional purification of niobium and tantalum can be achieved by washing the extracts with aqueous solutions. Making use of the obtained washing conditions for TBP, TIAP, CHN and MIBK extracts, there were isolated niobium and tantalum oxides in which the content of 16 controlled impurities declined to values below 0.001 mass.%. With the growth of the extractional properties of extractants the possibility of obtaining pure niobium and tantalum compounds becomes difficult.

INVESTIGATION OF THE EXTRACTION BEHAVIOUR OF HIGH TANTALUM 7-17
 AMOUNTS AND OF THE COMPOSITION OF TANTALUM COMPLEXES BY THEIR
 EXTRACTION INTO METHYLISOBUTYLKETONE FROM HF-H₂SO₄ MIXTURES

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The determination of trace impurities in pure tantalum requires the matrix separation $\overline{1}$, $\overline{2}$ in most cases. In the present work tantalum was extracted by methylisobutylketone (MIBK) from HF-H₂SO₄ solutions $\overline{3}$ - $\overline{5}$ and these investigations were accomplished by the study of the composition of extracted tantalum complexes.

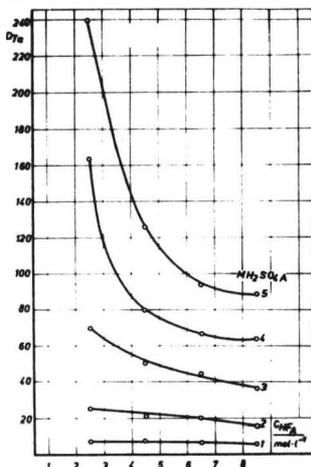
The solution were prepared as follows: 0.5 g of Ta were dissolved in 5 ml of a mixture of concentrated HF and HNO₃ (3:1), evaporated to dryness and dissolved in 10 ml of the HF-H₂SO₄ mixtures again.

The distribution of tantalum at its extraction into MIBK in dependence on HF and H₂SO₄ concentration is shown in Fig. 1. The increase of the H₂SO₄ concentration at the same HF concentration causes the increase of the tantalum distribution ratio. Fig. 2 shows the tantalum distribution ratio in dependence on the tantalum concentration. According to this, the two-fold extraction of tantalum from the solution containing 2.5 M of HF and 4 - 5 M H₂SO₄ allows to remove the tantalum to sufficient extent. The distribution ratio of tungsten at the extraction from the solution containing 5 M of H₂SO₄ equals to 0.04 and diminishes to 0.01 in the presence of 4 M H₂SO₄. The distribution ratios of the investigated trace elements at the extraction from the solution containing 2.5 M HF and 4 M H₂SO₄ are given in Table 1. Together with the

Table 1. Distribution ratios of the trace elements at the extraction of tantalum as matrix

Me	D	Me	D	Me	D	Me	D
Cs	$5 \cdot 10^{-3}$	Zn	$1 \cdot 10^{-3}$	V	$5 \cdot 10^{-4}$	Mo	0,12
Cu	$4 \cdot 10^{-4}$	Cd	$1 \cdot 10^{-4}$	Cr	$4 \cdot 10^{-4}$	W	0,01
Ag	$2 \cdot 10^{-3}$	Ga	$1 \cdot 10^{-3}$	Mn	$1 \cdot 10^{-4}$	Eu	$1 \cdot 10^{-4}$
Ca	$4 \cdot 10^{-3}$	In	$2 \cdot 10^{-3}$	Fe	$6 \cdot 10^{-3}$	As	0,24
Sr	$1 \cdot 10^{-3}$	Zr	$7 \cdot 10^{-4}$	Co	$4 \cdot 10^{-4}$	Au	$4 \cdot 10^3$
Ba	$1 \cdot 10^{-2}$	Hf	$7 \cdot 10^{-4}$	Ni	$1 \cdot 10^{-4}$	Re	1,0

Fig.1. Distribution ratio of tantalum in dependence on HF and H₂SO₄ concentration



tantalumfluorocomplexes also HF, H₂SO₄ and H₂O are extracted into MIBK phase $\overline{6}$, $\overline{7}$.

The composition of the tantalumfluorocomplexes is investigated by the modified equilibrium shift method by Bent and French $\overline{8}$: $\log D_{\text{Me}} = K + n \log \overline{\text{HA}}_0$. The extraction equilibrium of the tantalum can not be shifted by the change of hydrofluoric acid concentration, but only by the change of H₂SO₄ (Fig. 1). In the solution with the ration of F⁻ : Ta < 8 - 9 the hydrolysis of tantalum occurs and the precipitate does not dissolve even in concentrated H₂SO₄. In presence of free HF in the water phase the hydrofluoric acid will be extracted into MIBK phase $\overline{7}$. With the assumption of formation of only one tantalumfluorocomplex in the water and organic phase and under consideration of the HF distribution ratio D_{HF} $\overline{7}$ the equation for the total concentration of fluoride in the organic phase C_{F_0} can be written as:

$$C_{\text{F}_0} = n \overline{\text{TaF}_{n-}}_0 + \overline{\text{HF}}_0 \quad \text{or}$$

$$C_{\text{F}_0} = n \overline{\text{TaF}_{n-}}_0 + \frac{(C_{\text{F}_{\text{tot}}} - nC_{\text{Ta}_{\text{tot}}}) \cdot D_{\text{HF}}}{1 + D_{\text{HF}}}$$

The index 'tot' means total concentration in the initial water phase. If the values of $C_{\text{F}_{\text{tot}}}$, $C_{\text{Ta}_{\text{tot}}}$ as well as $\overline{\text{TaF}_{n-}}_0$ and D_{HF} at several H₂SO₄ concentrations are known, then the theoretical

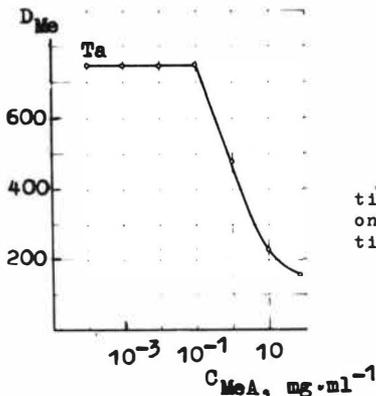


Fig. 2. Tantalum distribution ratio in dependence on the tantalum concentration

concentration of HF in the organic phase C_F can be calculated for several ligand numbers n . The comparison of plots of theoretical values of C_F vs. $\sqrt[n]{TaF_n}$ with the experimental values of C_F determined by titration of F^- in organic phase allows to make a conclusion about the ligand number in $\sqrt[n]{TaF_n}^{-(n-5)}$. Fig. 3 shows the experimental points lie on a straight line with the slope of 7.9, that means, that tantalum will be extracted into MIBK as H_3TaF_8 complex.

The determination of the solvation number of tantalum complex was done by straight line slope of the function $\log D_{Ta} = f(\log \sqrt[MIBK]{O})$ in a solution of 2 M HF, 4 M H_2SO_4 and 0.056 M Ta, the dilution of MIBK was done by benzene. The solvation number was determined to 4, Fig. 4. The determination of water in the organic phases by its titration with Fischer reagent allows to determine the hydration number of extracted complex to 8. The IR-spectra of organic phase containing tantalum show in the region of $3700 - 3350 \text{ cm}^{-1}$ a wide absorption band which belongs to OH-groups of strong fixed water. The maximum of C=O band is shifted from 1725 to 1710 cm^{-1} and is probably overlapped with the absorption band maximum of H_3O^+ ions

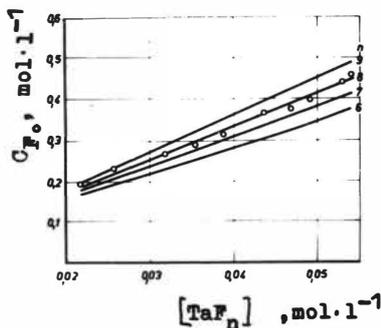
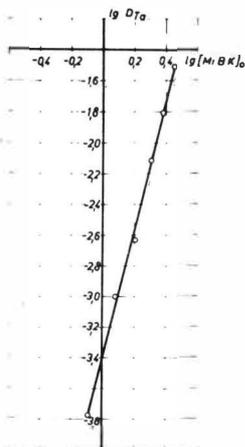
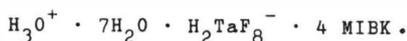


Fig. 3. Determination of the ligand number in tantalum-fluoro-complex

Fig. 4. Determination of the solvation number of tantalum complex



at 1700 cm^{-1} . These results allow to assume that the extraction of tantalumfluorocomplex occurs according to the extraction mechanism of strong acids [9, 10]. Therefore the composition of the tantalum complex in the MIBK phase can be written as:



References

1. I.M. Gibalo, *Analiticheskaya Khimiya Niobiya i Tantara*, Nauka Moskow, 1967.
2. R. Caletka, V. Krivan // *Fresenius Z. Anal. Chem.* 313 (1982).125.
3. C.R. Waterburg, C.E. Bricker // *Anal. Chem.* 29 (1957).1474.
4. K. Nishimura, H. Irokava // *Japan Analyst.* 12 (1963).933.
5. R. Caletka, V. Krivan // *Fresenius Z. Anal. Chem.* 321 (1985).61.
6. R. Bock, M. Herrmann // *Z. Anorg. Allg. Chem.* 284 (1956).288.
7. O. GroBmann, A.V. Karjakin // *Z. Phys. Chem. Leipzig*, 258 (1977). 3, 469.
8. H.E. Bent, C.L. French // *J. Amer. Chem. Soc.* 63 (1941).568.
9. D.G. Tuck, R.M. Diamond // *J. Phys. Chem.* 65 (1961).193.
10. Ju.A. Zolotov // *Uspechi Chimii.* 32 (1963).220.

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The extraction of tungsten(VI) from hydrochloric acid solutions in the presence of tartaric acid has been investigated using tributyl phosphate, trioctyl phosphine oxide, dihexyl sulfoxide, trioctylamine and trioctylmethylammonium chloride in benzene.

Introduction

Solvent extraction of tungsten(VI) from acid solutions has been studied by some researchers. However, since the solubility of tungstates to mineral acid is generally low, there are only a few limited literatures. De et al. [1] examined the extraction from hydrochloric acid by tributyl phosphate (TBP), and Palant et al. [2] extracted using trialkylamines from aqueous solutions at pH2. In order to obtain further information on solvent extraction of tungsten(VI), the extraction from hydrochloric acid solutions in the presence of tartaric acid added to prevent the precipitation of tungstates has been investigated by using neutral organophosphorus compounds (tributyl phosphate, TBP; trioctyl phosphine oxide, TOPO), sulfur-containing compound (dihexyl sulfoxide, DHSO, R₂SO) and high-molecular weight amines (trioctylamine, TOA, R₃N; trioctylmethylammonium chloride, TOMAC, R₃R⁺NCl).

Experimental

Chemicals. TBP (Daihachi Chemical Industry Co., Ltd.) was purified by usual method [3] and TOPO (Hokko Chemical Industry, Co., Ltd.), TOA and TOMAC (Koei Chemical Co., Ltd.) were used without further purification. DHSO was synthesized by oxidation from dihexyl sulfide (DHS, Daihachi Chemical Industry Co., Ltd.). The synthesis was carried out as follows: 1) 35 cm³ each of acetic acid and acetic anhydride and 20 cm³ of aqueous solution of hydrogen per-

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oxide in 30 % was added to 50 cm³ of DHS dropwisely for during 1 h; the mixture was cooled with ice, and then the resulting mixture was stirred for 3 h at 0°C. 2) After end of the reaction was confirmed by TLC, DHSO extracted into chloroform was washed at first with water and with 10 % sodium carbonate, and finally with water again. 3) White crystal got from the removal of chloroform by evaporater.

A stock solution of tungsten(VI) was prepared by dissolving sodium tungstate at the concentration in 1 g dm⁻³ in deionized water, and diluted to a selected concentration of hydrochloric acid in the presence of tartaric acid. Aqueous solutions containing sodium tungstate in 0.1 g dm⁻³ were generally used in the present examination. All chemicals used of analytical reagent grade.

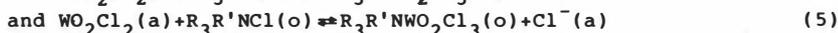
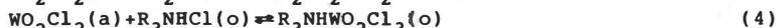
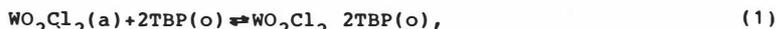
Extraction and analytical procedures. Equal volumes (15 cm³ each) of the aqueous and organic phases, placed in 50 cm³ stoppered conical flasks, were shaken in water bath maintained by thermostat at 20°C, except the examination of temperature effect. Preliminary experiments showed that the equilibration was completed for 10 min. The mixture was centrifuged and separated, and then the aliquots of both phases were pipetted to determine the distribution coefficient (the ratio of the concentration of tungsten(VI) in organic phase to that in aqueous phase, E_a^o). Tungsten(VI) in organic phase was stripped with aqueous solution of sodium hydroxide in 2 mol dm⁻³ for all extractants. The concentration of tungsten (VI) in aqueous solution was determined spectrophotometrically [4] : 2-4 cm³ of aqueous solution containing in below 1×10^{-2} mg dm⁻³ was transferred to 10 cm³ volumetric flask; to this, 4 cm³ of 7 % tin(II) chloride in concentrated hydrochloric acid was added, mixed well and placed for 20 min in a thermostatted water bath at 60°C; it was cooled by cold water, then 1 cm³ of 20 % potassium thiocyanate was added and diluted with water; after it was placed for 10 min at room temperature, the absorbance of the yellow colored solution was measured at 400 nm using water as a reference. The solutions of tin(II) chloride and potassium thiocyanate were prepared whenever the absorbance was measured, and spectrophotometric measurement was carried out with a Hitachi 340 UV-VIS recording spectrophotometer using 1x1 cm glass cell.

Infrared spectrophotometry The infrared spectra of the samples prepared by evaporation of the organic diluent were measured on the Japan Spectroscopic Co., Ltd. grating models IRA-1(4000-650 cm⁻¹) and IR-F(700-200 cm⁻¹) using a capillary film between thallium halide plates or polyethylene films.

Results and Discussion

Extraction isotherms. When tungsten(VI) is extracted by TBP, TOPO, TOA and TOMAC in benzene from aqueous solutions containing hydrochloric acid in the presence of tartaric acid, the extraction efficiency for tungsten(VI) is in the order TOPO DHSO TOMAC TOA TBP, but the shape of those extraction curves resemble each other. The distribution coefficients rise steeply with increasing aqueous acidity to maxima which occur at initial hydrochloric acid concentrations in 9, 6-7, 8, 7-8 and 8 mol dm⁻³ for TBP, TOPO, DHSO, TOA and TOMAC, respectively, and then fall. When hydrochloric acid in the aqueous phase is partly replaced by lithium chloride, the variation in the distribution coefficient with the total chloride concentration is essentially the same as that with hydrochloric acid concentration although the distribution coefficient by TBP is lower than that in the presence of hydrochloric acid alone at the same concentration owing to hydrolyses. These imply that the controlling factor is the total chloride concentration. Log-log plots of E_a^0 vs. [TBP], [TOPO], [DHSO] or [TOMAC] at constant hydrochloric acid concentrations give the straight lines with the slopes of 2 for TBP, TOPO and DHSO and of 1 for TOA and TOMAC: at 5, 6, 7, 8 and 9 mol dm⁻³ HCl, 2.3, 2.1, 1.9, 1.7 and 1.5, respectively, for TBP; 1.7, 1.6, 1.7, 1.6 and 1.7 for TOPO; 1.8, 2.2, 1.8, 1.9 and — for DHSO; 0.98, 1.13, 1.01, 1.05 and 1.03 for TOA; 0.96, 1.01, 0.93, 0.93 and 0.93 for TOMAC. From this it is seen that the distribution coefficients by TBP, TOPO or DHSO and by TOA or TOMAC have the second- and first-power dependencies, respectively, on the concentration of extractants.

Hence it is expected that the extraction equilibria by TBP, TOPO, DHSO, TOA and TOMAC are expressed by the respective following equations:



where (a) and (o) denote aqueous and organic phases, respectively.

The formation of the extracted species according to Eqns. (1) - (5) is supported by the stoichiometry due to the loading test of tungsten to the organic phases and infrared spectral results for the organic extracts. In the extraction from aqueous solution at the concentration of hydrochloric acid in 6 mol dm⁻³ with 0.002 mol dm⁻³ TOPO in benzene, the molar ratio [W]/[Cl]/[TOPO] in organic

phase approaches a limiting value of 1:2:2 as the concentration of tungsten(VI) in aqueous phase is increased. Additionally several times repeated extractions of tungsten(VI) from fresh aqueous solution containing tungsten salt at the concentration of hydrochloric acid in 7 mol dm^{-3} with $0.002 \text{ mol dm}^{-3}$ TOA or TOMAC in benzene gave the $[W]/[Cl]/[TOA]$ or $[TOMAC]$ of 1:3:1 in the organic phase. The infrared spectra of the organic extracts exhibit the following absorptions: for TBP, the W-Cl absorption band at 277 and 243 cm^{-3} ; for TOPO, the W=O stretching band at 955 and 910 cm^{-1} , the WO_2 bending mode at 380 cm^{-1} and the W-Cl stretching absorption at 312 and 250 cm^{-1} ; for DHSO, the W=O stretching band at 925 and 895 cm^{-1} , the WO_2 bending band at 450 cm^{-1} and the W-Cl stretching frequency at 325 and 260 cm^{-1} ; for TOA, the W=O stretching band at 960 and 890 cm^{-1} , the WO_2 bending band at 435 and 400 cm^{-1} and the W-Cl stretching vibration at 335 cm^{-1} ; for TOMAC, the W=O stretching band at 970 and 915 cm^{-1} , the WO_2 bending band at 445 cm^{-1} and the W-Cl stretching band at 365 cm^{-1} .

In these extraction systems, however, the extraction efficiencies of every extractants for tungsten(VI) are lowered with increasing the amount of tartaric acid added, but the presence of tartaric acid prevents the precipitation of tungsten salt.

Temperature effect. Distribution data of tungsten(VI) extracted from hydrochloric acid solutions in the presence of tartaric acid by TBP, TOPO, DHSO, TOA and TOMAC in benzene as a function of temperature indicate that the distribution coefficients for tungsten(VI) by those extractants decrease with rising temperature, although the exothermic effect on the extractions is in the order $DHSO > TBP > TOPO > TOA > TOMAC$.

Acknowledgements

We wish to thank Messrs.T.Takagi and M.Ukita for assistance with the experimental work, and also thank the Daihachi Chemical Industry Co., Ltd. for the samples of TBP and DHS, the Hokko Chemical Industry Co., Ltd. for the sample of TOPO and the Koei Chemical Industry Co., Ltd. for the samples of TOA and TOMAC.

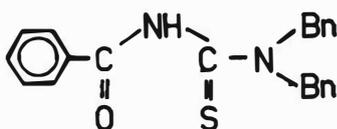
References

1. De A.K. and Rahaman M.S.// Talanta.1964. Vol.11. P.601.
2. Palant A.A., Rezuichenko V.A., Nikiforva S.E.//Zh. Neorg. Khim. 1980. Vol.25. P.826.
3. Alcock K., Grimly S.S., Healy T.V., Kenedy J., McKay H.A.// Trans. Faraday Soc. 1956. Vol.52. P.39.
4. Somdell E.B.// Colorimetric determination of traces of metals. Interscience, N.Y., 3rd Ed., 1957. P.888.

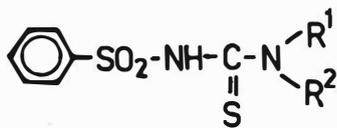
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Noble metals and their compounds are widely used in electronic and chemical industry. Therefore a recycling of those metals from secondary sources is very important. Liquid-liquid extraction is a useful method for the concentration and separation of such metals. Extractants with sulfur donor atoms effect an important progress regarding an increased selectivity in comparison with amines or TBP.

This paper gives results on the extraction of silver, gold, palladium and mercury with oxygen, sulfur and nitrogen containing extractants from type 1-4.



1 N,N'-dibutyl benzoyl thiourea



2 N-benzenesulfonyl thiourea
 $R^1, R^2 = H, \text{Alkyl}, \text{Aryl}$



3 oxa thia alkanes
 $X, Y, Z = O, S$
 $R = Bu, Hex$

4 thia aza alkanes
 $X, Y, Z = O, NR$
 $R = Bu, Hex, H$

Gold(III), silver(I), palladium(II) and also mercury(II) are extracted with the acidic chelating extractants 1 and 2 from strong acidic solutions and can be easily separated from base metals [1, 27]. Distribution ratios of about 10^3 from 1 M mineralic acid are observed even at relative low extractant concentrations. Stripping is possible in presence of complexing agents forming strong water soluble complexes, e. g. thiourea, or by direct reduction to metals from the organic phase. Palladium(II) forms normal 1:2 complexes with 1, whereas the silver complex with 1 has the composition $AgR \cdot HR$ in the

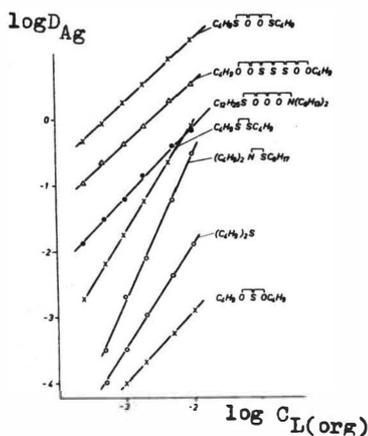


Fig. 1. Extraction of Ag(I) with oxathia alkanes

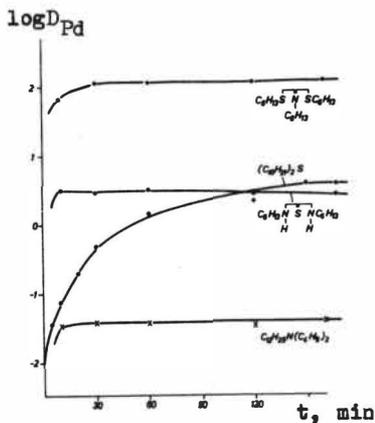


Fig. 2. Kinetics of Pd(II) extraction with thiaaza alkanes

organic phase. Investigations on solid complexes gave also such results [3]. Gold(III) forms with 1 a mixed complex in which 2 chlorine atoms and one chelating group are bonded, similar to the results of ZOLOTOV et al. [4] at thiopicoline amides.

Favourable extraction properties show the neutral sulfur containing compounds 3 and 4 with respect to noble metals. Some results are given in Fig. 1 for silver with such extractants. In relation to dialkyl sulfides the introduction of further sulfur atoms in the molecule leads to a higher extraction of silver. A dioxadithia alkane shows the best extraction power from all the investigated compounds. This result is caused by the formation of very stable four-dentate 1:1 complexes. In case of gold(III) the order of extraction for various compounds from type 3 and 4 is quite different. The highest distribution ratios are determined for compounds, which contain only sulfur donor atoms.

It is well-known, that dialkyl sulfides are excellent extractants for palladium(II). Their disadvantage is the slow kinetics of the extraction reaction. Our investigations with oxaza alkanes show, that these compounds are not only effective extractants for palladium(II), but have also a fast extraction kinetics. The results are illustrated by Fig. 2 [5]. The extraction of palladium(II) with the dithiamonoaza alkane is greater than in the case of dialkyl sulfide which is represented in higher D-values by more than 1 order of magnitude; the

extraction equilibrium is reached in a few minutes. It is pointed out, that the extractant molecule is an intramolecular accelerator for palladium(II). Probably the first step is the phase transfer of the PdCl_4^{2-} anion via a complex with nitrogen coordination, and the second step is the formation of the stable sulfur bonded metal complex in the organic phase.

In contrast to gold(III) and silver(I) mercury(II) prefers nitrogen donors. Therefore high complex stability constants and high extraction constants are determined for diaza and triaza alkanes [6].

Another point of investigation results from the idea, that C = C double bonds in sulfur-containing extractants can act as additional coordination centre for noble metals. The extraction properties of alkylalkene sulfides as extractants have been tested for silver, mercury and palladium and compared with dialkyl sulfides. The remarkable higher extraction yield for such unsaturated sulfides show the contributions of the C = C bond to the stability of the formed metal complexes. A dependence of the extraction ratios on the distance of the C = C bond from the sulfur donor atom is observed caused by the stability of the formed complex in connection with the ring size of the considered chelate complex [7].

The investigations carried out were the basis for the development of processes for the recovery of noble metals from secondary sources. The increased volume of waste material from microelectronics contain favourably silver, palladium, gold, ruthenium and different base metals, e. g. copper, nickel, bismut, lead.

A special leaching process, combined with a solvent extraction route for noble metals and the separation from the base metals has been developed.

References

1. P. Mühl, K. Gloe, F. Dietze, E. Hoyer, L. Beyer// Z. Chem. 26 (1987).81.
2. K. Gloe, P. Mühl, E. Uhlig, M. Döring// GDR-Patent 231 495 (1986).
3. F. Dietze, unpublished results .
4. A. N. Skil, E. G. Ruchadee, J. A. Zolotov// Koord. Chim. 13 (1987).1352.
5. K. Gloe, R. Jacobi, P. Mühl, J. Beger// Isotopenpraxis in press.
6. J. Beger, R. Jacobi, K. Gloe, P. Mühl// Poster ISEC'88, Moscow 1988.
7. P. Mühl, K. Gloe, V. G. Torgov, V. V. Tatarčuk// Isotopenpraxis in press.

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Tri-n-octylamine salts as platinum metals extractants are well known
have been thoroughly investigated, the complexity of these extraction
systems has been shown in [1]. Additional effects appear when salts of
tri-n-octylamine and organic acids (R_3NHA) as extractants are used.

This paper studies extraction of H_2PtCl_6 and H_2PdCl_4 from chloride
solutions by different R_3NHA salts. R_3NHA solutions in toluene obtained
by mixing equimolar amounts of R_3N and HA were used for extraction.
The following organic acids were used: p-tret-butylphenol, caprylic
acid, di-(2-ethylhexyl)phosphoric acid ($(RO)_2P(O)OH$), 5-tret-butyl-
2-hexadecyloxibenzenesulphoric acid (RSO_3H). Fig.1 shows the dependen-
ces of distribution coefficients of Pt and Pd on the acidity of the
aqueous phase when extracting by R_3NHA solutions, and for comparison,
by R_3NHCl solutions in toluene at constant concentration of chloride
ions. When using tri-n-octylamine chloride as extractant, pH increase
doesn't vary D_{Pt} and D_{Pd} values, though in the presence of organic acids
pH increase results in significant decrease of the distribution
coefficients of Pt and Pd. In the regions of comparatively high acidity
(1-3 M HCl) the D_{Pt} and D_{Pd} values don't depend on acidity under
the conditions of constant chloride-ion concentration, this fact cor-

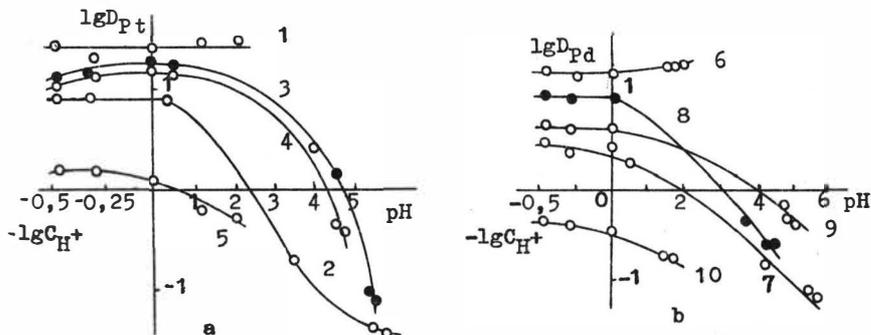
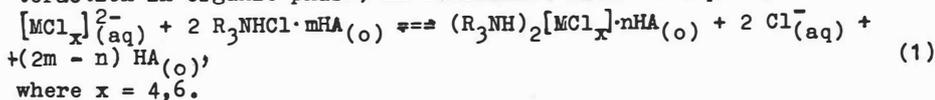


Fig.1. Extraction of H_2PtCl_6 (a) and H_2PdCl_4 (b) with tri-n-octylamine
salts as a function of aqueous phase acidity
1,6- R_3NHCl ; Tri-n-octylamine salts: p-tret-butylphenolate (2,7), cap-
rylate (3,8), di-(2-ethylhexyl)phosphate (4,9), alkylsulphonate (5,10)
 $C_{Pt} = 1,97 \cdot 10^{-3}$ M, $C_{Pd} = 3,0 \cdot 10^{-3}$ M, $C_e = 0,025$ M, $C_{HCl} + C_{LiCl} = 3,0$ M

responds to anion-exchange process (taking into account possible interaction in organic phase) in accordance with the equation:



The data on the chloride-ion distribution in systems with various R_3NHA salts depending on aqueous phase acidity confirm the anion-exchange mechanism of extraction in the region of $C_{HCl} > 1 M$. It has been experimentally shown (Table 1) that under these conditions nearly all tri-n-octylamine is present in the form of R_3NHCl (with the exception of the system with RSO_3H). The D_M values in systems with R_3NHA

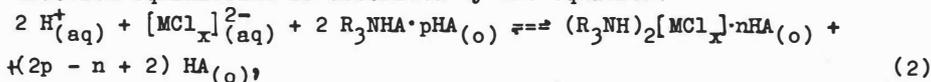
Table 1. Extraction of HCl with tri-n-octylamine and organic acid salts

R_3NHA	C_e, M	C_{HCl}, M	pH	$C_{Cl(o)}, M$
p-tret-butylphenolate	0,025	0,58 2,3	6,98	0,0016
			5,57	0,0095
				0,024
				0,025
caprylate	0,025	0,50 1,0 2,0		0,021
				0,022
				0,022
di-(2-ethylhexyl)phosphate	0,030	0,50 1,1 2,3		0,022
				0,027
				0,029
alkylsulfonate	0,050	0,58 1,1 3,5		0,0043
				0,0046
				0,0063

decrease compared to the distribution coefficients of Pt and Pd for R_3NHCl , probably due to the prevailing influence of the interaction of R_3NHCl with HA compared to the interaction of $(R_3NH)_2MCl_x$ with HA. In this case $(2m - n) > 0$ in Equation 1.

In the region of low aqueous solution acidity and in the presence of various organic acids, tri-n-octylamine forms R_3NHA salts due to their special stability in heterogeneous extraction system

because of the organic cation and anion hydrophobicity. At this, the component distribution between the phases is determined by the mechanism of acid binary extraction. Taking into account possible interactions of the binary extractant with extracted compounds in organic phase the extraction equilibrium is described by the equation:



where p , n and m -values can vary. Comparison of Equations (1) and (2) shows, that in binary extraction of H_2PtCl_6 and H_2PdCl_4 (not as in anion-exchange extraction) the distribution of Pt and Pd depends on activity of hydrogen ions in aqueous phase which is confirmed by the experimental data of Fig. 1.

Under the condition of constant ratio of coefficients of component activity in aqueous and organic phases obtain from Equation (2) the fol-

following expression for concentration constant of binary extraction of H_2MCl_x :

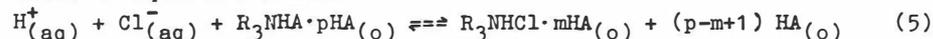
$$\bar{K}_{H_2MCl_x} = \frac{C_{M(o)} \cdot C_{HA(o)}^{2p-n+2}}{C_{M(aq)} \cdot \alpha_{H^+(aq)}^2 \cdot C_{R_3NHA(o)}^2} \quad (3)$$

where

$$\lg D_M = \lg \bar{K}_{H_2MCl_x} + 2 \lg C_{R_3NHA(o)} - (2p-n+2) \lg C_{HA(o)} - 2 \text{ pH} \quad (4)$$

Therefore, at binary extraction the D_M may be influenced not only by varying C_{R_3NHA} and pH of aqueous phase, but by varying the correlation of two extracted compounds in organic phase, e.g. by adding extra amount of HA. Thus, in stripping platinum metals with water from organic phase, containing the mixtures of HA and $(R_3NH)_2MCl_x$, the increase of organic acid concentration results in significant raising of platinum and palladium extraction in aqueous phase, and contrary to stripping with 3 M HCl solution, when stripping follows the anion-exchange type. On the other hand, it has been shown experimentally that increase of chloride ion concentration doesn't affect D_M under the conditions of binary extraction.

One of the main problems in studying binary extraction is the problem of extraction power of binary extractants of various compositions. Paper [2] showed that in extracting mineral acids with binary extractants with different anions and the same cation the binary extraction constant is determined mainly by the acid dissociation constant of organic acid. The experimental data (Fig.1) show, that in binary extraction region (pH 2-5,5) the extraction power of binary extractants in the series "caprylate > di-(2-ethylhexyl)phosphate > p-tret-butylphenolate > tri-n-octylamine alkylsulphonate" corresponds qualitatively to the decrease of acid dissociation constants of corresponding organic acids, except for the system with tri-n-octylamine p-tret-butylphenolate. This can be explained by good stability of tri-n-octylamine chloride solvated with phenole, and also at relatively high pH-values (5-7) of aqueous phase (pK_a of p-tret-butylphenol ~ 10), which leads to decreasing binary extractant concentration and of platinum metals distribution coefficients. To understand the binary extractants solvation, the stripping of HCl with water from organic phase at various ratios of R_3NHCl and HA (Fig.2) has been studied. It is clear from the obtained data that the increase of the HA concentration leads to equilibrium shift:



tending to binary extractant forming and stripping of platinum metals in systems with RSO_3H and $(RO)_2P(O)OH$. All amount of chloride-ion is displaced in aqueous phase at $R_3NHCl:HA$ ratio - 1:1 and 1:2, which corresponds to the formation of R_3NHA for RSO_3H and $R_3NHA \cdot HA$ for

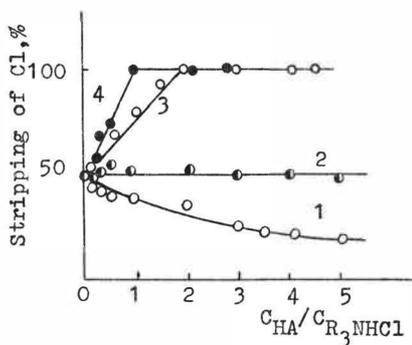


Fig.2. Stripping of chloride ions with water from the mixture $R_3NHCl + yHA$ in systems with p-tret-butylphenol (1), caprylic acid (2), $(RO)_2P(O)OH$ (3), RSO_3H (4). $C_{R_3NHCl_{init.}} = 0,025 M$

abnormal position of tri-n-octylamine p-tret-butylphenolate in the low acidity region. Platinum metals stripping with water in systems with salts of tri-n-octylamine and organic acids is given for comparison, where R_3NHCl doesn't form. As it can be seen from Table 2, the extraction power of binary extractants in this case correlates with the values of acid dissociation constants of the corresponding organic acids.

di-(2-ethylhexyl)phosphoric acid. The solvation of tri-n-octylamine alkylsulphonate with organic acid molecules is seemingly slowed down due to the hydration of alkylsulphonic acid in contact with aqueous solutions. Increase of HA concentration in the mixtures of tri-n-octylamine chloride and caprylic acid doesn't affect chloride-ion distribution. The decrease of the chloride-ion stripping in addition of p-tret-butylphenol to R_3NHCl is probably connected with the strong interaction of R_3NHCl with HA in organic phase. It's due to the formation of stable solvates $R_3NHCl \cdot mHA$ that the D_M values are low under the conditions of anion-exchange extraction (Fig.1). The same is true for the

Table 2. Distribution of Pt and Pd in the system $(R_3NH)_2MCl_x + HA$ in toluene-water

HA	$C_{HA} : C_{R_3NH^+}$	Extraction, %	
		Pt	Pd
p-tret-butylphenol	1:1	2,66	< 0,6
caprylic acid	1:1	3,07	< 0,6
$(RO)_2P(O)OH$	1:1	36,5	19,0
RSO_3H	1:1	70,5	96,0

References

- Ivanova S.N., Gindin L.M., Chernyaeva A.P.// Izv. Sib.Otd.AN SSSR. 1978. Ser. khim. nauk. N 14. Vyp.6. P.68.
- Kholkin A.I., Kuzmin V.I.// Zh. neorg. khimii.1982. Vol.27. P.2070.

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The kinetics of extraction of palladium(II) with N_{510} (2-hydroxy-5-sec-octylbenzophenone oxime) from chloride medium was studied by using two phase fully mixed method.

1. Determination of the apparent extraction rate equation

According to the experimental results, it can be seen that the bigger the shaking speed of the system is, the faster the extraction rate is, but when the shaking speed is over 300 oscillations/min, the extraction rate has nothing to do with it, then the extraction kinetics will be related with chemical reaction mechanisms other than diffusion mechanisms.

Supposing the extraction is a first order reversible reaction with Pd(II):



then the extraction rate of Pd(II) can be expressed as follows:

$$-\frac{d[\text{Pd(II)}]}{dt} = k_f[\text{Pd(II)}] - k_b[\text{Pd(II)}]_{(o)}, \quad (2)$$

where k_f and k_b represent the total forward and backward rate constant respectively, the footnote (o) indicates the organic phase and the aqueous phase has no sign.

The relations between k_f , k_b and the concentrations of the components are shown in Fig.1, Fig.2 and Fig.3, where HL represents the mo-

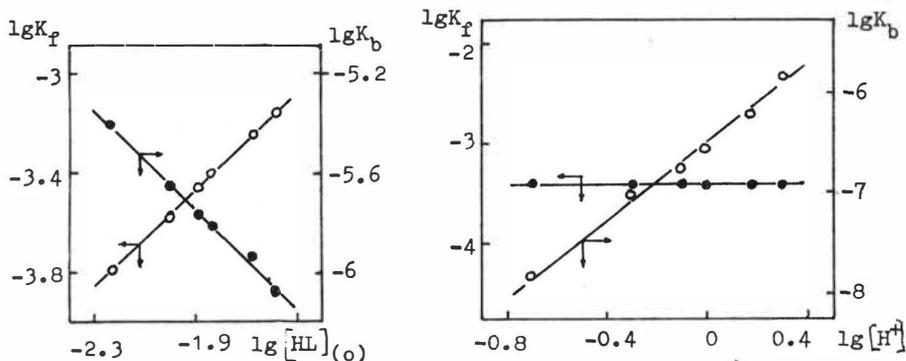


Fig.1. The relation between k_f , k_b and the concentration of HL in organic phase. $[\text{Cl}^-]$: $1.00 \text{ mol}\cdot\text{dm}^{-3}$; $[\text{H}^+]$: $2.00 \text{ mol}\cdot\text{dm}^{-3}$; $[\text{PdCl}_4^{2-}]^0$: $1.00\cdot 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$; Temperature: 25°C .

Fig.2. The relation between k_f , k_b and the concentration of H^+ in aqueous phase. $[\text{Cl}^-]$: $1.00 \text{ mol}\cdot\text{dm}^{-3}$; $[\text{HL}]_{(o)}$: $0.0146 \text{ mol}\cdot\text{cm}^{-3}$; $[\text{PdCl}_4^{2-}]^0$: $1.00\cdot 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$; Temperature: 25°C

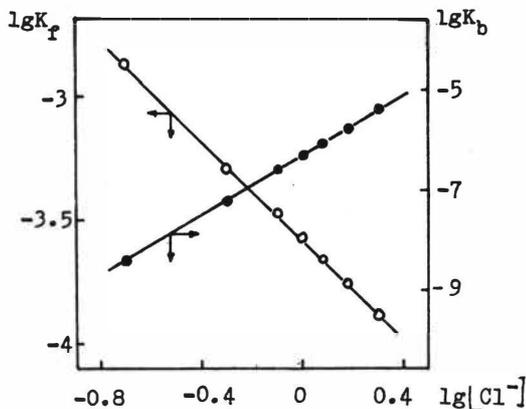


Fig.3. The relation between K_f , K_b and the concentration of Cl^- in aqueous phase. $[\text{H}^+]$: $1.00 \text{ mol} \cdot \text{dm}^{-3}$; $[\text{HL}]_{(o)}$: $0.0100 \text{ mol} \cdot \text{cm}^{-3}$; $[\text{PdCl}_4^{2-}]^0$: $1.00 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$; Temperature: 25°C

number of N_{510} , $[\text{PdCl}_4^{2-}]^0$ represents the initial concentration of Pd(II) in aqueous phase. It is evident, in these figures, that K_f is directly proportional to $[\text{HL}]_{(o)}$ and inversely proportional to $[\text{Cl}^-]$ but independent of $[\text{H}^+]$, K_b is directly proportional to $[\text{H}^+]^2 [\text{Cl}^-]^3$ but inversely proportional to $[\text{HL}]_{(o)}$, so equation(2) can be shown as follows:

$$-\frac{d[\text{Pd(II)}]}{dt} = k_f [\text{Pd(II)}] [\text{HL}]_{(o)} [\text{Cl}^-]^{-1} - k_b [\text{H}^+]^2 [\text{Cl}^-]^3 [\text{HL}]_{(o)}^{-1} [\text{Pd(II)}]_{(o)} \quad (3)$$

where k_f and k_b represent the apparent rate constant of forward reaction and backward reaction respectively. $k_f = 10^{-1.58} \text{ s}^{-1}$ and $k_b = 10^{-8.25} \text{ mol}^{-4} \cdot \text{dm}^{12} \cdot \text{s}^{-1}$ was measured at the temperature of 25°C .

2. Deduction of the reaction mechanism

The measurement of interfacial tension of N_{510} -kerosene/water system indicates that as $[\text{HL}]_{(o)}$ is over $1.00 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ the interface is saturated with HL, then the interfacial concentration of HL will not be increased with the increase of $[\text{HL}]_{(o)}$, however Fig.1 indicates that in the range of $5.92 \cdot 10^{-3}$ to $2.62 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ $[\text{HL}]_{(o)}$ still has a first order effect on the forward reaction rate, so the extraction rate has nothing to do with the interfacial concentration of HL, then the interfacial mechanism can be eliminated. Referring to the extraction mechanism of Pd(II) with other hydroxy-oxime of the same kind; [1,2] the extraction mechanism for this system can be deduced as follows:

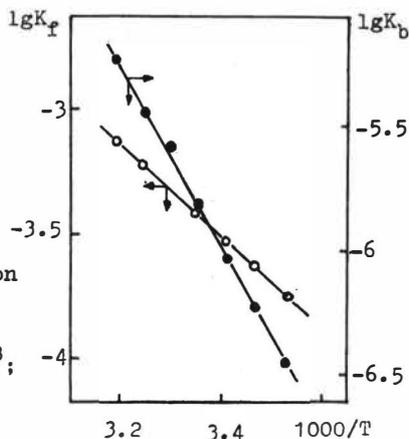


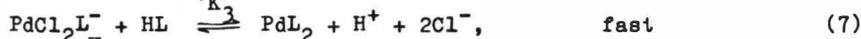
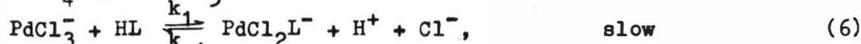
Fig.4. The effect of temperature on

K_f and K_b

$[Cl^-]: 1.00 \text{ mol} \cdot \text{dm}^{-3}; [H^+]: 1.00$

$\text{mol} \cdot \text{dm}^{-3}; [HL]_{(o)}: 0.0146 \text{ mol} \cdot \text{dm}^{-3};$

$[PdCl_4^{2-}]_{(o)}: 1.00 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$



where equation (6) is the rate-determining step.

3. Effect of temperature on the extraction rate

In the range of 10°C to 40°C, the effect of temperature on K_f and K_b is shown in Fig.4.

According to the Arrhenius formula:

$$\lg K_f = \frac{-\Delta E_f}{2.303RT} + c_1, \quad (9)$$

$$\lg K_b = \frac{-\Delta E_b}{2.303RT} + c_2, \quad (10)$$

where ΔE_f and ΔE_b represent the apparent activation energy of the forward and backward reaction respectively, it can be obtained that $\Delta E_f = 35.2 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta E_b = 68.2 \text{ kJ} \cdot \text{mol}^{-1}$ their difference chiming in with the extraction equilibrium constant $K_{ex} = -32.6 \text{ kJ} \cdot \text{mol}^{-1}$ [3].

References

1. Enxin M., Friser H. // Solv.Extr. and Ion Exchange 1983. Vol.1(3). P.485-496.
2. Enxin M., Jiansheng G. // Acta Chem. Sinica. 1986. Vol.44. P.1087.
3. Song Q.Sh., Sun S.X., Gao Z.L., Shen J.L. // XXV Intern. al Conf. on Coordination Chem. Book of Abstracts. Nanjing, China, July 26-31. 1987. P.347.

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Salts of tertiary amines and quaternary ammonium bases are effective extractants for extractive separation of platinum metals from moderately acid solutions. Quantitative regularities of the extraction of stable complex platinum metal anions in an excess of extractant were found in [1]. The extraction constants of ML_n^{2-} -complexes in different extraction systems are given in Table 1 where $K_1 = [R_4NL]_0 \cdot [ClO_4^-]_{aq} / [R_4NClO_4]_0 \cdot [L^-]_{aq}$ is the exchange constant of simple anions, $K_2 = D_M \cdot [L^-]_{aq}^2 / [R_4NL]_0^2$ and $K_3 = D_M \cdot [ClO_4^-]_{aq}^2 / [R_4NClO_4]_0^2$. The extraction

Table 1. The extraction constants of ML_n^{2-} with R_4NL , R_4NClO_4 (1-12) and R_3NHL (13-18), ($R = C_8H_{17}$); $M = 4.0$

No	ML_n^{2-}	K_1	K_2	$K_3 = K_2 \cdot K_1^2$
1	PtF_6^{2-}	$9.9 \cdot 10^{-9}$	$3.6 \cdot 10^5$	$3.5 \cdot 10^{-11}$
2	IrF_6^{2-}	$9.9 \cdot 10^{-9}$	$1.5 \cdot 10^7$	$1.4 \cdot 10^{-9}$
3	$PtCl_6^{2-}$	$8.4 \cdot 10^{-6}$	$2.5 \cdot 10^9$	$1.8 \cdot 10^4$
4	$IrCl_6^{2-}$	$8.4 \cdot 10^{-6}$	$4.8 \cdot 10^9$	$3.4 \cdot 10^{-1}$
5	$PtCl_4^{2-}$	$8.4 \cdot 10^{-6}$	$2.0 \cdot 10^6$	$1.4 \cdot 10^{-4}$
6	$PdCl_4^{2-}$	$8.4 \cdot 10^{-6}$	$4.8 \cdot 10^6$	$3.4 \cdot 10^{-4}$
7	$PtBr_6^{2-}$	$3.1 \cdot 10^{-4}$	$5.5 \cdot 10^8$	$5.3 \cdot 10^1$
8	$IrBr_6^{2-}$	$3.1 \cdot 10^{-4}$	$8.2 \cdot 10^8$	$7.9 \cdot 10^1$
9	$PtBr_4^{2-}$	$3.1 \cdot 10^{-4}$	$1.8 \cdot 10^6$	$1.7 \cdot 10^{-1}$
10	$PdBr_4^{2-}$	$3.1 \cdot 10^{-4}$	$3.4 \cdot 10^6$	3.26
11	PtJ_6^{2-}	$2.2 \cdot 10^{-2}$	$5.2 \cdot 10^7$	$2.5 \cdot 10^4$
12	PtJ_4^{2-}	$2.2 \cdot 10^{-2}$	$3.7 \cdot 10^5$	$1.8 \cdot 10^2$
13	$PdCl_4^{2-}$	-	$4.7 \cdot 10^4$	-
14	$PdCl_2^{2-}$	-	$1.1 \cdot 10^6^*$	-
15	$PdBr_4^{2-}$	-	$4.7 \cdot 10^4$	-
16	$PdBr_2^{2-}$	-	$1.7 \cdot 10^6^*$	-
17	PdJ_4^{2-}	-	$8.8 \cdot 10^4$	-
18	PdJ_2^{2-}	-	$5.7 \cdot 10^8^*$	-

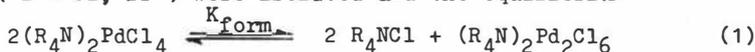
*Diluents : 1,2-dichloroethane, toluene

of three charged complexes ML_3^{3-} ($M = Rh, Ir, Ru$) is under these conditions insignificant. The separation of metals was found to be affected by their tendency to form bi- and polynuclear halogen-bridged complexes under a ligand shortage [2-3].

This is particularly characteristic of Pd (II), Rh(III), Ru(III), Ir(III). In the extraction in halogenide systems acting as a ligand in the organic phase is the anionic part of the extractant.

As a result, the equilibrium shifts towards formation of polynuclear species as the concentration of the metal increases and that of the extractant decreases.

The stability of these species, the rate of their formation and destruction depend on the nature of the diluent, the central atom, and the ligand (Table 2 where $K_{form} = C_{dim} \cdot C_L^2 / C_{mon}^2$). For Pd this process proceeds quickly. The compounds $[(C_8H_{17})_4N]_2[Pd_2L_6]$ ($L = Br, J$) and $[(C_8H_{17})_3NH]_2[Pd_2L_6]$ ($L = Cl, Br$) were isolated and the equilibrium



was studied spectrophotometrically (Fig. 1). For the complexes

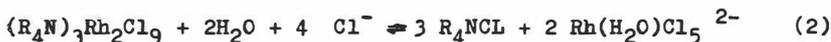
$(R_3NH)_2[Pd_2Cl_6]$ there is an increase in the formation constant with increasing solvating power of the diluent (Fig. 2). The distribution data shown in Table 3 confirm the existence in the extraction systems of binuclear compounds along with mononuclear species. All of the diluents used showed an increased content of Pd in the organic phase ($TOAHCl: Pd < 2$).

Table 2. Formation constants of binuclear Pd-complexes in nonaqueous solvents

Complex	Extractant	Solvent	K_{form}
$(R_3NH)_2Pd_2J_6$	R_3NHJ	$C_2H_4Cl_2$	$2.9 \cdot 10^{-1}$
$(R_3NH)_2Pd_2Br_6$	R_3NHBr	$C_6H_5CH_3$	$3.2 \cdot 10^{-5}$
$(R_4N)_2Pd_2Br_6$	R_4NBr	$C_2H_4Cl_2$	$1.4 \cdot 10^{-2}$
$(R_3NH)_2Pd_2Cl_6$	R_3NHCl	$C_2H_4Cl_2$	$2.3 \cdot 10^{-5}$
$(R_3NH)_2Pd_2Cl_6$	R_3NHCl	$C_6H_5CH_3$	$3.2 \cdot 10^{-5}$
$(R_3NH)_2Pd_2Cl_6$	R_3NHCl	$C_6H_{12}O$	$9.3 \cdot 10^{-4}$
$(R_3NH)_2Pd_2Cl_6$	R_3NHCl	C_3H_6O	$2.1 \cdot 10^{-3}$
$(R_3NH)_2Pd_2Cl_6$	R_3NHCl	$(C_2H_4Cl)_2O$	$6.3 \cdot 10^{-3}$

This makes possible to change the composition of the extracted compounds and the extractant capacity by changing the solvents. For metals in the oxidation state of III determination of the stability constants is difficult because of the small reaction rates of (1). Earlier it was shown that Rh(III) is extracted with tetraoctylammonium in the form of $[(C_8H_{17})_4N]_2[Rh_2Cl_9]$.

Its stripping with 3 to 6 mol / l of hydrochloric acid



proceeds slowly being limited by "depolymerization" in the organic phase. In an excess of extractant the rate of Rh back extraction is

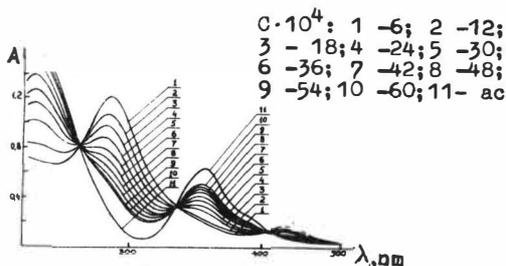


Fig. 1. The electronic absorption spectra of equilibrium mixtures of R_4NBr , $(R_4N)_2Pd_2Br_6$ and $(R_4N)_2PdBr_4$ in $C_2H_4Cl_2$

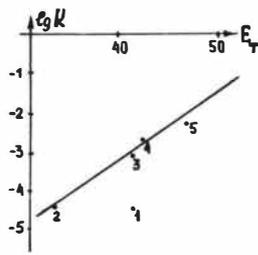


Fig. 2. $\lg K_{form}$ for $(R_3NH)Pd_2Cl_6$ as a function of the diluent solvating power E_t (1 - $C_2H_4Cl_2$, 2 - $C_6H_5CH_3$, 3 - $C_6H_{12}O$, 4 - C_3H_6O , 5 - $(C_2H_4Cl)_2O$)

Table 3. Solvent effect on the composition of the extracted Pd-compounds. $C_{Pd} = 0.3$ g-ion/l, $C_{TOAHCL} = 0.3$ mol/l

Diluent	$(\frac{TOAHCL}{Pd})_0$	D_{Pd}
Methylisobutylketone	1.30	3.30
Tetrachloroethylene	1.40	2.30
Toluene	1.60	1.70
Dichloroethane	1.67	1.80

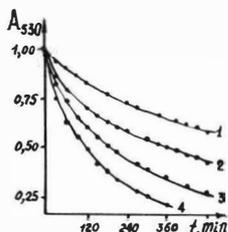


Fig. 3. Kinetic back extraction curves of Rh with 3M HCl from toluene solutions of $(R_4N)_3Rh_2Cl_9$: T, °C: 15(1), 20(2), 25 (3), 30(4)

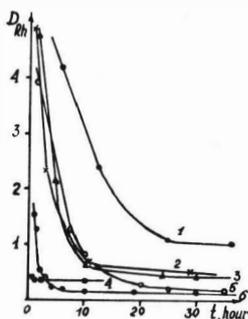
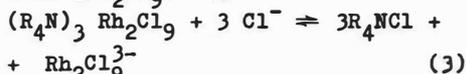


Fig. 4. The effect of solvent on the Rh back extraction rate. 1.-nitrobenzene, 2.-dichloroethane, 3.-toluene, 4.-toluene + 40% caprylic acid, 5.-dichloroethane + 10% 2-ethylhexanol, 6.-methylhexylketone

independent of the H^+ , Cl^- , Rh_2 -concentrations ($k = 3.7 \cdot 10^{-5} s^{-1}$, $t = 25^\circ C$). Fig. 3 shows kinetic back extraction curves at different temperatures. The dependence of the rate constant on $I/[R_4NCl]$ is a straight line. This permits us to write the following law for the rate: $W = k_I \cdot [Rh_2] + k_{II} \cdot [Rh_2]/[R_4NCl]$. The values of k_I and k_{II} are given in Table 4. Fig. 4 shows the effect of solvent on the rate of Rh back extraction. Back extraction of Rh with concentrated HCl occurs in the form $[Rh_2Cl_9]^{3-}$:



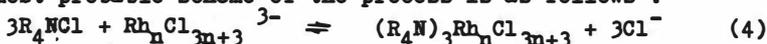
und further "depolymerization" takes place in the aqueous phase in two stages. This is confirmed spectrophotometrically and by kinetic studies.

The rate constants of the first "depolymerization" stage in the back-extraction liquid and in the solutions of $[(CH_3)_4N]_3Rh_2Cl_9$ are close to each other ($1.51 \cdot 10^{-3} s^{-1}$ and $1.36 \cdot 10^{-3} s^{-1}$, respectively). The rate constant of the second stage is $6 \cdot 10^{-6} s^{-1}$ (for $C_{HCl} = 11$ mol/l, $t = 25^\circ C$). The reason for the occurrence of the slow stage is the presence

Table 4. Rate constants of Rh back extraction in the system $(R_4N)_3Rh_2Cl_9$ - toluene- 3 mol/l HCl

t°C	k_I, s^{-1}	$k_{II}, mol \cdot s^{-1}$
15	$(7.6 \pm 0.7) \cdot 10^{-6}$	$(8.9 \pm 0.9) \cdot 10^{-8}$
20	$(1.5 \pm 0.1) \cdot 10^{-5}$	$(1.4 \pm 0.1) \cdot 10^{-7}$
25	$(3.3 \pm 0.1) \cdot 10^{-5}$	$(2.2 \pm 0.1) \cdot 10^{-7}$
30	$(6.2 \pm 0.6) \cdot 10^{-5}$	$(3.5 \pm 0.1) \cdot 10^{-7}$

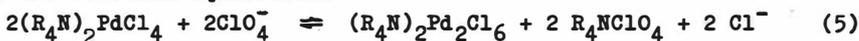
in the organic phase and in the back extraction liquid of Rh species with a nuclearity greater than 2 which have high distribution coefficients but are unstable with time. This explains the presence of a maximum in the dependence of the Rh distribution coefficient on the extraction time for freshly prepared solutions (Curve 1, Fig. 5). A similar but more complex behaviour is also observed for ruthenium. The most probable scheme of the process is as follows:



Dissolution of $(RhCl_3)_n$ in a toluene- R_4NCl mixture gives rise to a compound of the composition $[(C_8H_{17})_4N]_4H_3O[Rh_3Cl_{14}]$. Its structure was studied by X-ray method, NMR ^{103}Rh spectra were measured (for $(R_4N)_4H_3O[Rh_3Cl_{14}]$ - 95.5 m.p., for $(R_4N)_3Rh_2Cl_9$ - 120 m.p.) relative $Rh(acac)_3$ [4].

The increased extractability of polynuclear complexes is of interest for extraction of metals from aqueous solutions but at the same time it complicates its separation. But "depolymerization" of the solution prior to the extraction and the use of more hydrophylic diluents allow the separation process in these systems to be made fully reversible.

In some cases the polynuclear complexes are formed in the back extraction. Thus, in contrast to Pt, back extraction of Pd with diluted HNO_3 and $HClO_4$ is less effective. This is explained by a shift in the reaction equilibrium:



towards formation of binuclear Pd complexes as a result of decreased ligand concentration in the organic phase. In the back extraction of Ir using reducers, a ligand shortage also results in the formation of polynuclear complexes whose back extraction proceeds very slowly.

Thus, the study allows a substantiated approach to the choice of systems in the extraction and back extraction of platinum metals.

References

1. S.N. Ivanova, L.M. Gindin, A.P. Chernayeva // *Izv. SO AN SSSR*. 1974. N 4. Ser. Khim. Nauk. V. 2. P. 3.
2. L.M. Gindin, S.N. Ivanova, A.A. Mazurova et al. // *Solvent extraction chemistry*. Amsterdam, 1967. P. 433.
3. I.A. Selezneva, S.N. Ivanova, L.M. Gindin // *Izv. SO AN SSSR*. 1982. N 14. Ser. Khim. Nauk. V. 6. P. 107.
4. S.N. Ivanova, I.A. Druzhinina, O.V. Shuvayeva // *Zh. Neorg. Khim*. 1986. T. 31. N 8. P. 2069.

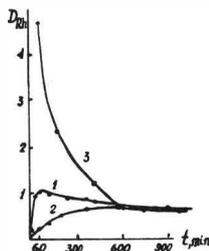


Fig. 5. Kinetic Rh extraction curves. 1 - from freshly prepared samples, 2 - from aged samples, 3 - back extraction with 3mol/l HCl

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There are two problems on the way of wide application of oxygen containing extractants for separation and extraction of platinum group metals, namely unreproducibility of results of different researchers and relatively low distribution and selectivity ratios [1]. The reasons for the absence of reproducibility can be best regarded on a system: chloride solutions-tributylphosphate (TBP). The highest variance of extractivity results for chloride complexes with TBP is registered for Os (IV) and Ir (IV). To find out the reason of this variance we used iridium and osmium chloride complexes solutions prepared by diluting metallic samples primarily activated with thermal neutrons in indirect electric field. Two series of osmium and iridium samples were prepared varying hydrochloric acid concentration, temperature and retention time. Judging by absorption spectra they seemed absolutely identical and corresponded to OsCl_6^{-2} and IrCl_6^{-2} . At the same time distribution ratios of osmium and iridium identified in the course of extraction, reextraction and back extraction differed by two orders. Element identification in aqueous and organic phases was based on γ -spectra of corresponding isotopes. Test solutions were prepared on the basis of primarily activated metals. Thus low kinetics of isotope exchange between different forms of their presence in solution while introducing a radioactive tracer could not be a possible reason for error. Thus the existence of variance of acquired data can be accounted for only by the existence in solution of several osmium and iridium complexes with different extraction properties.

To prove the correctness of this assumption in the present study we made an attempt of extraction-chromatographic separation in the same system HCL TBP. In all instances there were prepared several fractions of one element. The difference of chromatograms within the series of the solutions is confined to variation in individual component concentration. With osmium absorption spectrography shows washing $\text{Os}(\text{H}_2\text{O})_2\text{Cl}_4^0$, OsCl_6^{-2} , $\text{Os}(\text{H}_2\text{O})\text{Cl}_5^{-2}$ out of the column (Fig.1, a). In the case of iridium along with similar complexes in the first fraction Ir(III) compounds were detected. The chromatogram showed as well a peak for previously unknown Ir(IV) compound - presumably dimere complex (Fig. 1,b). These results are in agreement with the existing understanding of extractability of a complex depending on its loading with oxygen-containing extractants. It must be

A · 10³ c.p.m.
6 M HCl 0.2 M HCl H₂O

4M H₂SO₄ +
0.1 M HCl 3M HCl 0.1 M HCl

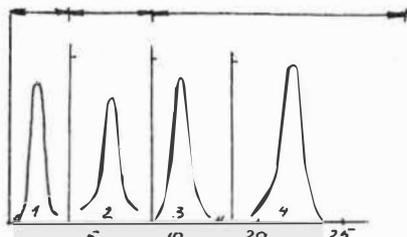
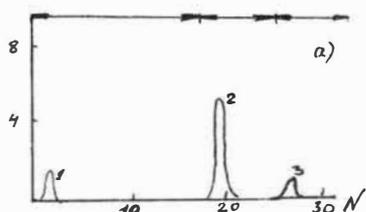


Fig. 1. Extraction-chromatographic separation of chloride and aqua-chloride complexes Os(IV): (a) 1 - $\text{Os}(\text{H}_2\text{O})_2\text{Cl}_4^0$; 2 - OsCl_6^{-2} ; 3 - $\text{Os}(\text{H}_2\text{O})\text{Cl}_5^-$ and Ir(IV); (b): 1 - Ir(III) + $\text{Ir}(\text{H}_2\text{O})_2\text{Cl}_4^0$; 2 - dimere; 3 - IrCl_6^{-2} ; 4 - $\text{Ir}(\text{H}_2\text{O})\text{Cl}_5^-$

noted that there is a considerable difference in distribution ratios of individual complexes (Table 1).

It is also necessary to dwell on another possible reason for data variance on extraction, particularly, for iridium. To stabilize iridium in the form of Ir(IV) compounds the usual practice is to saturate the solution with gaseous chlorine. The study of Ir(IV) chloride complexes extraction behaviour in HCl-TBP system showed deviations of distribution data for static extraction and extraction with chromatography. Attachment of chloride complexes to a column proved much lower than it could be expected from extraction data. To clarify this phenomenon we carried out a series of experiments. In the course of it distribution ratios of iridium (IV) in 3 M HCl-TBP were determined under different conditions of aqueous and organic phases saturation with chlorine (Table 2).

The above data show sharp rise in chlorine solubility in TBP-HCl system in comparison to that in solvents taken separately. The presence of chlorine in the system noticeably decreases distribution ratio. Saturating solutions with chlorine can be used for extractive and

Table 1. Values of D for chloride and aqua-chloride complexes, Ir(IV) and Os(IV) in system 6 M HCl-TBP

Complex	$[\text{Os}(\text{H}_2\text{O})_2\text{Cl}_4]^0$	$[\text{OsCl}_6]^{-2}$	$[\text{Os}(\text{H}_2\text{O})\text{Cl}_5]^-$	$[\text{Ir}(\text{H}_2\text{O})_2\text{Cl}_4]^0$	$[\text{IrCl}_6]^{-2}$	$[\text{Ir}(\text{H}_2\text{O})\text{Cl}_5]^-$
	0,067	53	250	<1,0	23	≥200

Table 2. Ir(IV) extraction in 3 M HCl-TBP system in the presence of dissolved chlorine

Conditions of aqueous and organic phases chlorine saturation	$Cl_2^{org}_{(m)}$	D_{Ir}
1. Separately before contacting	0,07	26 ± 2
2. In contact during 10 min	0,8	$4,6 \pm 0,2$
3. In contact during 15 min	1,1	$3,0 \pm 0,2$
4. No saturation	-	28 ± 2

extraction-chromatographic separation of various PGM mixtures. So the influence of Cl_3^- coextraction will tell on distribution ratios not only of iridium but other PGM as well.

Thus the reason for data variance for PGM extraction with oxygen-containing extractants becomes clear. For correct data interpretation, first of all, reliable data on PGM relative contents in aqueous solution is necessary. The fact that absorption spectra in the visible range are identical is not sufficient to testify that solutions have identical contents. Maximums for absorption of aqua-chloride and chloride complexes within visible range are very close, their relative contents can be up to 10 per cent and even above 10 per cent. Thus their direct spectrophotometric identification is absolutely impossible.

The analysis of reasons for unreproducibility of data of PGM extraction with oxygen containing extractants has an important practical consequence. Slow kinetics of ligand substitution complicates stabilizing PGM in a definite form in solutions, sometimes this stabilization is absolutely impossible. Thus one must probably withdraw from attempts to work out an extraction technology for individual separation of PGM in the form of one fraction. Instead having reliable information on extraction behaviour of individual forms of elements it seems in principle possible to design a process aimed at separating a number of fractions corresponding to relatively stable states of an element in a primary solution.

The second problem on the way of PGM extraction with oxygen containing extractants is that of providing high values for distribution ratios and selectivity ratios. In accordance with currently existing ideas of the process of PGM extraction with oxygen containing extractants the presence of a maximum on the curve representing D - depending on HCl concentration for chloride complexes is accounted for by counter-action of increasing concentrations of hydrogen and chloride ions. Negative influence of chloride ions in their competition for the extractant is obvious. Explaining of determining effect of hydrogen ions concentration by the formation of cation hydrosolwates seems arbitrary. The data on electro dialysis of platinum and palladium chloride complexes through liquid extraction membranes based on TBP show the

determining role of the process of suppressing dissociation of corresponding halogenometallides of hydrogen [2]. Thus the optimum composition of aqueous phase used for the extraction of PGM chloride complexes with oxygen containing extractants must correspond to requirements for maximum possible chloride ion concentration with reference to prevention of intra-sphere substitution of ligands and relatively concentration of oxygen ions which promotes suppressing the second stage of hydrogen halogenometallide dissociation. In general these conditions must be realised on mixtures of hydrochloric acid with any other strong acid having lower extractability than that of hydrochloric acid. Fig.2 presents the curves for distribution ratios of PtCl_6^{-2} (1) and PdCl_4^{-2} (2) extracted from solutions with TBP (a) and n-heptanol (b).

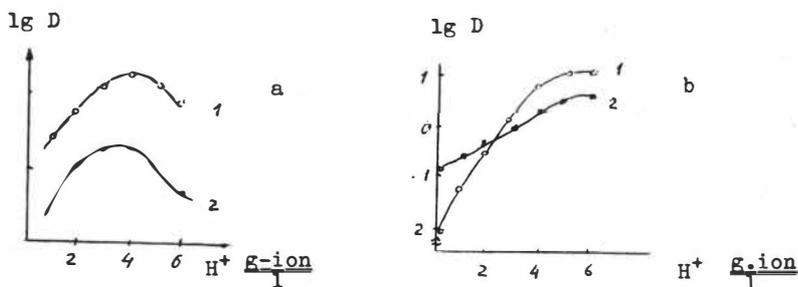


Fig.2. PtCl_6^{-2} (1) PdCl_4^{-2} (2) extraction from 0,1 M $\text{HCl}+\text{H}_2\text{SO}_4$ with TBP (a) and n-heptanol (b)

Along with high values of distribution ratios the extraction systems in question have another advantage: decreasing of chloride ions concentration in solution brings about a considerable decrease in D-value for the majority of basic metals. Under optimum conditions the selectivity ratio for PGM versus other most typical byproduct elements exceeds the value of 10^4 [3]. This value corresponds to the level of values achieved when using nitrogen and sulphur containing extractants, at that the proposed systems have obvious advantages of full reversibility of extraction process.

References

1. Mojsky M. // Chem. Anal. (PRL). 1980. V.25. p.919.
2. Moskvina L.N., Krasnoperov V.M., Chereshevich Yu.L. // Izv. SO AN SSSR. 1974. Ser. Khim. nauk. Vyp.2. P.53.
3. Moskvina L.N., Krasnoperov V.M., Grigor'ev G.L. // ZhAKh. 1982. Vol.37. P.942.

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Strong changes of phase volumes, resulting under certain conditions in the change of the number of phases (third liquid phase formation), the effect of diluent, synergistic enhancement, strong sensitivity to small temperature changes and mutual influence of metals have been observed in the course of extraction of metals as chlorometallic acids by diisopropyl ether or solvents containing diisopropyl ether (IPE). Therefore the systems which could be presented with the general formula: $\text{MeCl}_3\text{-HCl-H}_2\text{O-S}$, where Me is Fe(III), Ga(III) or Au(III) and S is solvent containing IPE, are very interesting. Good results of extraction can be attained with pure IPE as solvent if initial concentration of hydrochloric acid exceeds $7 \text{ mol}\cdot\text{dm}^{-3}$ [1,2]. Then, under properly chosen conditions, the third liquid phase with a very high metal content appears. At a lower initial acid concentration e.g. $5 \text{ mol}\cdot\text{dm}^{-3}$ the system is under no circumstances a three-phase one and extraction with pure IPE is much less effective. In that case good results of extraction can be obtained with a mixed solvent producing a synergistic effect. As earlier results of iron(III) extraction by mixed solvents IPE-n-pentyl alcohol [3] and IPE-n-hexyl alcohol [4] show synergistic enhancement of extraction, it appeared advisable to undertake also the extraction of gold(III) with the above mixed solvents.

EXPERIMENTAL

IPE was purified and distilled. Other chemicals and solvents used were of analytical reagent grade.

The separation were made in 15 ml separation funnels having a calibrated stem and/or in 15 ml graduated cuvettes. The systems were prepared by vigorous shaking of components and placed in water bath with a thermostat kept by automatic control at $20.0 \pm 0.05^\circ\text{C}$. The shaking was repeated in the same manner at 15 min intervals for 1 h. The initial volume ratio of the organic phase to the aqueous phase (r^i) was always 1.0. The volume of the equilibrated phases were determined before sampling. Sampling for analysis, by pipettes thermostated at the temperature of extraction, was carried out directly (from the cuvette) or after removal of the separated phases (from the funnel). The concentration of metals in the samples of the aqueous phase and in pretreated samples of the organic phase was determined by ICP spectrometry, by complexometric titration (for larger quantities of iron), and gravimetrically (for larger quantities of gold).

RESULTS AND DISCUSSION

Investigation of the effect of initial hydrochloric acid concentration in the system $\text{AuCl}_3\text{-HCl-H}_2\text{O-IPE}$ on phase volumes shows that the system transforms from a three-phase one to a two-phase one (at initial acid concentration $c_{\text{HCl}}^i = 10.0\text{-}10.5 \text{ mol}\cdot\text{dm}^{-3}$)

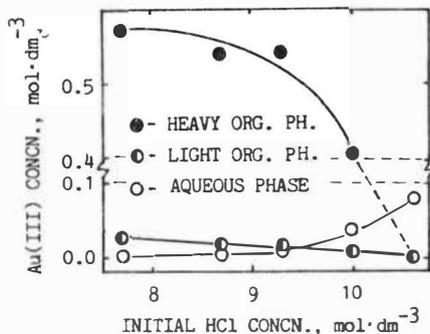
Fig.1.

Gold(III) concentration in equilibrated phases vs. initial acid concentration.

System: $\text{AuCl}_3\text{-HCl-H}_2\text{O-IPE}$,

$$c_{\text{Au}}^i = 0.14 \text{ mol}\cdot\text{dm}^{-3},$$

$$c_{\text{IPE}}^i = 7.1 \text{ mol}\cdot\text{dm}^{-3}$$



and then to a homogeneous system (at $c_{\text{HCl}}^i = 10.5\text{--}11.2 \text{ mol}\cdot\text{dm}^{-3}$) along with a continuous increase in the aqueous phase volume. Fig.1 shows the change of gold(III) concentration in equilibrated phases in dependence on initial acid concentration.

With increase of initial acid concentration gold(III) concentration in the heavy organic phase decreases at first slightly (7.7–9.3 mol·dm⁻³) and later on more remarkably until the heavy organic phase disappears. In the light organic phase gold(III) concentration slightly decreases in the full range of initial acid concentrations, while in the aqueous phase it increases at first slightly and later on (9.3–10.6 mol·dm⁻³) more strongly. By proper choice of initial acid concentration (e.g. 8 mol·dm⁻³) it is possible to obtain the partial distribution ratio between the heavy organic phase and the aqueous phase (D_{c}^{h}) higher than 500.

Fig. 2 shows the change in volume fraction of organic phases in dependence on alcohol content in mixed solvent. At a given initial acid concentration (5 mol·dm⁻³) the composition of mixed solvent does not affect significantly the organic phase volume, in distinction from the system with a higher initial acid concentration (8 mol·dm⁻³).

Fig.2.

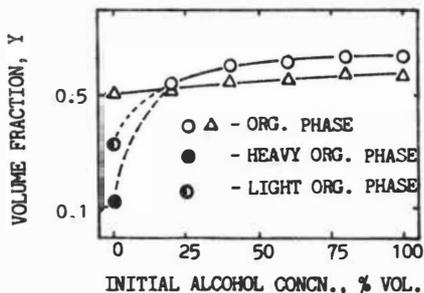
Volume fraction of organic phase vs. initial concentration of n-hexyl alcohol in mixed solvent.

System: $\text{AuCl}_3\text{-HCl-H}_2\text{O-IPE-CH}_3(\text{CH}_2)_5\text{OH}$,

$$c_{\text{Au}}^i = 0.15 \text{ mol}\cdot\text{dm}^{-3},$$

$$c_{\text{HCl}}^i = 5.0 \text{ mol}\cdot\text{dm}^{-3} (\Delta)$$

$$= 8.0 \text{ mol}\cdot\text{dm}^{-3} (\circ)$$



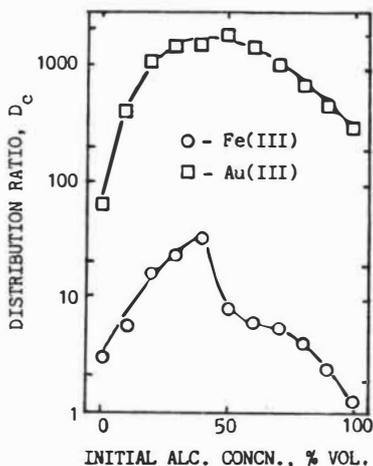


Fig. 3.

Distribution ratios of gold(III) and iron(III) vs. initial concentration of n-hexyl alcohol in mixed solvent.

Systems: $\text{AuCl}_3\text{-HCl-H}_2\text{O-IPE-CH}_3(\text{CH}_2)_5\text{OH}$,

$\text{FeCl}_3\text{-HCl-H}_2\text{O-IPE-CH}_3(\text{CH}_2)_5\text{OH}$,

$c_{\text{Fe}}^i = 0.15 \text{ mol}\cdot\text{dm}^{-3}$,

$c_{\text{Au}}^i = 0.15 \text{ mol}\cdot\text{dm}^{-3}$,

$c_{\text{HCl}}^i = 5.0 \text{ mol}\cdot\text{dm}^{-3}$

Fig. 3 shows the effect of composition of the mixed solvent IPE-n-hexyl alcohol on gold(III) extraction. As in iron(III) extraction under identical conditions a synergistic effect was observed, but in contrast to iron(III) extraction pure alcohol was found to extract gold(III) better than pure IPE.

The synergistic effect was much more expressed in the case of gold(III) extraction than in the case of iron(III) extraction. For instance, in the extraction with IPE-n-hexyl alcohol mixture the magnitude of synergistic enhancement was about 9 for iron(III) (maximum value at $c_{\text{alc}}^i = 40\%$ vol.) and about 1600 for gold(III) (maximum value at $c_{\text{alc}}^i = 50\%$).

The effect of mixed solvent composition on the extraction of iron(III) and gold(III) was also investigated in the system containing both metals in equimolar concentrations at $5 \text{ mol}\cdot\text{dm}^{-3}$ initial acid concentration. Fig. 4 shows metal content in

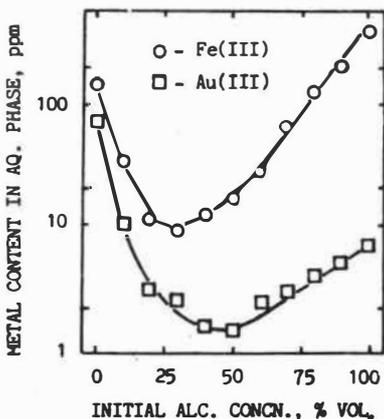


Fig. 4.

Iron(III) and gold(III) content in the aqueous phase vs. initial n-hexyl alcohol concentration in mixed solvent.

System: $\text{AuCl}_3\text{-FeCl}_3\text{-HCl-H}_2\text{O-IPE-CH}_3(\text{CH}_2)_5\text{OH}$,

$c_{\text{Me}}^i = 0.15 \text{ mol}\cdot\text{dm}^{-3}$,

$c_{\text{HCl}}^i = 5.0 \text{ mol}\cdot\text{dm}^{-3}$

the equilibrated aqueous phase depending on mixed solvent composition. The magnitude of synergistic enhancement was about 1900 for gold(III) (maximum value at $c_{alc}^i=50\%$).

Gold (III) extraction with n-pentyl alcohol and with the mixed solvent IPE-n-pentyl alcohol was investigated. The results were compared with the results of extraction in systems containing n-hexyl alcohol. Table gives the calculated distribution ratios for pure solvents and their mixtures and the magnitude of synergistic enhancement (ΔD).

Distribution ratios for different pure solvents and their mixtures and magnitude of synergistic enhancement. System: $AuCl_3-HCl-H_2O-IPE-CH_3(CH_2)_nOH$ ($n=4$ and 5), $c_{Au}^i=0.15 \text{ mol}\cdot\text{dm}^{-3}$, $c_{HCl}^i=5.0 \text{ mol}\cdot\text{dm}^{-3}$

SOLVENT	IPE	IPE - 10% n-pentyl alcohol	IPE - 30% n-pentyl alcohol	n-pentyl alcohol	IPE - 10% n-hexyl alcohol	IPE - 30% n-hexyl alcohol	n-hexyl alcohol
Distribut. ratio D_c	65.6	792.3	2178.6	291.8	419.7	1505.6	323.1
ΔD		434.9	1821.1		31.0	1116.8	
$\Delta D = D_c - (D_{c_{IPE}} + D_{c_{alc}})$							

The effect of temperature on phase volume in the systems containing n-pentyl alcohol and n-hexyl alcohol was investigated in the range $15-40^\circ\text{C}$. In these systems no significant effect was observed in contrast to systems without alcohol.

High distribution ratios as well synergistic enhancement were found at moderate acid concentration. It can be concluded that the systems investigated are very promising for gold(III) extraction and deserve more detailed examination.

References

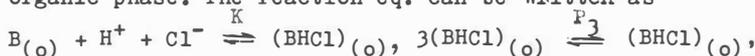
1. Maljković Da., Maljković Du., Branica M. // Croat. Chem. Acta 1979. Vol. 52. P.191.
2. Maljković Da., Maljković Du., Branica M. // Sep. Sci. Technol. 1981. Vol. 16. P.315.
3. Maljković Du., Maljković Da., Paulin A. // Proceedings of Intern. Solvent Extract. Conf. (ISEC'83). Denver, Colorado, 1983. P.242.
4. Maljković Du., Maljković Da. // Preprints of Intern. Solvent Extract. Conf. (ISEC'86). München, FRG, 1986. Vol. II. P.471.

EXTRACTION EQUILIBRIA OF GOLD(III) WITH A MIXTURE OF
PRIMARY AMINE N1923 AND MONOALKYLPHOSPHORIC ACID P538 IN KEROSENE

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The mechanism of the extraction of gold(III) ($C_{Au} = 4.00 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) from $1.00 \text{ mol} \cdot \text{dm}^{-3}$ (Na,H)Cl solution with a mixture of primary amine N1923 ($R' > \text{CH-NH}_2, R' + R = \text{C}_{19-23}, \text{B}$) and monoalkylphosphoric acid P538 ($\text{RO-PO}(\text{OH})_2, R = \text{C}_{12-18}, \text{H}_2\text{A}$) in kerosene at 25°C has been studied. The experimental results are as follows.

1. The determination of an aggregation number of amine salts, BHCl, formed by reaction of N1923 (B) dissolved in kerosene with hydrochloric acid from aqueous solution have been performed by two phase emf titration. When the concentration of N1923 in organic phase is in the range of $0.001-0.01 \text{ mol} \cdot \text{dm}^{-3}$, the formation of an aggregate as trimer was observed, by assuming the ideal behavior of each species in organic phase. The reaction eq. can be written as



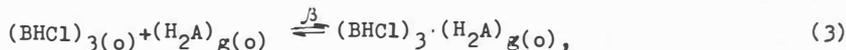
where $\log K + \log 3P_3 = 7.46$.

2. The extraction results of Au(III) with N1923 kerosene solution ($C_{\text{BHCl}(o)} = 0.003-0.019 \text{ mol} \cdot \text{dm}^{-3}$) show that the extraction mechanism is anion exchange reaction described by eq.(1):



where $a = 1.31$ $\log K_{ex} = 4.30$.

3. The extraction equilibrium of Au(III) with a mixture of P538 ($C_{\text{H}_2\text{A}(o)} = 0-0.05 \text{ mol} \cdot \text{dm}^{-3}$) and N1923 ($C_{\text{BHCl}(o)} = 0-0.06 \text{ mol} \cdot \text{dm}^{-3}$) in kerosene can be represented by



$$\text{and } C_{\text{BHCl}(o)}^0 = 3\mathcal{L}(\text{BHCl})_3 \mathcal{J}'(o) + 3\mathcal{L}(\text{BHCl})_3 (\text{H}_2\text{A})_g \mathcal{J}'(o) + 3a' \mathcal{L}[\text{Au}]_{(o)} \approx 3\mathcal{L}(\text{BHCl})_3 \mathcal{J}'(o) + 3\mathcal{L}(\text{BHCl})_3 (\text{H}_2\text{A})_g \mathcal{J}'(o), \quad (4)$$

$$C_{\text{H}_2\text{A}(o)}^0 = q\mathcal{L}(\text{H}_2\text{A})_g \mathcal{J}'(o) + q\mathcal{L}(\text{BHCl})_3 \cdot (\text{H}_2\text{A})_g \mathcal{J}'(o). \quad (5)$$

From eqs. (2)-(5) and $\text{Cl}^- = 1.00 \text{ mol} \cdot \text{dm}^{-3}$, the eq. (6) can be obtained:

$$C_{\text{BHCl}(o)}^0 = 3(D/K_{ex})^{1/a'} + 3q^{-1} \mathcal{L} \beta^{-1} (D/K'_{ex})^{-1/a'} + 1 \mathcal{J}'^{-1} C_{\text{H}_2\text{A}(o)}^0 \quad (6)$$

The experimental results show that the plots of $C_{\text{BHCl}(o)}^0$ vs. $C_{\text{H}_2\text{A}(o)}^0$ gave a good straight line at constant $D = C_{\text{Au}(o)} / C_{\text{Au}}$. The values of intercepts $b = 3(D/K'_{ex})^{1/a'}$, and slopes, $s = 3q^{-1} \mathcal{L} \beta^{-1} (D/K_{ex})^{-1/a'} + 1 \mathcal{J}'$ are changed by varying the values of D. Therefore, the values of a', K'_{ex}, q can be calculated, thus $a = 1.66$; $\log K'_{ex} = 5.14$

and $q=4.75$. From this, it can be seen that the extracted species, $(BH)AuCl_4 \cdot (BHCl)_4$, in this system is larger than that formed in the system containing N1923 only, and that P538 does not enter into it. The acidity in aqueous phase does not affect the extraction equilibrium of Au(III).

$C_{(o)}^{\circ}$ stands for the initial concentration of species in organic phase, $[]_{(o)}$ and $[]$ stand for the equilibrium concentrations of species in the organic phase and in the aqueous phase respectively.

Reference

1. Grinsterd R.R. // J.Phys.Chem. 1968. Vol.72. P.1630.

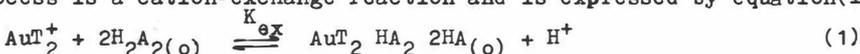
A EQUILIBRIUM AND KINETIC STUDY OF THE EXTRACTION OF Au(I) FROM AQUEOUS THIOUREA SOLUTION BY HDEHP AND HEH(EHP)

7-26

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Equilibrium and kinetics of extraction of Au(I) from aqueous thiourea solution by HDEHP and HEH(EHP) in various diluents have been investigated respectively at 25°C. The initial concentration ranges for each component in these systems are: $C_{Au}^{\circ} = (0.4 \sim 1.2) \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$; $C_{HA(o)}^{\circ}$ (HA denotes HDEHP or HEH(EHP)) = $0.05 \sim 0.5$) $\text{mol} \cdot \text{dm}^{-3}$; C_T° (T denotes CS $(NH_2)_2$) = $(0.2 \sim 3) \cdot 10^{-4}$; $C_{Cl}^{\circ} = 0.1 \sim 1.0 \text{ mol} \cdot \text{dm}^{-3}$; pH = $2 \sim 5$. Concentration of Au(I) in aqueous phase was determined with the method of HDEHP extraction-TMK colorimetry.

Results of extraction equilibrium studies show that: extraction process is a cation-exchange reaction and is expressed by equation(I)



chloride ion not enter into the extracted complex. IR spectra of this extracted complex can further prove that anion AuT enters into it.

This extraction mechanism is unchanged in various diluents. Values of K_{ex} obtained are listed in Table.

Equilibrium constant for the extraction of Au(I) by HDEHP and HEH(EHP) ($C_{Au(I)} = 1.00 \cdot 10^{-3}$, $C_{NaCl} = 0.40$, $C_T = 0.10$, $C_{HA(o)} = 0.50 \text{ mol} \cdot \text{dm}^{-3}$)

Diluent	Kerosine	n-Hexane	CCl_4	Benzene	$CHCl_3$	MIBK
HDEHP	$\bar{\epsilon}$ -1.16	-1.18	-1.20	-1.34	-1.54	-1.83
HEH(EHP)	-2.18	-2.22	-2.30	-2.58	-2.68	-3.07
$\bar{\epsilon}$ d	7.8	8.2	8.6	9.15	9.3	8.4

$\bar{\epsilon}$ solubility parameter of n-Dodecane

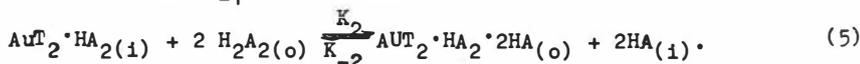
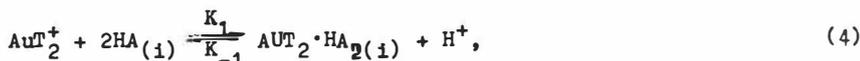
By treating the relation between the extraction equilibrium constant and the solubility parameters of diluents with Regular solution theory the following equations are obtained.

$$\log K_{\text{ex}}^{\text{HDEHP}} = -0.24\delta_d^2 + 3.95\delta_d - 17.2, \quad (2)$$

$$\log K_{\text{ex}}^{\text{HEH(EHP)}} = -0.21\delta_d^2 = 3.19\delta_d - 14.5. \quad (3)$$

In these equations there is an exception for MIBK, since there is the stronger interaction between MIBK and the extractant in the organic phase so it can't be treated simply with Regular Solution Theory 2.

Results of studies on the kinetics for the extraction process show that the extraction of Au(I) by HDEHP(EHP) (or HEH(EHP)) from aqueous thiourea solution is a first order reaction. The variation of K and K with varying the extractant concentration and the acidity of aqueous phase can be obtained respectively by using the pseudo-first order approximation, from the knowledge of the interfacial activity of HDEHP and HEH(EHP) two interfacial equations can be obtained as follows:



Equation (5) may be considered as the rate-determining step for the extraction by HDEHP. By using the steady-state approximation, K_f and K_b can be obtained as

$$K_f = K_2 K_e \frac{[\text{HA}]_{(1)}^2 \cdot [\text{H}_2\text{A}_2]_{(o)}^2}{[\text{H}^+]}, \quad (6)$$

$$K_b = K_{-2} \frac{[\text{HA}]_{(1)}^2}{[\text{H}^+]}, \quad (7)$$

where $K_e = K_1/K_{-1}$.

Equations (6) and (7) are in accordance with the results obtained from the thermodynamic studies. Equations (4) and (5) may be considered as the rate-determining steps for the extraction by HEH(EHP) K_f and K_b obtained can also explain the experimental results i.e.

$$K_f = \frac{K_1 K_2 \frac{[\text{HA}]_{(1)}^2}{[\text{H}^+]} \frac{[\text{H}_2\text{A}_2]_{(o)}^2}{[\text{H}^+]}}{K_{-1} \frac{[\text{H}^+]}{[\text{H}^+]} + K_2 \frac{[\text{H}_2\text{A}_2]_{(o)}^2}{[\text{H}^+]}} ,$$

$$K_b = \frac{K_{-1} K_{-2} \frac{[\text{HA}]_{(1)}^2}{[\text{H}^+]}}{K_{-1} \frac{[\text{H}^+]}{[\text{H}^+]} + K_2 \frac{[\text{H}_2\text{A}_2]_{(o)}^2}{[\text{H}^+]}} . \quad (8)$$

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Nitrogen-containing organic reagents have found the greatest application in the extraction chemistry of rhenium. Aliphatic amines are of great importance among them, mainly the tertiary alkylamines derived from C_7-C_9 alcohols. Since, the capabilities of these extractants have been exhausted in the most cases, the further increase of effectiveness of rhenium extraction may be accomplished by involving more perfect structures of phosphorus- and nitrogen-containing organic reagents.

It is to be noted, that a lot of rhenium extraction processes are carried out as a sulfuric acid variant, thus rhenium-containing sulfuric acid solutions became the object of studies.

The results of the investigation (Table) have shown, that out of the whole series of studied extractants, the priority has given to quaternary ammonium base (QAB) (See NN2 and 3, Table). The distribution coefficients D_{Re} for QAB are tens of times as much as those for neutral organophosphorus compounds (NOPC) (See NN5-7, Table) and for several orders higher than for cation-exchange organic reagents (NN 10-12).

According to the data on rhenium extraction (VII), one can obtain the reactivity series, showing the extractants strength increasing from phosphorus- through phosphorus and nitrogen- towards nitrogen-containing organic reagents.

However, high distribution coefficients of QAB considerably hinder the stripping of rhenium. The concentrated solutions of mineral acids are necessary to be used for a complete rhenium reextraction from saturated QAB, otherwise this will effect unfavourably the economics of the whole recovery process. The optimal structure of the extractant of rhenium will be such a compound with D_{Re} less than 10-20. In this case (NN 4, 7, Table) the extraction and stripping processes will be supplement one another.

Cation-exchange organophosphorus reagents (NN 9-12) under the chosen conditions have D_{Re} value 0.01-0.001. Taking into account the reactivity of these extractants when recovering molybdenum as a constant companion of rhenium (sulfuric acid solutions with pH=2-3), one can recommend with a good reason these compounds for preliminary selection of molybdenum.

Extraction and stripping of rhenium(VII) with
phosphorus- and nitrogen-containing organic reagents

Extractant	pH 1.1		pH 3.0		pH 4.5		pH 6.2	
	D _{extr.}	D _{strip.}						
1	2	3	4	5	6	7	8	9
1.Trialkylamine	220	187	17.5	44.5	3.1	2.5	2.1	6.6
2.Trialkylmethyl- ammonium nitrate	366	0.0031	1110	0.003	240	$4 \cdot 10^{-3}$	980	$1 \cdot 10^{-4}$
3.Trialkylmethyl- ammonium carbo- nate	366	0.0030	555	0.001	1200	$8 \cdot 10^{-4}$	980	$5 \cdot 10^{-4}$
4.Octaalkyltetra- aminephosphoni- um bromide	3.8	0.0840	10.1	0.036	9.2	$4 \cdot 10^{-3}$	8.65	$2 \cdot 10^{-3}$
5.Tributylphos- phate	0.03	16	0.049	32.5	0.13	0.18	0.043	0.67
6.Disoamylmethyl- phosphonate	0.0018	10.8	0.13	23.2	0.006	8.3	0.017	3.60
7.Trialkylphos- phineoxide with different radicals	3.3	415	0.0023	120	0.023	0.81	0.058	0.70
8.Phosphoric acid hexabu- tyltriamide	0.046	47	0.0440	25.9	0.110	0.44	0.046	0.39
9.Dialkylphos- phinic acid	0.070	3.1	0.0210	24.4	0.044	0.51	0.060	0.74
10.Di-2-ethylhe- xylphosphoric acid	0.025	20	0.0015	0.25	0.038	0.11	0.042	0.81
11.Dioctylphe- nylphosphoric acid	0.030	21.7	0.0020	0.33	0.060	0.18	0.048	0.87
12.Poly-2-ethyl- hexylphospho- nitric acid	0.012	13.1	0.0086	47.5	0.110	0.11	0.053	0.26

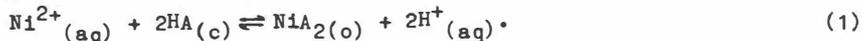
Notes: Re (VII) concentration in a sulfuric acid solution: 550 mg/l;
Phases ratio: O:W=1:1; Contact time: $\tau_{extr.}$ = 5 min., $\tau_{strip.}$ =
5 min ; Organic reagents concentrations: NN 1,4+11 - 0,1 mol ,
NN 2 , 3, 12 - 5 %; Temperature: 20 °C; Strip. solution:
2% NH₄OH.

According to the obtained results some advantageous phosphorus- and nitrogen-containing organic reagents have been determined, allowing to select rhenium (VII) from sulfuric acid aqueous solutions with subsequent recovery of pure ammonium perrhenate salts.

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Di(2-ethylhexyl)dithiophosphoric acid (DTPA) and its salts are promising metal extractants in particular, extractants based on DTPA can be used for separating of Co and Ni, extracting and concentrating of Cu. DTPA is a strong acid, it can extract metal cations from strongly acid media. One of the important properties of this extractant is its ability to reversible oxidation-reduction, it is evident at the extraction of Co and Cu. DTPA is weakly hydrated in organic solvents and is present mainly in monomeric form.

Extraction of Ni(II) with DTPA. This process isn't complicated by oxidation-reduction. The mechanism of the process is of cation-exchanging type, it affects the dependence between Ni-distribution coefficients and hydrogen ion concentration (Fig.1). Based on data on organic phase saturation with Ni and on metal distribution as a function of extractant concentration (Fig.2), the conclusion is made that the process of extraction of Ni with DTPA is described by the following equation



The electron spectrum analysis of Ni-extracts shows that NiA_2 has square-plate structure and low-spin configuration. Diamagnetism is confirmed by the measurements of magnetic susceptibility of extracts.

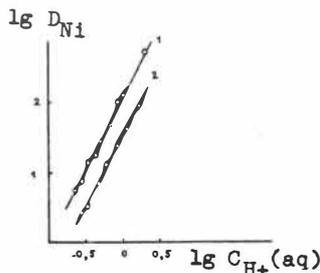


Fig.1. Extraction of Ni with 0,5M solution of DTPA in decane from nitrate (1) and chloride (2) solutions $J = 4,8 \text{ mol/l}$

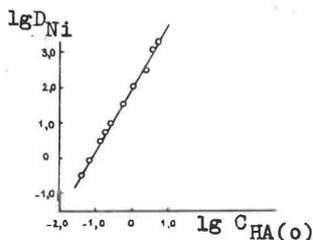
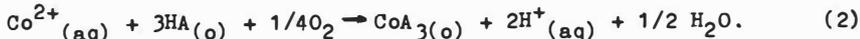


Fig.2. Ni-distribution coefficient as a function of DTPA concentration in decane at extraction from 1,26M solution of HCl containing 0,05mol/l of NiCl_2

Extraction of Co(II) with DTPA. It's known that labile compound of cobalt(II) - CoA_2 - is formed in the first step of extraction in organic phase. This compound is unstable, it's transformed into inert difficultly-backextracted compound of Co(III) - CoA_3 - in the presence of oxygen and excess of DTPA. The ratio of oxidized cobalt amount to absorbed oxygen amount is found by volumetric measurements. This ratio corresponds to the process



It's found that reducing properties of DTPA become more evident in the system being investigated. Thus, the absorption bands of Co(II)-complexes appear in electronic absorption spectrum after some time passed after high dilution of extracts containing Co(III). The reducing of Co is connected with reversible reaction

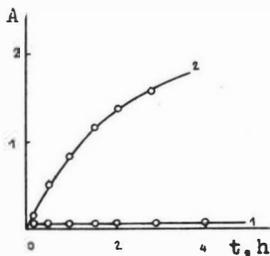
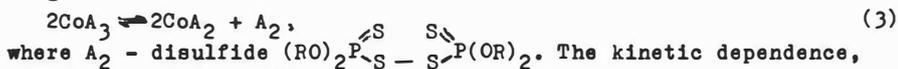


Fig. 3. Optical density of absorption of cobalt dithiophosphate solutions as a function of time:

1 - CoA_2 (10^{-3} mol/l)

2 - CoA_2 (10^{-3} mol/l) + A_2 (0.4 mol/l)

showing the reverse reaction-interaction of CoA_2 with disulfide is shown in Fig. 3. The rate of Co-oxidation depends on various aspects. It decreases significantly under addition of oxygen containing electron donors in the solution: alcohols, tributylphosphate. Secondary amine $(\text{C}_8\text{H}_{17})_2\text{NH}$ is found to stabilize thermodynamically Co(II), displacing equilibrium (3) to the right nearly in general.

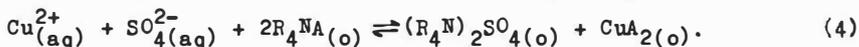
Separation of Co and Ni. DTPA can be used both for extraction of Ni from Co-solutions and for reverse process. Extraction continues for 0,5-2 hours in the first case, so equilibrium with Ni is created, and Co isn't oxidized yet, it's extracted much worse ($\beta_{\text{Ni}/\text{Co}} \sim 15$). Much higher distribution coefficients are obtained using DTPA mixtures with diheptyldithioethane ($\beta_{\text{Ni}/\text{Co}} \sim 500$). On the other hand, the extraction of Co from Ni-solutions becomes possible using DTPA mixtures with oxygen-containing compounds because the extraction rate of Ni is slowed and the extraction rate of Co remains high. It's found that the values of $\beta_{\text{Ni}/\text{Co}} \sim 200$ can be obtained at short phase contact.

Extraction of Cu with DTPA salts. It's known that Cu can be selectively extracted in the wide range of acidity with dialkyldithiophos-

phoric acids. However, the Cu-stripping in these systems is impossible due to high stability of extracting Cu-complexes.

Binary extractants - salts of dialkyldithiophosphoric acid and of quaternary ammonium bases - were investigated for selective extraction of Cu from sulfate Fe-containing solutions. The extractants were obtained by mixing equimolar amounts of di(2-ethylhexyl)dithiophosphoric acid and tetractylammonium salt in organic solvent and by washing organic phase in water.

The extraction with binary extractants differs from the cation-exchanging extraction of Cu with dialkyldithiophosphoric acid, it's characterized by coextraction of Cu-cation and sulfate-ion (bisulfate-ion at extraction from acid solutions) in organic phase:



The results of extraction of Cu and Fe with 0,6 M solution of trialkylmethylammonium di(2-ethylhexyl)dithiophosphate in kerosene with the addition of TBP (10%) are shown in Fig.4. The decreasing of effectiveness of Cu and Fe separating was observed at pH increase with Cu,

Fe being independent, therefore exchanging extraction of these metals doesn't occur. It seems to be connected with the formation of anionic Fe(III) sulfate complexes at these pH-values of aqueous phase and their extraction with tetraalkylammonium salt. Extracted Fe is easily washed off with dilute sulfuric acid eolutions, Cu remains in organic extract practically on the whole.

The investigations showed high extraction rate of Cu for various extractant concentrations, the time of equilibrium obtaining is not more than 1,5 min.

The presence of sulfate-ion in organic phase and the stability of binary extractant in two-phase system

create the conditions, under which Cu can be stripped out by cation bonding in aqueous phase, e.g. at settling of Cu hydroxide (solid phase stripping) or by reaction with ammonia:

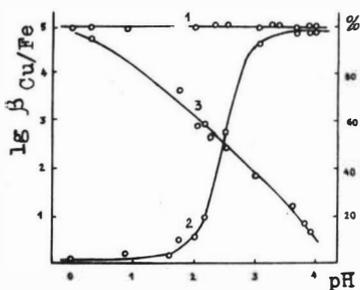
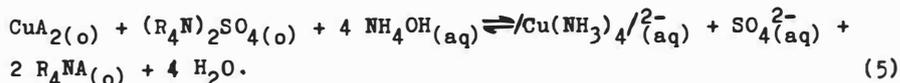


Fig.4. Effect of pH of water phase on extraction of Cu(1) and Fe(2) and the values of $\beta_{\text{Cu/Fe}}$ (3) at extraction with 0,6 M solution of trialkylammonium di(2-ethylhexyl)-dithiophosphate in kerosene (10% of TBP)

More than 90% of Cu is stripped for three countercurrent steps with 10% ammonia aqueous solution at $V_0:V_{aq}=3:1$, Cu concentration in organic stripped product reaches 45 g/l, residual Cu concentration in organic phase being equal to 2 g/l (Fig.5).

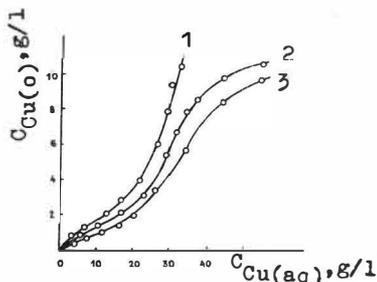


Fig.5. Isotherm of Cu-stripping with ammonia water solutions from organic phase, %: 5,0 (1); 10,0 (2); 15,0 (3)

Oxidation-reduction disproportioning of Cu(II)-dialkyldithiophosphate with formation of Cu(I)-dialkyldithiophosphate and disulfide takes place at extraction of Cu with binary extractant as well as in system with initial dialkyldithiophosphoric acid. Extractant isn't destroyed at extraction-stripping cycle due to reversibility of the process. In particular, no changing of extractant capacity and other extraction properties was observed in 10 extraction-stripping cycles.

Thus, the obtained data show, that the extractant capacity, the extraction rate of Cu, the separation coefficient $\beta_{Cu/Fe}$, the binary extraction rate are significantly higher than these for extractants of hydroxyoxime type. The extractant can be used for selective extraction of Cu from sulfate Fe-containing solutions with consequent ammonia stripping. The possibility of extraction of Cu from acid and strongly-acid solutions makes perspectives for extraction of Cu not only from ore-leaching solutions, but also for selective extraction of Cu from galvanic and etching industrial solutions, at regeneration of waste Cu electrolytes, for concentrating and obtaining pure Cu product from eluates, obtained in sorption systems for processing of Cu-containing products. In the case of the high concentration of the silica-contained compounds in the initial aqueous solutions the formation of the stable emulsions is observed. In order to process such solutions it is worth-while using the combined schemes: on the first stage - the ion-exchange for the recovery of the copper from the ore-leaching solutions, for example, as for oxide copper ores, on the second stage - extraction with the binary extractant so as to obtain the commodity copper product from the eluates.

Copper can be extracted from ammonia stripping product in powdered form by reducing to metal form with sulfur gas or in form of solid complex salt $Cu(NH_3)_4SO_4 \cdot H_2O$ by blowing with ammonia.

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In synergic extraction, the aqueous phase composition plays a main role in achieving the synergic phenomenon [1-6]. The presence of certain chemical composition in the aqueous medium was found to be required for the formation of the synergic species to be extracted [7]. In previous publications synergic extraction of divalent cobalt by the systems thenoyltrifluoroacetone (HTTA)-crown ether [8] and HTTA-amine [9] was investigated using perchlorate aqueous media. In the present work, the extraction of tetrahedral and octahedral divalent cobalt from nitrate buffer aqueous media is investigated using mixed extractants of 8-hydroxyquinoline and amine or crown ether in chloroform.

Experimental

Radiotracers and Chemicals

The radiotracer used, Co-60, was prepared by neutron irradiating of A.R. grade cobalt carbonate for 48 hours in the ET-RR-1 reactor [10]. The irradiated material was divided into two parts. One part was dissolved in a minimum amount of perchloric acid, leading to the formation of octahedral cobalt species [11]. The other part was dissolved in a suitable amount of 1:1 hydrochloric acid forming the tetrahedral cobalt species [11]. The solutions were adjusted to constant ionic strength of 0.1 by sodium nitrate. The octahedral and tetrahedral cobalt structures of the solutions were confirmed spectrophotometrically.

8-hydroxyquinoline (HOX) and sodium nitrate were A.R. grade and obtained from Veb Labor. Chemie Apolda. 15-crown-5 (15C5) was purchased from Fluka AG, Buchs SG. Dibenzo-18-crown-6 (Dbl8C6) was supplied by Aldrich Chemical Company. Dibenzylamine (DBA) was Light and Co Label. Tridodecylamine (TDA) and chloroform were supplied from Prolabo, Italy. The different extractants and the diluent were used without any chemical treatment.

The extraction procedure and the radiometric assay were done as previously reported [8,9].

Results and Discussion

Synergic Extraction of Divalent Octahedral Cobalt

The extraction of octahedral Co(II) was investigated by the system 8-hydroxyquinoline (HOX)-crown ether (dibenzo-18-crown-6 (Db18C6) or 15-crown-5 (15C5)). The extraction was performed by a chloroform solution of the respective extractants from nitrate buffer aqueous medium. Different enhancements in the extraction were obtained with the respective extractant mixtures used, Fig. 1-A. On the other hand, when the extraction was carried out for the tetrahedral cobalt species no enhancement was obtained by the same extractant mixtures, Fig. 1-B. The different parameters affecting the extraction of the octahedral cobalt by the different extractants from the aqueous medium at pH 5.2 as well as at $diff. pH_s$ were elucidated and the data were represented in Figs. 2-5. Based on slope analysis of the extrac-

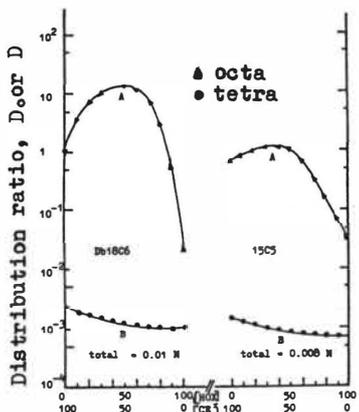


Fig. 1

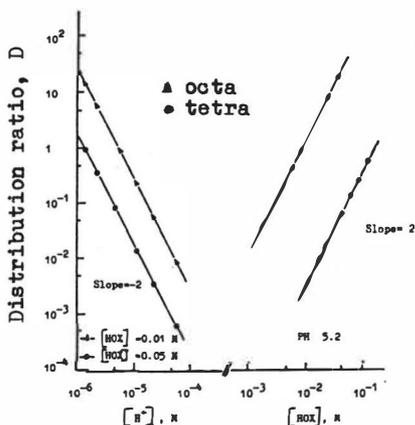


Fig. 2

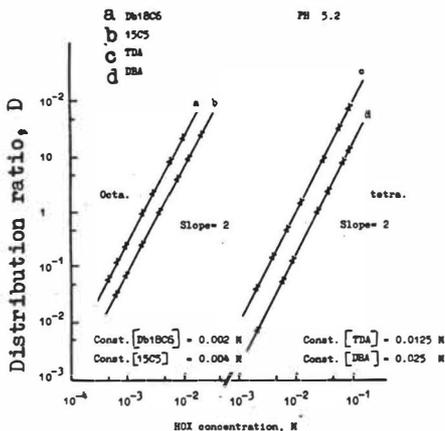


Fig. 3

Fig. 1. Extraction of Co(II) by HOX, CE and their mixtures

Fig. 2. Effect of $[H^+]$ and $[HOX]$ on the extraction of Co(II)

Fig. 3. Effect of $[HOX]$ on Co(II) extraction of at const. $[CE]$ or $[am]$

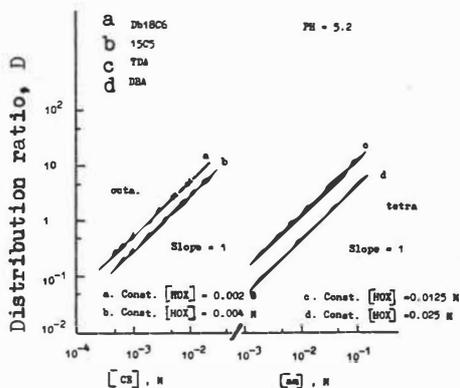


Fig. 4. Effect of $[CE]$ or $[am]$ on the extraction of Co(II) at const. $[HOX]$

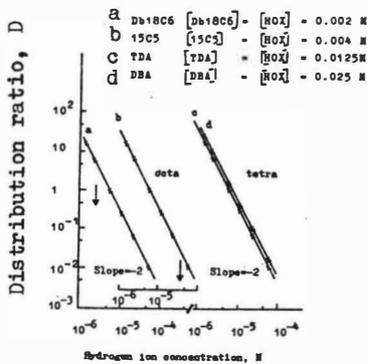


Fig. 5. Effect of $[H^+]$ on Co(II) extraction by HOX+CE or HOX+am

tion experimental results the stoichiometric formulae of the extracted species were found to be $Co(OX)_2$ and $Co(OX)_2.CE$; $CE = Dbl8C6$ or $15C5$, for the chelate and the synergic species extracted of the octahedral cobalt, respectively. The different constants for these species are summarized in Table 1, together with the maximum synergic factors [12].

Synergic Extraction of Divalent Tetrahedral Cobalt

The extraction of tetrahedral Co(II) was investigated by a chloroform solution of HOX and dibenzylamine (DBA) or tridodecylamine (TDA) from nitrate buffer aqueous solution. In parallel, the extraction of the octahedral Co(II) was also tested. The enhancement in the extraction was only obtained for the tetrahedral Co(II), Fig. (6-A), while no enhancement was obtained for the octahedral Co(II) extraction; Fig. 6-B. The different parameters affecting the extraction of the chelate and

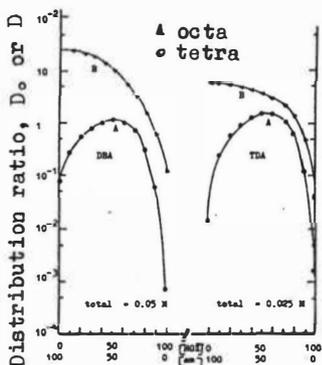


Fig. 6. Extraction of Co(II) by HOX and their mixtures

synergic species of the tetrahedral Co(II) were elucidated; Figs. 2-5.

The stoichiometric formulae of the extracted chelate and synergic species of the tetrahedral cobalt were found to be $\text{Co}(\text{OX})_2$ and $\text{Co}(\text{OX})_2 \cdot \text{am}$ (am=DBA or TDA), alternatively. The different constants for the extracted species as well as the maximum synergic factors are given in Table.

Extraction of octahedral and tetrahedral divalent cobalt by 8-hydroxyquinoline (HOX) and HOX-crown ether or amine *

Species	Constant**			
	$-\log K_{20}$	$-\log K_{21}$	$\log B_{21}$	S.F. ***
Octahedral extraction	6.43			
$\text{Co}(\text{OX})_2$				
$\text{Co}(\text{OX})_2 \cdot 1.5\text{G5}$		3.17	3.27	6.7
$\text{Co}(\text{OX})_2 \cdot \text{Db18C6}$		2.3	4.13	65
Tetrahedral extraction	9.02			
$\text{Co}(\text{OX})_2$				
$\text{Co}(\text{OX})_2 \cdot \text{DBA}$		5.53	3.49	75
$\text{Co}(\text{OX})_2 \cdot \text{TDA}$		4.46	4.56	380

* The standard deviations [13] in K_{20} and K_{21} are $\pm 2\%$ and in B_{21} are $\pm 3\%$.

** $K_{20} = \frac{D_0 [\text{H}^+]^2}{[\text{HOX}]^2}$, $K_{21} = \frac{D [\text{H}^+]^2}{[\text{HOX}]^2 [\text{L}]}$ and $B_{21} = \frac{K_{21}}{K_{20}}$,

$D_0 = \frac{[\text{Co}(\text{OX})_2]}{[\text{Co}^{2+}]}$, $D = \frac{[\text{Co}(\text{OX})_2 \cdot \text{L}]}{[\text{Co}^{2+}]}$; L = CE or am, *** S.F. = $\frac{D_{\text{HOX}} + L}{D_{\text{HOX}} + D_L}$.

Conclusions

- The extraction constants obtained show the following :
- Octahedral cobalt is highly extracted than tetrahedral cobalt by HOX, where K_{20} for octahedral cobalt, 3.7×10^{-7} , is much higher than the corresponding value for tetrahedral cobalt extracted, 9.6×10^{-10} . This can be explained by the restricted stable tetrahedral configuration to form a chelate compound with the bulky oxime anion. This is contrary to the octahedral structure, where the two oxime anions can chelate cobalt by substituting the four water molecules surrounding the middle plane of the octahedral structure.
 - The mixed extraction constant, K_{21} , for the octahedral cobalt extracted as $\text{Co}(\text{OX})_2 \cdot \text{CE}$ is also higher than of the tetrahedral cobalt extracted as $\text{Co}(\text{OX})_2 \cdot \text{am}$; Table 1. This is due to the cooperative extraction of both the cobalt chelate and adduct of octahedral extraction.

c) The formation constant, B_{21} , of the tetrahedral cobalt extracted as $\text{Co}(\text{OX})_2$ is relatively stable than the octahedral cobalt extracted as $\text{Co}(\text{OX})_2$. This is reflected by the high synergic factors obtained for the extracted tetrahedral cobalt species. The formation of the adduct between the CE and the octahedral oxime cobalt chelate could be achieved through substitution of the CE with one of the water molecules on the perpendicular axis of the octahedral molecule, where a square pyramidal configuration for the adduct is formed. The high B_{21} values for the tetrahedral cobalt adduct can be related to the relatively high hydrophobic property of the octahedral cobalt adduct which contains one water molecule compared to the tetrahedral structure.

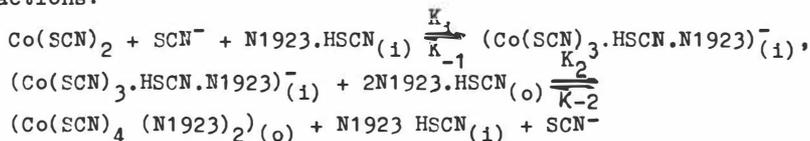
Further thermodynamic and structural elucidations are under consideration to add more verification for the previous conclusions.

References

1. Healy T.V. // J. Inorg. Nucl. Chem. 1961. Vol. 19. P. 314 and P. 328.
2. Irving H. // Solvent Extraction Chemistry of Metals. Macmillan, London, 1966. P. 91.
3. Taketatsu T.T., Toriami N. // J. Inorg. Nucl. Chem. 1969. Vol. 31. P. 2235.
4. Aggett J. // J. Inorg. Nucl. Chem. 1970. Vol. 32. P. 2767.
5. Subramanian M.S., Pai S.A. // J. Inorg. Nucl. Chem. 1970. Vol. 32. P. 3677.
6. Tikhomirov V.I., Ionov V.P. // Radiokhimiya 1967. Vol. 9. P. 427.
7. Deptula C., Minc S. // J. Inorg. Nucl. Chem. 1967. Vol. 29. P. 159.
8. Aly H.F., El-Dessouky M.M., Khalifa S.M., Navratil J.D., Shehata F.A. // Solv. Extr. Ion Exch. 1985. Vol. 3(6), 867.
9. Aly H.F., Raieh M., Mohamed S. (Khalifa S.M.), Abdel-Rassoul A.A. // J. Inorg. Nucl. Chem. 1978. Vol. 40. P. 567.
10. Hamuda I., El-Mofty O., El-Mashad Y., El-Nagdy M. // Proc. 3rd. Intern. Conf. Peac. Uses At. Energy, Geneva 1964. A/Conf./28/P. 453.
11. Phillips C.S.G., Williams R.J.P. // Inorganic Chemistry. Part II. N.Y.: Oxford University Press, 1966.
12. Khalifa S.M., Zakareia N., Shehata F., Aly H.F. // J. Radioanal. Nucl. Chem. 1984. Vol. 82/1. P. 75.
13. Eckschlager K. // Errors, Measurements and Results in Chemical Analysis. London, 1969.

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The extraction kinetics of cobalt(II) thiocyanate with N1923 kero-
sene solution has been studied by growing drop method at 25°C. The
schematic diagram of experimental apparatus is shown in Fig.1. The expe-
rimental results shown in Fig.2 to 6 indicate that the rate-determin-
ing steps of this extraction process may be the following interfacial
reactions:



the forward initial rate of this extraction process can be expressed
as follows:

$$R_f = \frac{K_1[\text{Co(SCN)}_2] [\text{SCN}^-] [\text{N1923.HSCN}]_{(o)}^2}{K_{-1} + K_2[\text{N1923.HSCN}]_{(o)}^2}$$

where $K = K_1 K_2 [\text{N1923.HSCN}]_{(i)}$. $[]_{(i)}$ denotes the interfacial concen-
tration.

The activation energy of this process was calculated to be
15.1 kJ·mol⁻¹.

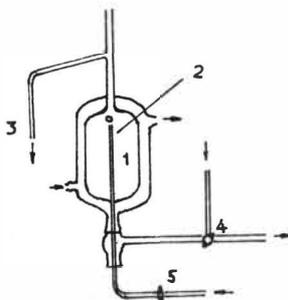


Fig.1. Schematic diagram of experimental apparatus for growing
drop method

- 1 - extraction cell with a volume of 150 cm³;
- 2 - capillary; 3 - spillover tube;
- 4 - three way cock; 5 - glass cock

Fig.2. The curve of $\text{Log}(A/t)$ vs. $\text{Log}[\text{Co}]$; $[\text{SCN}^-] 1.00\text{M}$; $\text{pH} 3.13$; $[\text{N}1923.\text{HSCN}]_{(o)} 0.046\text{M}$

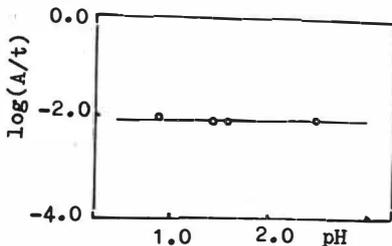
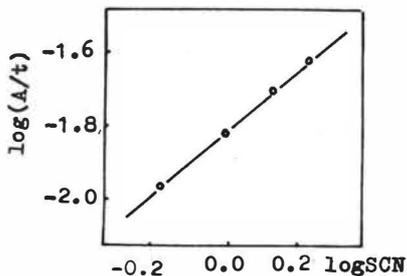
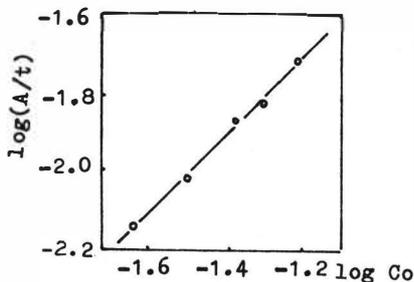


Fig.3. The curve of $\text{Log}(A/t)$ vs. $\text{Log}[\text{SCN}^-]$; $[\text{Co}] 0.0540\text{M}$; $\text{pH} 2.46$; $[\text{N}1923.\text{HSCN}]_{(o)} 0.046\text{M}$

Fig.4. The curve of $\text{Log}(A/t)$ vs. pH ; $[\text{Co}] 0.0540\text{M}$; $[\text{SCN}^-] 0.508\text{M}$; $[\text{N}1923.\text{HSCN}]_{(o)} 0.046\text{M}$

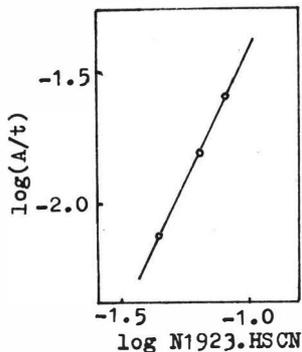
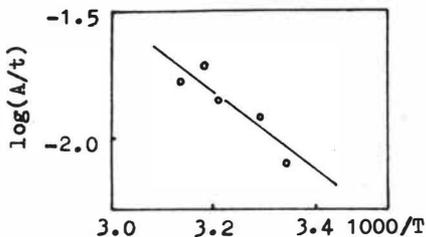


Fig.5. Effect of temperature on the extraction rate; $[\text{Co}] 0.0540\text{M}$; $\text{pH} 2.45$; $[\text{SCN}^-] 0.508\text{M}$; $[\text{N}1923.\text{HSCN}]_{(o)} 0.046\text{M}$

Fig.6. The curve of $\text{Log}(A/t)$ vs. $\text{Log}[\text{N}1923.\text{HSCN}]_{(o)}$; $[\text{Co}] 0.540\text{M}$; $\text{pH} 2.45$; $[\text{SCN}^-] 0.508\text{M}$

Note: 1. The A is the absorbance the organic phase loading Co(II) and is used to express the concentration of Co(II) in organic phase.

2. $[]$ and $[]_{(o)}$ denote aqueous and organic phase species respectively.

Reference

1. Hughes M.A.//T.Zhu. Hydrometallurgy. 1985. Vol.13. P.249.

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The extraction of Co(II) ions from sulphate solutions with aliphatic (n-hexanoic, n-octanoic and n-decanoic) and aromatic (benzoic and o-toluic) acids and with their mixtures with aliphatic (n-amyl, n-heptyl, n-nonyl) alcohols has been studied. It has been found that aliphatic carboxylic acids extract Co(II) ions from the aqueous into organic phase, whereas aromatic acids do not extract Co(II) from sulphate solutions, besides sparingly soluble deposits precipitate themselves in the system studied [1-3].

Extraction of Co(II) with mixtures of carboxylic acids and aliphatic alcohols in sulphate systems

Extractant	Complex	Opt.pH	R _%	K _{ex}
1	2	3	4	5
Hexanoic acid in decane	CoR ₂ ·2HR	5,5 - 6,5	95	(1,78±0,2)·10 ⁻¹²
Octanoic acid in decane	CoR ₂ ·2HR	5,5 - 6,5	95	(2,82±0,2)·10 ⁻¹²
Decanoic acid in decane	CoR ₂ ·2HR	5,5 - 6,5	95	(5,01±0,3)·10 ⁻¹²
Hexanoic acid with heptyl alcohol in decane	CoR ₂ ·HR	6,5 - 7,5	95	(3,05±0,38)·10 ⁻⁶
Benzoic acid in benzene	no extr.	2 - 8	0	-
o-Toluic acid in benzene	no extr.	2 - 8	0	-
Benzoic acid with amyl alcohol in benzene	CoR ₂ ·2HR	7,5	55	(3,78±0,18)·10 ⁻¹⁰
o-Toluic acid with amyl alcohol in benzene	CoR ₂ ·2HR	7,0	55	-

An addition alcohol to the extraction solvent brings about the synergic effect, particularly apparent in case of benzoic and o-toluic acids, and enables the extraction of Co(II) ions over a wide pH range of the aqueous phase. It has been proved that the extraction of Co(II) ions is not considerably affected by the kind of alcohol used.

The composition of Co(II) complexes in the organic phase were determined. The presence of Co(II) complexes of $\text{CoR}_2 \cdot 2\text{HR}$ and $\text{CoR}_2 \cdot \text{HR}$ composition was found in the organic phase. Since alcohol is not contained in the composition of Co(II) complexes in the organic phase, but merely affects the monomer - dimer equilibria of carboxylic acids, an indirect influence of the other extraction reagent on the synergic effect was assumed. This is particularly apparent in case of aromatic carboxylic acids.

Co(II) ions extraction with simple and complex extraction solvents containing acid (HR) and alcohol into a non polar solvent (n-decane, benzene) was described appropriately with chemical equations and the values of the concentration constants of the extraction were calculated (Table).

References

1. Kopacz S., Szantula J. // *Mat.Science*. 1978. Vol.4. P. 27.
2. Tanaka M., Nakasuka N., Goto S. *Solvent extraction chemistry*. Amsterdam: North-Holland, 1967. P. 154.
3. Szantula J. // *Prace Inst. Technol. Chem. N 2. Politechnika Rzeszowska*. Rzeszów, 1982. P. 61.

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Organophosphorus acids, mainly D2EHPH, are widely used for the extraction of metals. It is common knowledge that these reagents are also employed for the extraction of heavy non-ferrous metals: copper, zinc, cobalt and nickel. For example, D2EHPH is recommended for separating zinc from copper [1] and cobalt from nickel. The latter two metals are being separated in production quantities [2,3]. Up to now primary attention has been focussed on the extraction properties of D2EHPH, but recently there have appeared a number of reports on the successful employment of some other more effective organophosphorus acids which are either stronger or weaker than D2EHPH [4,5].

This paper considers the properties of dioctylphenylphosphorus acid (DOPPH) - $(i-C_8H_{17}-\text{C}_6\text{H}_4)_2\text{PO}(\text{OH})$ which is a stronger acid compared to D2EHPH. The constant of acid dissociation pK_a is 1.39 for DOPPH whereas it is 2.23 for D2EHPH [4]. In addition, we have considered the properties of dialkylphosphine acid (DAPH) - $R_2\text{PO}(\text{OH})$ where $R = C_5-C_8$. Acid properties of this reagent are weaker than those of D2EHPH. The extraction of Cu^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} with organophosphorus acids occurs in accordance with the cationexchange mechanism, and therefore the acidity of the aqueous phase (in equilibrium state) will have a pronounced effect on metal extraction. The growth of aqueous phase acidity will suppress the extraction, and the stronger reagents will more efficiently extract metals from the stronger acid solutions. In this case the extractability of metals from acid solutions increases as follows: $\text{DAPH} < \text{D2EHPH} < \text{DOPPH}$.

The isotherms of extraction of zinc, copper, nickel and cobalt from sulphate solutions at pH=4 with 0.35 M DOPPH in kerosine are shown in Fig.1. One can see that the extraction of metals into the organic phase is increased in the following order: $\text{Ni(II)} < \text{Co(II)} < \text{Cu(II)} < \text{Zn(II)}$. A similar dependence is also observed when D2EHPH and DAPH are used.

Temperature requirements during the process are very important factors affecting metal extraction with acid phosphororganic reagents. Our experimental results (Fig.2) show that a rise in temperature leads to an increased extraction of copper and cobalt into the organic phase, whereas the dependence of nickel extraction on temperature changes in the studied interval is insignificant. This leads to the increased effectiveness of metal separation. When DOPPH is used the separation factors are $\beta_{\text{Cu/Ni}} = 5.3$ and 15.2 at 20° and 63°C , respectively. For the cobalt-nickel pair $\beta = 3.0$ and 4.6 at 22° and 62°C ,

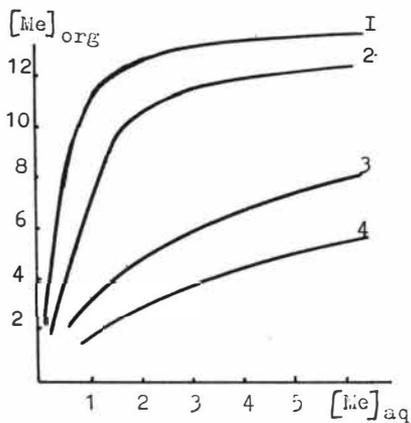


Fig. 1. Isoterm of Me^{2+} extraction with DOPPH Zn(I), Cu(2), Co(3) and Ni(4)

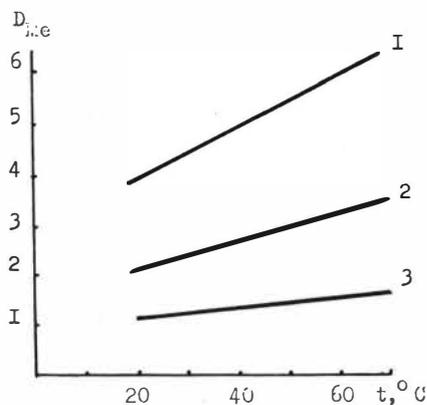


Fig. 2. Dependence of Cu(I), Co(2) and Ni(3) extraction with 0,35M DOPPH in kerosine on temperature at pH 2

respectively. Such dependence of cobalt-nickel separation effectiveness on temperature can be explained by the existence (in the organic phase) of metal complexes with organophosphorus acids: octahedral $MeA_2 \cdot 2H_2O$ (the O_h symmetry group), tetrahedral $MeA_2(T_d)$ or plane-tetragonal $MeA_2(D_{4h})$. With a rise in temperature the fraction of better extracted nonaqueous complex $CoA_2(T_d)$ or the $CuA_2(D_{4h})$ complex increases, which leads to the increase of copper and cobalt extraction into the organic phase. Such a transfer for nickel, and likewise the growth of D_{Ni} , becomes possible only at much higher temperatures.

If one takes into account that the formation of polymer complexes is possible in the organic phase, especially the nickel one, then we may find at the stripping stage the presence of the kinetic separation factor for the copper and nickel and also for cobalt and nickel.

The effect of phase contact time on the separation efficiency for cobalt and nickel has been studied in centrifugal extractors [6]. The experimental results have shown that the kinetics of extraction of these metals with acid phosphororganic reagents is rapid. The values of separation factors (β) for cobalt and nickel are weakly dependent on the phase contact time during extraction and stripping of the metals. At the same time, in the case of DAPH the effectiveness of the organic phase scrubbing depends on the phase contact time (see Table 1).

The process of cobalt and nickel separation with DAPH has been tested in mixer-settlers. The number of stages used in the process: extraction - 4; scrubbing - with a cobalt-bearing solution - 2; stripping with a sulphuric acid solution - 2.

Table 1. The effect of the phase contact time (τ) on the effectiveness of the extraction stage (E) and β Co/Ni for DAPH (O:A = 1:1, $t = 21^\circ\text{C}$).

Extraction: 0-0.35M DAPH in kerosine; A-pH=3.5-3.8; Co-0.42 g/l, Ni-26.5 g/l

Scrubbing: 0-0.35M DAPH, Co-0.42 g/l, Ni-0.84 g/l; A-pH=2.3-2.9, Co-11.7 g/l

Stripping: 0-0.35M DAPH, Co-0.9 g/l, Ni-0.13 g/l; A-H₂SO₄-50 g/l

Extraction				Scrubbing				Stripping			
τ_s	E ^{Co}	E ^{Ni}	β Co/Ni	τ_s	E ^{Co}	E ^{Ni}	β Co/Ni	τ_s	E ^{Co}	E ^{Ni}	β Co/Ni
0.3	0.81	0.84	6.5	0.4	0.77	0.01	1.2	0.4	0.42	0.08	6.3
1.0	0.76	0.84	7.2	1.0	1.00	0.02	2.4	1.1	0.49	0.09	6.5
3.7	0.95	0.89	8.5	2.8	1.00	0.06	6.5	4.4	0.61	0.12	6.2
10.5	1.00	0.98	9.4	11.6	0.88	0.15	15.0	12.0	0.78	0.18	5.0
23.6	1.00	0.89	9.3	27.7	0.83	0.43	40.0	24.6	0.88	0.25	4.2
48.7	1.00	0.91	9.5	52.3	1.00	1.00	113.0	29.9	0.88	0.26	4.0
								82.7	1.00	0.38	3.2

Note: Value E for extraction and scrubbing has been derived from the organic phase, and for stripping - from the aqueous phase. $E = (C_1 - C_f) / (C_1 - C_{eq})$, where C_1 , C_{eq} and C_f represent initial, equilibrium and final concentrations.

The extraction of cobalt from a sulphatic solution containing Co-1.33 g/l and Ni-34.2 g/l has been as high as 96.4%. The product solution with the content of Co-104 g/l and Ni-0.27 g/l can be used for electrolytic processing of cobalt.

Thus, our experimental results have shown that it is possible to employ acid phosphororganic reagents for the separation and concentration of copper, zinc, nickel and cobalt, when they are all present in aqueous solutions.

References

1. Forrest C., Hughes M.A. // Hydrometallurgy. 1978. V. 3, N 4. P. 327.
2. Preston J.E. // Hydrometallurgy. 1982. V. 9, N 2. P. 115.
3. Flett D.S. // Chem. Engn. 1981. V. 370. P. 321.
4. Travkin V.F., Loseva M.V. et al. // Zh. Neorg. Khim. 1987. V. 32. P. 732.
5. Danesi P.R., Reichley-Yinger Z. et al. // Solv. Extr. and Ion Exch. 1985. V. 3. P. 435.
6. Kuznetsov G.I., Pushkov A.A., Belyakov S.M. // Atomnaya Energia. 1986. V. 61. P. 23.

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In recent year the method of lixiviating nonferrous metals from their ores with the use of ammonia is finding increasing application. To fully utilize the advantages of this method, it is necessary to find more efficient and readily available extracting agents. Among them are oligomers derived from alkylphenols.

For extracting zinc and cadmium from ammonia solutions where these metals are in the form of soluble ammoniates, we have developed some alkylphenol oligomers. As nitrogen-containing oligomers we took p-t-butylaminophenolformaldehyde oligomer and as sulfur-containing oligomer - p-t-butylphenol and alkylphenoldisulfides (Fig.1).

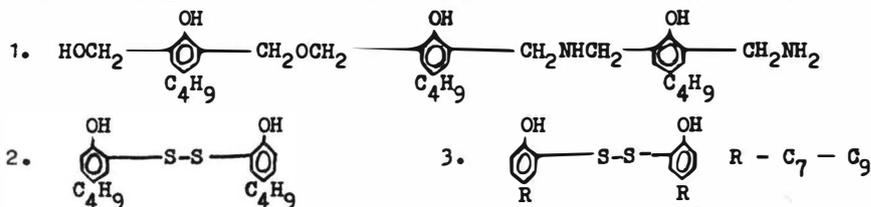


Fig. 1. Chemical formulas of alkylphenol oligomers: 1 - p-t-butylaminophenolformaldehyde; 2 - p-t-butylphenoldisulfide; 3 - alkylphenoldisulfide

In determining the main regularities in the extraction of zinc and cadmium, we have investigated the extraction with the aid of p-t-butylphenoldisulfide trace amounts of radioactive isotopes, Zn^{65} and $\text{Cd}^{115\text{m}}$. Preliminary results show that equilibrium was attained in 5 minutes. The extraction was carried out in separating funnels, the ratio of phase volumes being one.

Measurements showed that the angular coefficient of the relationship between the logarithm of the partition coefficient and the pH of the media for both metals equals two (Fig. 2). The logarithm of the partition coefficient as the function of the extractant's concentration in toluene was also close to two (Fig. 3). It could be assumed that in the extraction of zinc and cadmium with p-t-butylphenoldisulfide two protons of the hydroxyl group from the extractant become separated. In this process the metal forms a complex with the extractant, with the molar ratio metal:extractant being 1:2. This ratio was established under saturating conditions during the extraction of the metal at macro-concentration levels.

To confirm the composition of the metal-extractant complexes we have examined the infrared and ultraviolet spectra of the extractants

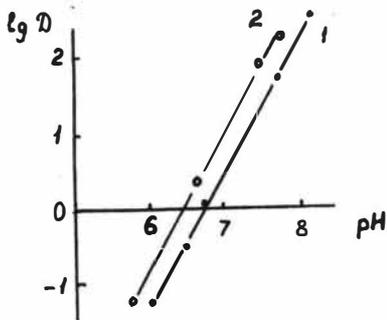


Fig. 2. Extraction of metals (present in micro-concentrations) with 0.25M toluene solution of p-t-butylphenoldisulfide: 1 - Cd; 2 - Zn

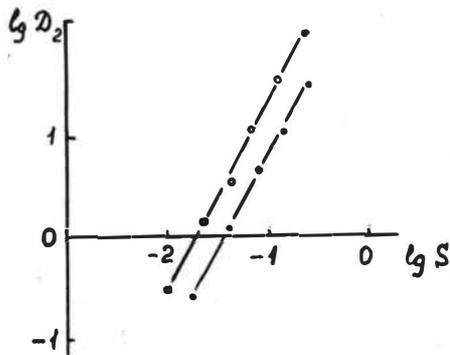
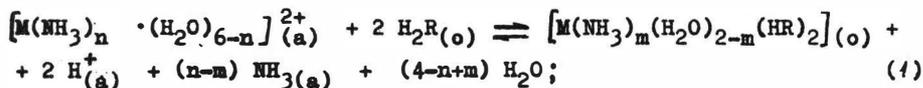


Fig. 3. Metal partition as the function of p-t-butylphenoldisulfide concentration in toluene: 1 - Cd; 2 - Zn

and the extracted compounds. The infrared spectrum of the starting p-t-butylphenoldisulfide was characterized by two absorption bands at 220 nm and 300 nm, which underwent a shift into a longer-wave region (by 10 nm for the 300 nm band) upon the formation of the complex with the metal. The shift in the absorption of benzene moiety during the formation of the complexes indicates the presence of phenolate structures. Therefore one can suppose that the complexes are formed by substituting protons in the hydroxyl group of p-t-butylphenoldisulfide by metal with the formation of a metal-oxygen bond. A comparison of the infrared spectra of zinc and cadmium complexes with those of p-t-butylphenoldisulfide showed a decrease in the integral intensity of absorption band at 2940 nm corresponding to oscillations of HO-group of the extractant. An analogous comparison of the same band of the extractant with that of p-t-butylphenoldisulfide supports the assumption that the proton in the hydroxyl group of the extractant is substituted by the extracted metal. The result of such a substitution is the formation of a metal-oxygen bond.

In the simultaneous extraction of ammonia and macro-concentrations of zinc and cadmium, we observed that, with an increase in the pH of aqueous ammonia solutions the NH_3 :metal ratio in the extracted compounds gradually increased from 0 to 2. Here account was taken of the co-extraction of ammonia ions of p-t-butylphenoldisulfide according to the cation-exchange mechanism.

On the basis of the state of the ions of zinc and cadmium in ammonia solutions and the results we obtained, the extraction process with p-t-butylphenoldisulfide can be described as follows:



where n - varies from 0 to 4 within the examined pH range; m - the ammonia-metal ratio in extracted complex, varying from 0 to 2, depending on the pH of the extracting media; M - Zn or Cd; HR - extractant.

Analogous results obtained in the extraction of zinc and cadmium from ammonia solutions with a nitrogen-containing extracting agent, *p-t*-butylphenolformaldehyde, indicate that Rx. (1) can be used to describe the extraction of these metals with a nitrogen-containing oligomer.

A comparison of the data on the extraction of zinc and cadmium with N- and S-containing oligomers (Fig. 4 and 5) shows that zinc is extracted more efficiently with *p-t*-butylaminophenolformaldehyde than with alkylphenoldisulfide. For the extraction of cadmium alkylphenoldisulfide was found to be more efficient. The results can be explained by the theory of mild and strong acids and bases, on the assumption that the extracted complex contains a coordination bond: metal donor atom of the extractant's molecule.

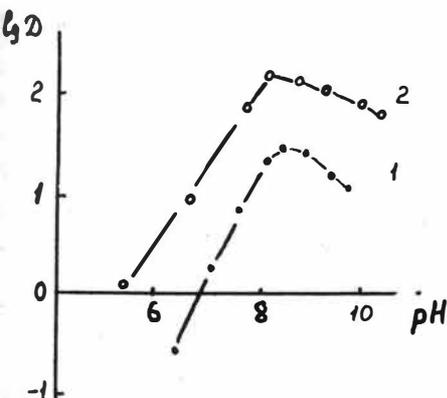


Fig. 4. Extraction of metals (present at concentration of g/l) with 0.25M kerosene solution of *p-t*-butylaminophenolformaldehyde: 1 - Cd; 2 - Zn

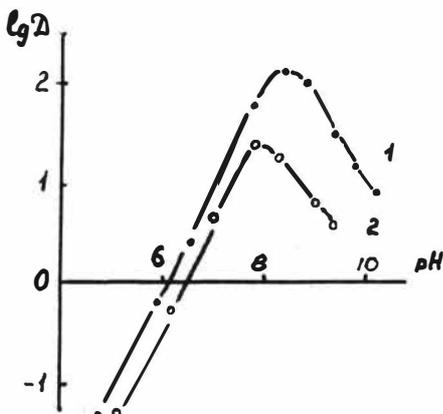


Fig. 5. Extraction of metals with 0.25M kerosene solution of alkylphenoldisulfide: 1 - Cd; 2 - Zn

The partition coefficient under optimal conditions was greater than 100 for the extraction of zinc from ammonia solutions with *p-t*-butylaminophenolformaldehyde at 0.25M concentration, and for the extraction of cadmium with alkylphenoldisulfide at the same concentration.

AMINE N₁₉₂₃ AND TBP*

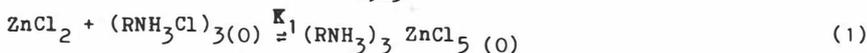
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Abstract. The synergic extraction of zinc(II) from hydrochloric acid by primary amine N₁₉₂₃ and TBP has been investigated. The composition of the synergic extracting complex and mechanism of the synergic extraction have been determined by the methods of slope analysis and constant mole. The dependences of solvents and temperature on the synergic extraction of zinc(II) and IR, NMR spectra of the synergic extracting complex have been studied. The equilibrium constants and the thermodynamic functions of the synergic reaction have been calculated as well.

The extraction of metal ions by primary amine alone has been well investigated [1-3]. However the binary synergic system of primary amine and neutral organophosphorus reagents has been reported to be much smaller. Although the synergic extraction of some metal ions such as Re(VII) [4], Au(CN)₂ [5] etc. has been reported, the synergic extraction of zinc(II) with primary amine N₁₉₂₃ (R₁¹/R₂²)CHNH₂, hereafter referred to as RNH₂) and tributylphosphate (TBP, B) has not been reported yet. In this paper, the synergic extraction of zinc(II) by primary amine N₁₉₂₃ and TBP has been therefore investigated in greater detail.

Extraction of zinc(II) with N₁₉₂₃ from hydrochloric acid

Previous investigations [2] have shown that extraction reaction of zinc(II) by primary amine N₁₉₂₃ from hydrochloric acid is as follows:



The equilibrium constant K₁ can be expressed as

$$K_1 = \frac{[(\text{RNH}_3)_3(\text{ZnCl}_5)](\text{O})}{[\text{ZnCl}_2][(\text{RNH}_3\text{Cl})_3(\text{O})]} = \frac{D_1(1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i)}{\beta_2 [\text{Cl}^-]^2 [(\text{RNH}_3\text{Cl})_3(\text{O})]} \quad (2)$$

Where D₁ stand for distribution ratio of zinc(II) with primary amine N₁₉₂₃. β represents the overall stability constant of zinc(II) with chloride ions. The subscript in parentheses, o, indicates that the substance is present in the organic phase and no subscript, that it is in aqueous phase.

Extraction of zinc(II) with TBP

The extraction of zinc(II) with neutral organophosphorus reagents has been reported [6], and the extracted species is ZnCl₂·2B. But under the present experimental conditions, the extraction of zinc(II) by TBP

* The Project Supported by National Natural Science Foundation of China.

was confirmed to be negligible, that is, the distribution ratio of zinc(II), D_2 , was smaller than 10^{-2} , then the extracted species of zinc(II) with TBP in the organic phase may be neglected approximately.

Synergic extraction of zinc(II) with N_{1923} and TBP

In order to ascertain the synergic effect of zinc(II) with primary amine N_{1923} and TBP from chloride system, it is first necessary to know the synergic diagram of zinc(II). Plots given in Fig. 1 represent the distribution ($D_{tot.}$) of zinc(II) between 1.5M HCl and mixtures of primary amine N_{1923} and TBP in the mole fraction range of N_{1923} in heptane at 25°C. As seen from Fig. 1 the $D_{tot.}$ of zinc(II) increase to a maximum in the mole fraction of N_{1923} up to 0.25 approximately and the synergic effect is observed obviously.

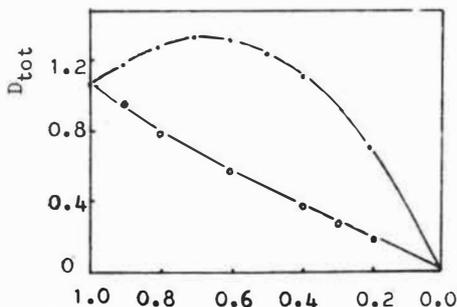


Fig. 1. Plots of $D_{tot.}$ vs X_{RNH_3Cl} at $C_{HCl} = 1.5M$, \circ - RNH_3Cl -TBP; \circ - o_2RNH_3Cl

Dependence of solvents on the synergic extraction of zinc(II)

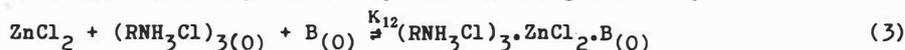
As seen from Table 1. the distribution ratios of zinc(II) with primary amine N_{1923} and TBP in various solvents have changed largely, and the distribution ratios of zinc(II) have increased with the dielectric constants of solvents in aromatic hydrocarbons and their derivatives but decreased with the dielectric constants of solvents in the nonaromatic hydrocarbons and their derivatives.

Table 1. The distribution ratios of zinc(II) with RNH_3Cl -TBP in various organic solvents

Solvent	Aromatic hydrocarbons and their derivatives			Nonaromatic hydrocarbons and their derivatives			
	Benzene	Xylene	Nitrobenzene	Heptane	Octane	Carbon tetrachloride	Chloroform
Dielectric constant	2.3	2.6	34.82	1.924	1.948	2.238	4.806
Distribution ratio	0.279	0.432	4.25	1.35	1.32	0.159	0.0421

Mechanism of the synergic extraction of zinc(II) from chloride system with primary amine N_{1923} and TBP in heptane

As seen from Fig. 2, 3, $\text{Log} D_{12}$ increase linearly with $\text{Log} [RNH_3Cl]_{(0)}$ and $\text{Log} [TBP]_{(0)}$ with slope of 1. Considering the polymerization degree of amine salts in octane [2] and reaction (1), the synergic reaction of zinc(II) can be represented by the following reaction, viz.



The addition reaction of synergic extracting complex in the organic phase can be represented by the following reaction, viz.

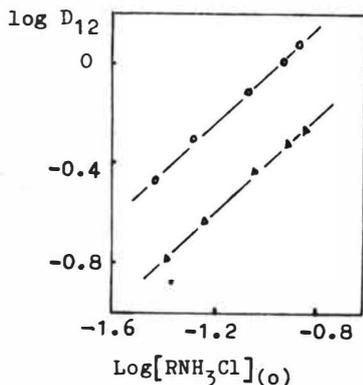
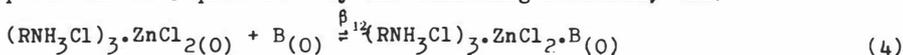


Fig. 2. Plots of $\text{Log} D_{12}$ vs $\text{Log} [\text{RNH}_3\text{Cl}]_{(\text{o})}$ at constant $[\text{TBP}]_{(\text{o})}$ Δ -0.04M; \circ -0.08M

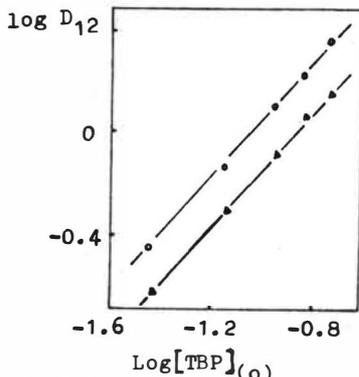


Fig. 3. Plots of $\text{Log} D_{12}$ vs $\text{Log} [\text{TBP}]_{(\text{o})}$ at constant $[\text{RNH}_3\text{Cl}]_{(\text{o})}$ Δ -0.08M; \circ -0.12M

Calculation of equilibrium constants of the synergic reaction and addition reaction of zinc(II) with primary amine N_{1923} and TBP

From the published data for [7] ($\beta_1=5.35$, $\beta_2=2.76$, $\beta_3=1.07$, $\beta_4=0.27$) the extraction constant $K_{12}=10^{1.75}$ calculated from the data obtained under the experimental conditions and pertinent values of $\text{Log} D_{12}$, $\text{Log} [\text{RNH}_3\text{Cl}]_{(\text{o})}$ and $\text{Log} [\text{TBP}]_{(\text{o})}$, the equilibrium constants of synergic reaction and addition reaction of zinc(II) can be calculated as $\text{Log} K_{12}=3.09$ $\text{Log} \beta_{12}=1.34$ respectively.

Calculation of the thermodynamic functions of the synergic reaction

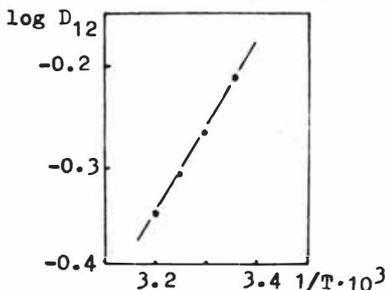


Fig. 4. Plot of $\text{Log} D_{12}$ vs $1/T$ at constant $[\text{TBP}]_{(\text{o})}=0.06\text{M}$, $[\text{RNH}_3\text{Cl}]_{(\text{o})}=0.14\text{M}$

Fig. 4 is the plot of $\text{Log} D_{12}$ against the reciprocal of the temperature. The value of enthalpy change (ΔH_{12}) for reaction (3) can be calculated to be $-15.91 \text{ KJ.mol}^{-1}$ with the slope of 830.7. The values of the corresponding free energy (ΔG^0) and entropy change (ΔS^0) can be calculated as $-17.63 \text{ KJ.mol}^{-1}$ and $5.77 \text{ J.mol}^{-1}.\text{K}^{-1}$ at 25°C respectively.

Studies on the IR and NMR spectra of the extracted species

As seen from Table 2. the RNH_3^+ group is still present in the synergic

extracting complex. The shift of the P=O stretching frequency from 1281cm^{-1} in the ligand TBP to $\nu(\text{P=O})$: 1254cm^{-1} in the $\text{RNH}_2\text{Cl-TBP}$ and 1211cm^{-1} in the synergic extracting complex indicates that the P=O group is involved in bonding. This could be attributed to the coordination with metal through the oxygen atom of P=O group. In addition, it has been shown in the proton magnetic resonance spectral data that RNH_3^+ group still exist in the synergic extracting complex. In a word, from what have been interpreted above, it can be confirmed that RNH_3Cl and TBP participate in the formation of synergic extracting complex.

Table 2. Observed vibrational frequencies of RNH_2Cl , TBP and synergic extracting complex

Frequency Species	Ways	$\nu_{\text{CH or NH}}$	$\delta_{\text{as NH}}$	$\delta_{\text{s NH}}$	$\nu_{\text{P=O}}$	$\nu_{\text{P-O-C}}$	Notes
RNH_3Cl		3000 vs, b, sh	1605 s	1512 s	--	--	1. $\nu_{\text{N-H}}$ or $\nu_{\text{C-H}}$ is overlapping at about 3000cm^{-1} .
$\text{RNH}_3\text{Cl-TBP}$		"	1605 s	1505 s	1254 s	1030 vs, b, sh	2. Little shift of $\delta_{\text{N-H}}$ or $\delta_{\text{N-H}}$ frequency may be due to the interaction of RNH_3Cl , TBP
$\text{RNH}_3\text{Cl-TBP-ZnCl}_2$		"	1605 s	1505 s	1211 s	1022 vs, b, sh	3. $\nu_{\text{P-O-C}}$ including $\nu_{\text{P-O-C}}$
TBP		2963 vs, sh	--	--	1281 s	1030 vs, b, sh	and $\nu_{\text{P-O-C}}$ is central value.

Legend: s, strong; vs, very strong; b, broad; sh, shoulder shape; ν , stretching; δ , bending or deformation.

Conclusions

The synergic effect of zinc(II) with primary amine N_{1923} and TBP in heptane is obvious. The dependence of solvents and temperature on the synergic reaction of zinc(II) has been studied. The mechanism of synergism has been determined by the methods of slope analysis and constant mole. The thermodynamic functions and equilibrium constants and IR, NMR spectra have been carried out.

References

1. Catrall R.N., Slater S.J.E.//Coord. Chem. Review.1973.Vol.11.P.227
2. Le Shaoming, Li Deqian, Ni Jiazan //J. Inorg. Chem.1987.Vol.3.P.80.
3. Singh J.M., Tandon S.N.//J. Inorg. Nucl. Chem. 1979.Vol.41. P.897.
4. Yu Shuchiou, Chem Chiayung //Hydrometallurgy. 1985. Vol.14. P.115.
5. Mooiman M.B., Miller J.D.//Hydrometallurgy. 1986.Vol.16. P.245.
6. Du Preez Rene, Preston Johns //S.Afr.J. Chem. 1986.Vol.39. P.89.
7. Sato T., Nakamura T.//J. Inorg.Nucl. Chem. 1977. Vol.39. P.1205.

SOLUTION BY N_{1923}

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The extraction mechanism of zinc(II) from thiocyanate solution by ternary amine has been reported[1], but the extraction of zinc(II) from thiocyanate solutions with primary amine has not been reported yet. The authors in present paper have studied the extraction of zinc(II) from chloride solutions by primary amine N_{1923} [2], In order to investigate the dependence of different inorganic anions on the extraction of zinc(II), the extraction mechanism of zinc(II) from thiocyanate solutions by primary amine N_{1923} has been studied. The extracted complexes of zinc(II) from thiocyanate solutions with both free amine(RNH_2) and its nitrate salt(RNH_3NO_3) have been confirmed. Moreover, the equilibrium constants and thermodynamic functions of both reactions have been measured and calculated. The IR and NMR spectra of the extracted complexes have been investigated as well.

Extraction of zinc(II) from thiocyanate solutions with free amine

As seen from Fig.1 LogDf, according to the method of Moriya[3], increases with $\text{Log}[\text{SCN}^-]$ and the slope of straight line is 2, which suggest that the species of $\text{Zn}(\text{SCN})_2$ in the aqueous solution has been extracted into the organic phase.

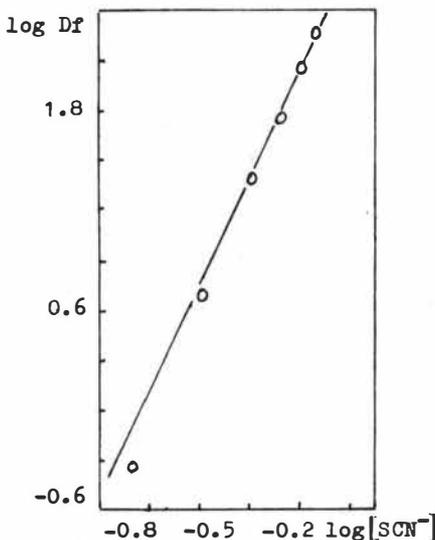


Fig. 1. Plot of LogDf vs $\text{Log}[\text{SCN}^-]$

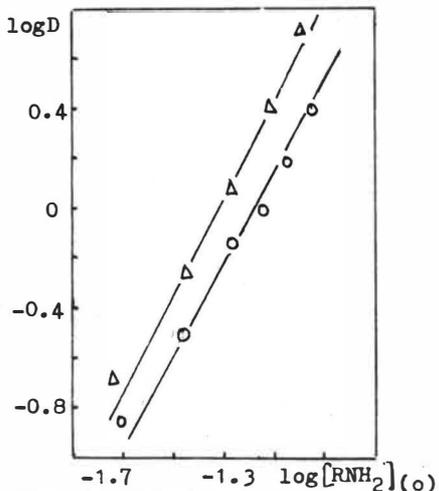
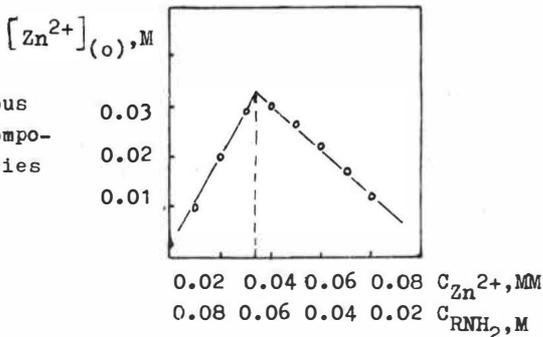


Fig. 2. Effect of RNH_2 concentration on $\text{Zn}(\text{SCN})_2$ extraction
 Δ - $[\text{SCN}^-]=0.0653\text{M}$, $[\text{Zn}^{2+}]=0.0522\text{M}$;
 \circ - $[\text{SCN}^-]=1.018\text{M}$, $[\text{Zn}^{2+}]=0.0815\text{M}$.

* To whom correspondence should be addressed.

Fig.3. Method of continuous variation to determine composition of extracted species (constant SCN^- conc.)



Plots given in Fig.2 are straight lines having a slope of 2. The results prove that a mole Zn(II) combines with two mole free amine RNH_2 .

Results shown in Fig.3 and Fig.4 indicate that the mole ratio of free amine RNH_2 , Zn(II) and SCN^- is 2:1:2 in the extracted species.

From what have been interpreted above, the composition of extracted complex is $(\text{RNH}_2)_2\text{Zn}(\text{SCN})_2$ and the extraction reaction of Zn(II) from thiocyanate solutions with free amine RNH_2 can be expressed as

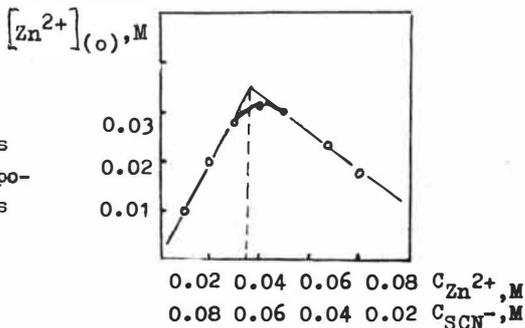


and the equilibrium constant K_1 can be represented by the following equation, viz.

$$K_1 = \frac{D(1 + \sum \beta_i [\text{SCN}^-]^i)}{\beta_2 [\text{RNH}_2]_{(o)}^2 [\text{SCN}^-]^2}, \quad (2)$$

where β represents the overall stability constant of Zn(II) with thiocyanate ions. The values β_i of Literature [4] was adopted.

Fig.4. Method of continuous variation to determine composition of extracted species (constant RNH_2 conc.)



Extraction of Zn(II) from thiocyanate solution with RNH_3NO_3

Plots shown in Fig.5 and Fig.6 suggest that the mole ratio of RNH_3NO_3 , Zn(II) and SCN^- is 2:1:4. Results indicate that the composition of the extracted complex could be $(\text{RNH}_3)_2\text{Zn}(\text{SCN})_4$. In order to ascertain the composition furtherly, the effect of RNH_3NO_3 concentrations

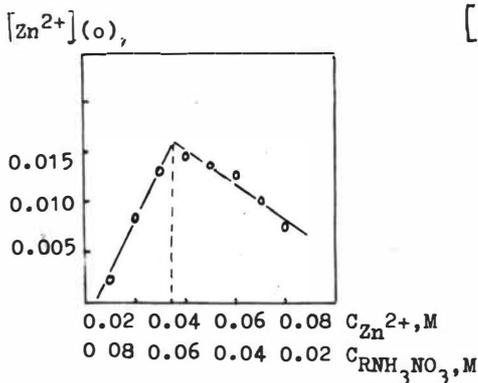


Fig.5. Method of continuous variation (constant SCN^- conc.)

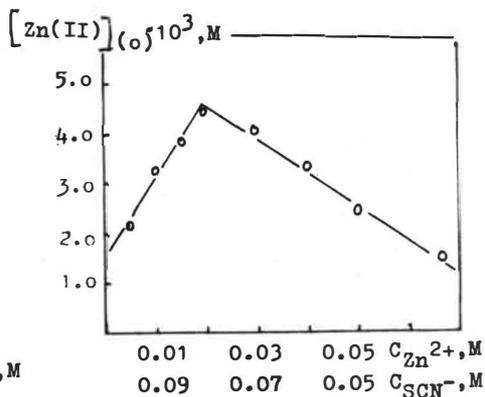
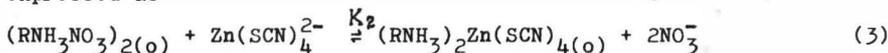


Fig.6. Method of continuous variation (constant RNH_3NO_3 conc.)

on the distribution ratio of Zn(II) has been shown in Fig.7. Plots given in Fig.7 are straight lines of slope 1. Considering the polymerization degree of RNH_3NO_3 in the organic phase, then the reaction can be expressed as



and the equilibrium constant K_2 can be represented by the following equation:

$$K_2 = \frac{D(1 + \sum \beta_1 [\text{SCN}^-]^i) [\text{NO}_3^-]^2}{\beta_4 [(\text{RNH}_3\text{NO}_3)_2(o)] [\text{SCN}^-]^4} \quad (4)$$

Calculation of equilibrium constants and thermodynamic functions

The equilibrium constants of Reaction (1) and (3) according to Equation (2) and (4) have been calculated to be $\text{Log}K_1 = 3.15$, $\text{Log}K_2 = 0.602$.

Fig.8 is the curves of relationship of $\text{Log}K$ to the reciprocal of the temperatures. Results indicate that Reaction (1) and (3) give out heat. The thermodynamic functions of Reaction (1) and (3) have been measured to be $\Delta H = -8.06 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta G = -16.86 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S = 29.53 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the $\text{RNH}_2\text{-Zn}(\text{SCN})_2$ system; $\Delta H = -4.12 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta G = -5.07 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S = 3.19 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the $\text{RNH}_3\text{NO}_3\text{-Zn}(\text{SCN})_2$ system at 25°C respectively.

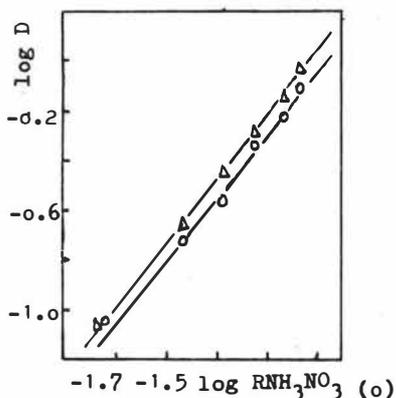


Fig. 7. Effect of RNH_3NO_3 concentration on the distribution ratio of Zn(II) - $[\text{SCN}^-]=0.795\text{M}$, $[\text{Zn}^{2+}]=0.0814\text{M}$; temperatures - $\text{RNH}_2\text{-Zn(SCN)}_2$; Δ - $[\text{SCN}^-]=0.580\text{M}$, $[\text{Zn}^{2+}]=0.0626\text{M}$

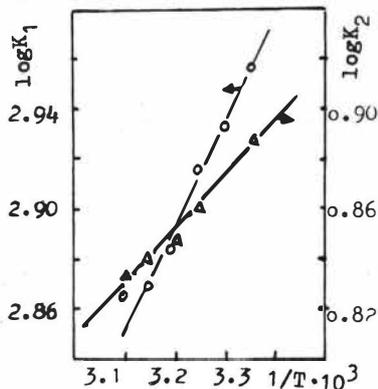


Fig. 8. Relationship of $\text{Log } K_1$ to the reciprocal of the temperature - $\text{RNH}_2\text{-Zn(SCN)}_2$; Δ - $\text{RNH}_3\text{NO}_3\text{-Zn(SCN)}_2$

IR and NMR spectra of the extracted complexes

In order to obtain the formations of the structures in extracted complexes, the IR spectra of two extracted complexes have been studied. Results suggest that free amine RNH_2 coordinates with Zn(II) in the extracted complex $(\text{RNH}_2)_2\text{Zn(SCN)}_2$ and amine salt cation ion RNH_3^+ still exists in the extracted complex $(\text{RNH}_3)_2\text{Zn(SCN)}_4$.

In addition, the ^1H NMR of the two extracted complexes have been investigated. Results are in good agreement with the IR spectra's.

Conclusions

The extraction mechanism of zinc(II) from thiocyanate solutions by primary amine N_{1923} has been studied. It has been found that zinc(II) can be extracted from thiocyanate solutions with both free amine (RNH_2) and its nitrate salt (RNH_3NO_3) by different extraction mechanism. It belongs to extraction mechanism of solvated complex using free amine as extractant and the extracted complex is $(\text{RNH}_2)_2\text{Zn(SCN)}_2$ formed with Zn-N coordination bond. While the RNH_3NO_3 is used as extractant, the extraction mechanism is anion exchange reaction. The equilibrium constants and the thermodynamic functions of both reactions have been calculated. The IR and NMR spectra of the extracted complexes also have been investigated.

References

1. Fridman Ya.D., Sarbaev D.S., Levina M.G. // Mater. Nauch. Konf., Posvyashch. 100-(sto) Letiyu Period. Zakona, Mendeleeva D.I. 1969. P.48.
2. Le Shaoming, Li Deqian, Ni Jiazan // J. Inorg. Chem. 1987. Vol. 3. P.80.
3. Moriya H., Sekine T. // Bull. Chem. Soc. Jap. 1971. Vol. 44. P. 3347.
4. Hogfeldt E. // Stability Constants of Metal-ion Complexes, Part A. IUPAC Chemical data. Series No. 21. Pergamon Press. Oxford. 1982. P.90.

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For the recovery of tin in hydrochloric acid solution, the precipitation [1,2] and replacement [3,4] methods are usually employed in industry. It has seldom been reported the use of extraction method in industry. However, the separation of tin by solvent extraction seems promising and may sometime replace the conventional methods. Reddy [5] studied the extraction of Sn^{2+} from hydrochloric acid solution by sulphoxide. In the separation of tin and indium with TBP from hydrochloric acid solutions, M. Golinski [6] indicated that the distribution coefficient under optimum conditions (7-9N HCl) are about two orders of magnitude higher than the maximum value of indium $D_{\text{In}^{3+}}$. With 0.1M acetylacetone-benzene, percentage extraction of Sn^{2+} is 75% at PH6 [7]. Sn^{4+} is almost completely extracted with 1% oxime- CHCl_3 at PH2.2-5.5 [8]. The present investigation is aimed at the utilization of the "ash" produced in the chloride volatilization of cassiterite, i.e. to recover tin and copper by solvent extraction.

Feed solutions were prepared by dissolving analytical grade reagents in hydrochloric acid of different concentrations. The concentrations of tin and copper were corresponding to the resulting aqueous hydrochloric acid solution obtained from the chloride volatilization of cassiterite [2]. Solvent used was methyl isobutyl ketone (MIBK) which was purchased in Shanghai market. Equilibration was carried out in separating funnels by contacting the aqueous and organic phases for ten minutes which were found to be sufficient. Then the concentration of tin and copper in aqueous phase were determined by EDTA titration and atomic absorption spectrometry.

RESULTS AND DISCUSSION

1. Time required to attain equilibrium

Table 1 shows that the time required is less than one minute. There is no difference for Sn or Cu or a mixture of both metals in the aqueous HCl solution.

Table 1. Variation of concentration for different time of equilibration

time, sec.	30	60	120	300	600
$[\text{Sn}^{4+}]_{\text{E}} \text{ Kmol/m}^3 \times 10^3$	95.5	95.5	95.8	95.8	95.5
$[\text{Cu}^{2+}]_{\text{E}} \text{ Kmol/m}^3 \times 10^3$	2.28	2.33	2.17	2.28	2.28
Aqueous, $[\text{Sn}^{4+}]$, 0.102 Kmol/m ³ ; $[\text{Cu}^{2+}]$, 0.152 Kmol/m ³ ; $[\text{HCl}]$, 6M; Solvent, MIBK; Phase ratio, 1; T, 283 K.					

2. Effect of temperature on equilibrium

As shown in Fig.1, experimental results indicate that distribution coefficient of tin ($D_{Sn^{4+}}$) decreases with increasing temperature. The increase in temperature from 10 to 70°C brings about a rise in $D_{Cu^{2+}}$ values from 0.016 to 0.032. From Fig.1, it is obvious the lower the extraction temperature, the higher will be the separation factor, $\beta = D_{Sn^{4+}}/D_{Cu^{2+}}$. It is also obvious that to carry out the extraction below the ambient temperature may be uneconomical, if not necessary. Therefore, operation at a temperature between 20 and 30°C seems appropriate, and the separation factor is still high enough, i.e. 300-500 (Fig.2), to separate these two metals with reasonable number of theoretical stages.

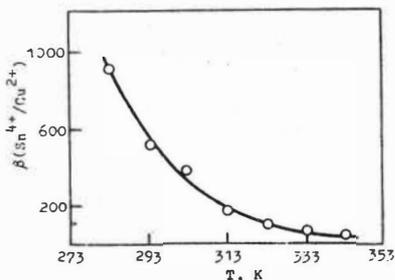
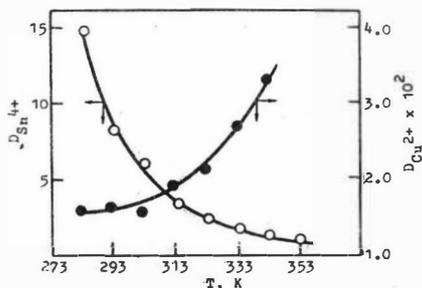


Fig.1. Effect of temperature on $D_{Sn^{4+}}$ and $D_{Cu^{2+}}$. Aqueous, $[Sn^{4+}]$, 0.102 $Kmol/m^3$; $[Cu^{2+}]$, 0.152 $Kmol/m^3$; $[HCl]$, 6M; Solvent, MIBK

Fig.2. Effect of T on $\beta(Sn^{4+}/Cu^{2+})$. Aqueous, $[Sn^{4+}]$, 0.102 $Kmol/m^3$; $[Cu^{2+}]$, 0.152 $Kmol/m^3$; $[HCl]$, 6M; Solvent, MIBK

3. Effect of HCl concentration

Fig.3 indicates the effect of HCl concentration on distribution of tin and copper between MIBK and aqueous solution. Both $D_{Sn^{4+}}$ and $D_{Cu^{2+}}$ increase with increasing HCl concentration. At 1.2N HCl, $D_{Sn^{4+}} = 0.833$ and $D_{Cu^{2+}} = 5 \times 10^{-4}$ thus $\beta = 1670$; at 6.8N HCl, $D_{Sn^{4+}} = 21$, $D_{Cu^{2+}} = 3.5 \times 10^{-2}$ and $\beta = 600$. In order to have a fairly large $D_{Sn^{4+}}$, it would appear preferable to use high concentration of HCl. But at a concentration of 8.5N the organic and aqueous phases become completely miscible. Hence 3-4N HCl is considered appropriate. Due to easy separation of Cu^{2+} from Sn^{4+} , the following has been emphasized on the extraction and stripping on tin.

4. Extraction isotherm

The extraction isotherm of Sn^{4+} and Sn^{2+} is shown in Fig.4. The curve of Sn^{4+} is always slightly higher than that of Sn^{2+} , particularly at higher concentration of tin. The relatively small differences of extraction between Sn^{4+} and Sn^{2+} can be explained by two opposing

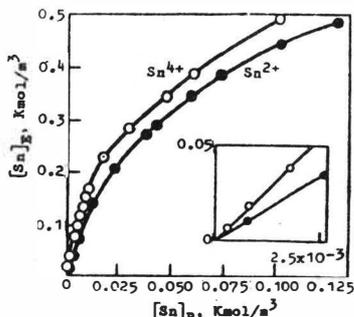
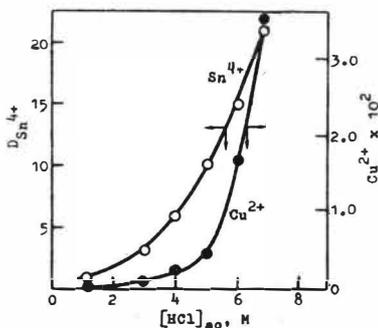


Fig. 3. Effect of $[HCl]$ on $D_{Sn^{4+}}$. Aqueous, $[Sn^{4+}]$, 7.88×10^{-2} $Kmol/m^3$; $[Cu^{2+}]$, 6.06×10^{-2} $Kmol/m^3$; T, 283 K; Solvent, MIBK

Fig. 4. Extraction isotherm of Sn^{4+} and Sn^{2+} . Aqueous, $[HCl]$, 6M; Solvent, MIBK; T, 283 K

factors, i.e. the Sn^{4+} ion probably has a higher tendency to polymerise than Sn^{2+} on one hand, but the former possesses greater ion potential than the latter on the other. The resulting effect is that Sn^{4+} appears a little better extracted than Sn^{2+} . At low concentration, i.e. below 2.5×10^{-3} $Kmol/m^3$ in aqueous solution, the isotherms can be seen in the enlarged diagram as indicated in the same figure.

At the low concentrations of both Sn^{4+} and Sn^{2+} , the extraction isotherms seem practically straight lines, the slopes of which are 20 and 13 respectively.

5. Choice of stripping agent for Sn^{4+}

It can be seen from the Table 2 that deionized water is a better stripping agent for Sn^{4+} than alkaline or acidic solutions due to the absence of precipitation and good phase separation with high percentage stripping. As it is known at pH values ≥ 4.7 , hydrolysis for Sn^{4+} will occur. When the loaded solvent is stripped with deionized water, it would seem that Sn^{4+} might tend to hydrolyze. In fact, this phenomenon does not appear, because MIBK also extract HCl from aqueous phase and during stripping the deionized water picks up HCl as well as Sn^{4+} and the resulting aqueous solution has a pH less than 4.7.

Table 2. Choice of stripping agent for Sn^{4+}

stripping agent	time of phase separation, sec	stripped solution, $Kmol/m^3$	% stripping
H_2O	30	0.151	97.3
2% NH_3 H_2O	precipitate	0.155	99.7
0.67M NaOH	precipitate	0.145	93.7
0.5M HCl	30	0.146	94.2
0.5M HNO_3	30	0.143	92.5
0.5M H_2SO_4	precipitate	0.142	91.7
0.5M NaCl	30	0.134	86.8

$[Sn^{4+}]$ in loaded solvent, 0.155 $Kmol/m^3$; Solvent, MIBK; Phase ratio, 1; T, 298K.

6. Effect of temperature on stripping for Sn^{4+}

Effect of temperature on stripping for Sn^{4+} from the loaded solvent with deionized water is listed in Table 3. Percentage stripping of Sn^{4+} increases with increasing temperature. When temperature is higher than 60°C , precipitates appear due to hydrolysis.

Table 3. Effect of temperature on stripping Sn^{4+}

temperature, K	293	298	303	313	323	333
stripping, %	94.8	97.3	98.5	99.5	99.8	Precipitate
$1/D_{\text{Sn}^{4+}}$	18.2	36.4	64.5	195	602	

Stripping agent, deionized water; Phase ratio, 1;
 $\angle\text{Sn}^{4+}$ in the loaded solvent, 0.155 Kmol/m^3 .

7. Change in enthalpy in extraction and stripping of Sn^{4+}

Fig.5 and Fig.6 show the plots of $\log D_{\text{Sn}^{4+}}$ and $\log(1/D_{\text{Sn}^{4+}})$ vs. $1/T$. The plots show good straight lines with slopes of 1.83×10^3 and -4.86×10^3 respectively. The enthalpy changes of extraction and stripping were found to be -3.62 and 9.82 Kmol/mol respectively.

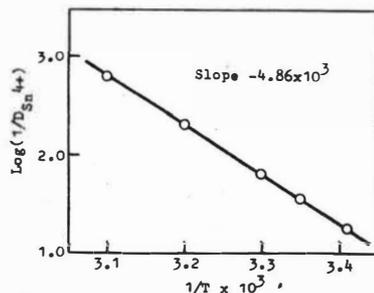
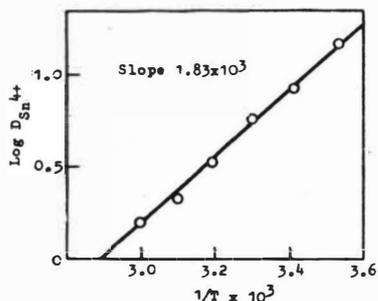


Fig.5. $\text{Log } D_{\text{Sn}^{4+}}$ vs. $1/T$. Aqueous, $\angle\text{Sn}^{4+}$, 0.102 Kmol/m^3 ; $\angle\text{HCl}$, 6M ; Solvent, MIBK

Fig.6. $\text{Log}(1/D_{\text{Sn}^{4+}})$ vs. $1/T$. $\angle\text{Sn}^{4+}$ in loaded solvent, 0.155 Kmol/m^3 ; Stripping agent deionized water; Phase ratio, 1

References

1. Zhu Yu-Qin // Youse Jinshu, Yelian Bofen. 1987.V.2.P.23.
2. Zhu Yu-Qin // Youse Jinshu, Yelian Bofen. 1986.V.1.P.12.
3. Fitchugh E.F., Seidel D.C.//U.S.Patent 3,499,756 (1970).
4. Yung Xian-Wan, Fei Xiu-Uin // Youse Jinshu, Yelian Bofen.1986.V.4. P.38.
5. Lakshmiipathi Reddy M. et al.// Radiochimica Acta.1985.V.38.P.161.
6. Golinski M.//Proc.of the Intern.Solvent Extraction Conference.The Hague,1971.Vol.1.Society of Chemistry Industry.London,1971.P.603.
7. Stary J., Hladyky E.//Anal.Chim.Acta. 1963.V.28.P.227.
8. Gentry C.H.R., Sherrington L.G.//Analyst. 1950.V.75.P.17.

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The major breakthrough in solvent extraction studies is the development of reagents known as chelating extractants [1]. Among these extractants, compounds marketed under the trade name "LIX" reagents has assumed great importance in the hydrometallurgy of copper [2]. In the present manuscript extraction of copper(II), antimony (III), zinc (II), cadmium (II), cobalt (II), nickel (II), manganese (II), palladium (II), lead (II), iron (II) and rhodium (III) using LIX26 extractant (substituted 8-hydroxyquinoline) has been investigated. Such a study would be helpful in providing basic information required for some separations and in the development of new analytical methods.

The extraction procedure and the mechanism of extraction has been given in detail in our earlier paper [3]. Presented in Table 1 are the data on the extraction of metals with 1% v/v LIX26 extractant in MIBK. The slopes of log D vs pH plot for some metals have been mentioned in Table 1. The slopes of the plots of logD

Table 1. Extraction data of some metals using 1% v/v LIX26 extractant in MIBK

Metal	pH _{1/2} value	pH for complete extraction	Shaking time (min)	Slope value (logD vs pH)	pH _{1/2} (0.01M oxine) [4]	logK _{ex}
Mn(II)	6.75	> 7.9	30	2.0	6.66	- 10.66
Co(II)	5.00	6.7	30	1.8	5.08	- 7.16
Ni(II)	6.15	> 7.8	30	1.72	3.16	- 9.46
Cd(II)	6.95	> 8.6	60	1.93	6.65	- 11.05
Zn(II)	5.40	6.7	30	1.73	5.20	- 7.95
Cu(II)	-	1.5 - 9.0	5	-	1.77	-
Pb(II)	6.40	> 8.5	30	2.1	6.04	- 9.95
Sb(III)	< 1.5	1.5	30	-	-	-
Fe(II)	3.8	> 5.0	60	1.88	-	- 4.76
Pd(II)	< 1.0	-	30	-	< 0	-
Rh(III)	-	25% extraction	120	-	-	-

vs log (LIX26) concentration in most systems is equal to $n/2$. The log K_{ex} values have been calculated for some metals using the experimental values of D and LIX26 concentration. Concentration of LIX26 extractant (a substituted 8-hydroxy quinoline) by indirect estimation has been found to be n 0.038M. The pH isotherms of LIX26 extractant with these selected metals are shown in Fig 1. The order of extraction of metals by LIX26 extractant as a function of pH_{1/2} value is as follows : Pd(II) < Cu(II) < Sb(II) < Fe(II) < Co(II) < Zn(II) < Ni(II) < Pb(II) < Mn(II) < Cd(II).

Except for Ni(II) and Cd(II) all the extraction data for LIX26 systems agree well with oxine systems [4]. Since LIX26 resembles oxine in its extractive properties towards metals, it seems reasonable to support that similarities exist in their properties. There is also a good agreement between extraction studies between LIX26 and Kelex 100 extractants. The extraction behaviour of these selected metals by LIX26 extractant can be briefly summarised as follows (i) Copper (II), antimony (III) and palladium (II) are extracted from acidic solutions. Antimony (III) gets extracted around pH9 using oxine, whereas with LIX26 an effective complete extraction is possible around pH 1.5. Palladium

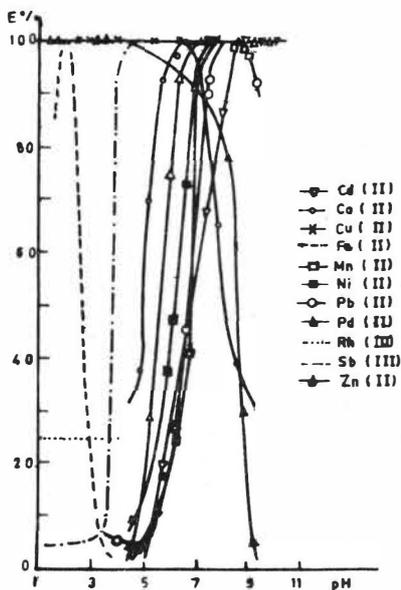


Fig.1. Percentage extraction versus pH plots

is extracted from highly acidic solutions thereby providing high selectivity in the recovery and purification of palladium. Effective separation of palladium is also achieved from nickel using this extractant (ii) Complete extraction of copper (II), manganese (II), nickel (II), zinc (II), lead (II), cadmium (II) and iron (II) by using LIX26 extractant is around pH 8.6, though copper (II) is also extractable from acidic solutions.

Thus a single extraction at pH 8.6 from a dilute solution of metals into a smaller volume of the organic solvent will be a rapid and effective method of preconcentration of metals before atomic absorption spectrophotometric determination [5]. Preconcentration of some selected metals Cu (II), Ni (II), Pb (II), Cd (II), Mn (II), Zn (II) and Fe (II) present in diluted water and urine samples using samples using LIX 26 extractant (1% v/v in MIBK) followed by their determination using atomic absorption spectrophotometer have been investigated. Results of preconcentration of trace metals present in water and urine samples are given in Table 2 and 3.

A ten times enhancement factor has been obtained in all the cases for the preconcentration of trace metals in water sample. Direct aspiration of the organic layer (MIBK) does not improve the detectability of measurement (\downarrow 2.5) as compared to aspiration of aqueous layer into atomic absorption spectrophotometer. In the case of trace metals in urine sample an actual enhancement of 2.5 times was observed in cases of all metals except manganese and lead (four times dilution of urine sample). Even after preconcentration, the lead and manganese contents in urine sample was not detected by flame atomic absorption spectrophotometer. All the results agree

Table 2. Results of preconcentration of trace metals in water by extraction with 1% v/v LIX26 extractant in MIBK.

Metal	Back Extraction		Direct aspiration	
	Initial concentration (μgml^{-1})	Final Concentration (μgml^{-1})	Initial Direct concentration (μgml^{-1})	Final concentration (μgml^{-1})
Mn(II)	0.042	0.42	0.02	0.21
Ni(II)	0.1	1.0	0.04	0.4
Pb(II)	0.1	1.0	0.04	0.38
Cu(II)	0.022	0.22	0.022	0.22
Cd(II)	0.08	0.69	0.032	0.31
Zn(II)	0.02	0.2	0.008	0.1
Fe(II)	0.002	0.018	0.001	0.011

Table 3. Preconcentration of trace metals present in urine sample extraction into 1% v/v LIX26 extractant in MIBK and back extraction into 8M HNO_3 .

Metal	Standard value of trace metals in urine (μgml^{-1})	Amount after Preconcentration (μgml^{-1})	In dilute urine solution (μgml^{-1})	In actual urine sample (μgml^{-1})
Mn(II)	0.001 - 0.01	-	-	-
Pb(II)	0.1	-	-	-
Ni(II)	0.05	0.1	0.01	0.04
Cu(II)	0.05	0.2	0.02	0.08
Cd(II)	0.001	0.01	0.001	0.004
Zn(II)	0.5	3.65	0.365	1.46

well with the data reported in the literature [6]. MIBK is chosen for this work as it is the ideal solvent for monitoring the metal concentrations by atomic absorption spectrophotometer.

LIX26 is a very cheap extractant as compared with many analytical reagents. It is for the first time that the utility of this commercially available extractant has been exploited, which had been used extensively for hydrometallurgical extractions earlier.

References

1. Ashbrook A.W. // Co-ord. Chem. Rev. 1975. Vol. 16, P. 285.
2. Burkin A.R. // Chem and Ind. 1983. P. 690.
3. Ramesh V., Rao G.N. // Proc. Ind. Acad. Sci. Chem. Sci. 1987. Vol. 98. P. 165.
4. Stary J. // Anal. Chim. Acta. 1968. Vol. 28. P. 132.
5. Cresser M.S. Solvent extraction in flame spectroscopic analysis. London, 1978.
6. Thompson K.C., Reynolds R.J. Atomic absorption, fluorescence and flame emission spectroscopy. London : Griffin and Co., 1978.

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A review of solvent extraction literature reveals considerable interest in d-transition elements extractions, especially those belonging to the VIII group of the periodic classification. Historically, extractions and separations are difficult because of the poor selectivity of available reagents, slow kinetics and pH control conditions.

In an effort to adress this problem, we investigated synergic mixtures, containing cationic exchangers such as dinonylnaphtalene sulfonic acid (HDNNS), plus a neutral polydentate nitrogen donor ligand, such as bipyridine or others aromatic polyimines.

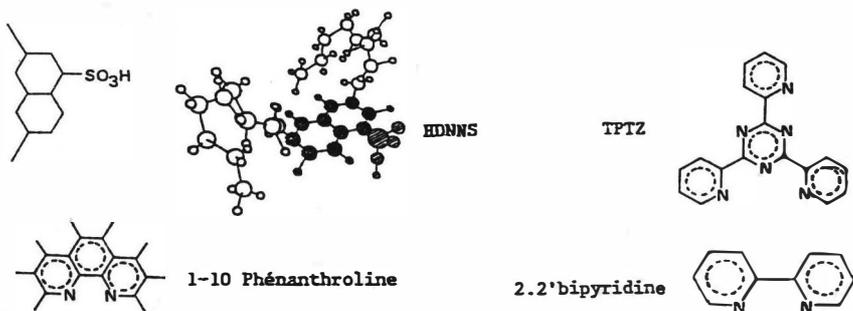


Fig.1 . HDNNS, bipyridine, phenanthroline, TPTZ (tripirydyltriazine)

The prospects of this system, which performs good extractions and separations from acidic media (0.1N - 2N), have been described previously (1). This system looks like synergic combinations, requiring HDNNS, such as the system presented in (2). The main difference, in our case, is that the ligand is water soluble.

The system is characterized by a mechanism in two steps. On the one hand, complexation of metallic cations, in acidic media, is operated by polyimines. This is the limiting step, from a kinetical point of view. On the other hand, extraction is performed by cationic exchanger, HDNNS, forming inverted micelles in the diluents we used (tertbutylbenzene or CCl₄).

Our aim was to identify and to quantify the chemical equilibria involved in the system, in order to elucidate the extraction mechanism, to explain its selectivity and to predict numerically the behaviour of a multicomponent system where few metals are initially present in aqueous media. Reactions in aqueous media were investigated within three aspects : kinetics of complexes formation with aromatic polyimines (especially when inert complexes are involved, such as ruthenium and rhodium in nitric acid medium), stability of metal complexes in acidic media and ionic associations between complexes and mineral anions present in acidic media. This last point

explains partly the selectivity of the system : the logarithms of the stability constants of these outer sphere complexes are linear functions of the corresponding heats of hydration of the anions. This ability of polyimine complexes to form ion pairs has been already studied (3) (4) (5) (6). The strength of the ion pairs, with a same anion, decreases in the ligand order and the central cation order according to phen > bipy > TPTZ (order of the shielding effect of the ligand) and Pd(II) > Rh(III) > Ru(II) > Ni(II) > Co(II) > Fe(II) (order of the soft character of the cations).

The behaviour of HDNNS was studied with numerous experimental means (I.R. spectroscopy, U.V. visible spectrophotometry, osmometric measurements, Karl Fisher water determinations in the organic phase, numerical treatments of extraction experimental results etc...), the micelle and the quantification of equilibria involved :



The micelles contain a large amount of water in their cores : 48 water molecules.

HDNNS shows little ability to separate individual metal ions from each others. The selectivity is due to the ligand.

Ligand extraction was studied, previously to metal complexes extraction, since the general mechanism of the system proceeds as competitive extractions of cationic species in aqueous media (protonated forms of the free ligand, cationic metal complexes, H⁺).

The modelling of different extraction experiments leads us to give an explanation to the mechanism of extraction. Let us take the modelling of bipyridine extraction as an example (Figure 2).

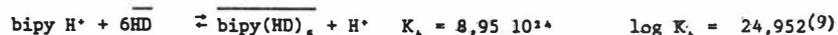
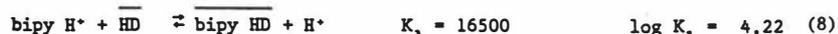
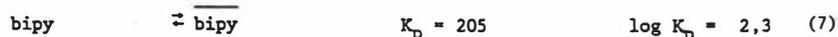
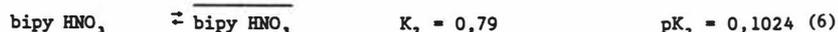
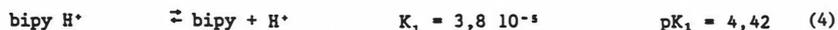
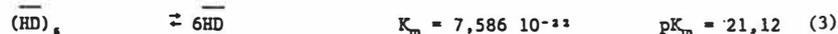
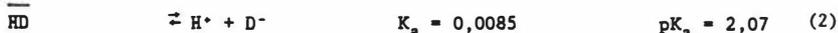
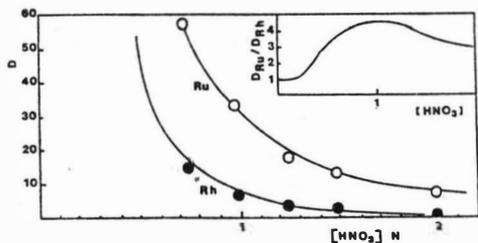


Fig.2. Modelling of bipyridine extraction by HDNNS from nitric acid medium

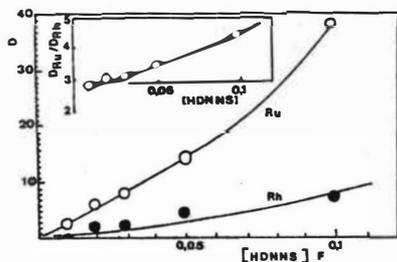
For low [ligand]/[HDNNS] ratios, cationic species are solubilised by micelles (equation (9)). At higher ratios, until ligand saturation conditions in the organic phase, micelles are destroyed and cationic species are extracted as associations with the monomeric forms of the extractant (equation (8)). This mechanism was observed in complexes extractions.

Figures 3 and 4 show two examples of metals separations, illustrating the two kinds of ligand selectivity.



$$[Ru] = [Rh] = 10^{-4} \text{ M}$$

$$[bipy]_{\text{free}} = 5.10^{-4} \text{ M}$$



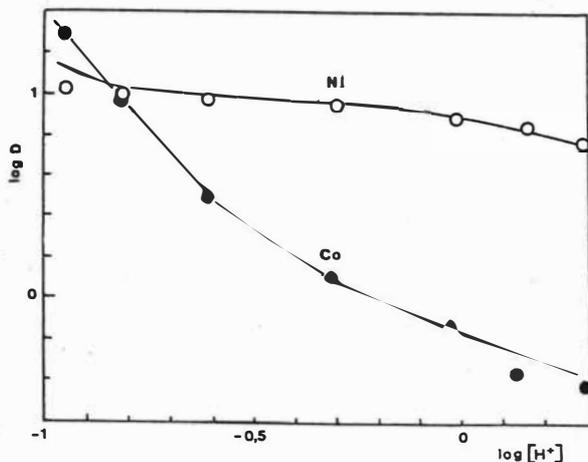
$$[HDNNS] = 0.1 \text{ F} \quad [HNO_3] \text{ varies}$$

$$[HNO_3] \approx 1 \text{ N} \quad [HDNNS] \text{ varies}$$

Fig. 3 . Ruthenium/rhodium separation from nitric acid media

The selectivity of this system is owing to ionic associations, in aqueous media, between bipyridine complexes of ruthenium and rhodium with nitrates, which are more important for rhodium complexes than for ruthenium ones. Ion pairing decreases the charge of metal complexes and significantly influences extraction by a cationic exchanger.

Nickel II complexes with bipyridine are stable in acidic media (H_2SO_4 , 1N for instance), cobalt II ones are not. Since only polyimines complexes are significantly extracted, the effect of selectivity, due to the ligand, is quite obvious for extractions from 1N sulfuric media. Selectivity over cobalt (ratio of distribution coefficients) is about 15. Experiments, illustrating the effect of varying acidities, show two areas of selectivities : when $[H^+] \leq 0.15\text{N}$, cobalt is most strongly extracted. In such conditions, cobalt is complexed by bipyridine and the modelling of the extraction system shows that such complexes extraction constants are greater than the nickel complexes ones. When $[H^+] \geq 0.15\text{N}$, nickel is more strongly extracted since its complexes with bipyridine are stable and the cobalt ones are not. When $[H^+] = 0.15\text{N}$, the balance of these two effects induces coextraction of nickel and cobalt.



[Ni] = [Co] = $2,5 \cdot 10^{-3}$ M [bipy] = $5 \cdot 10^{-2}$ M [HDNNS] = 0.05 F
 [H₂SO₄] varies

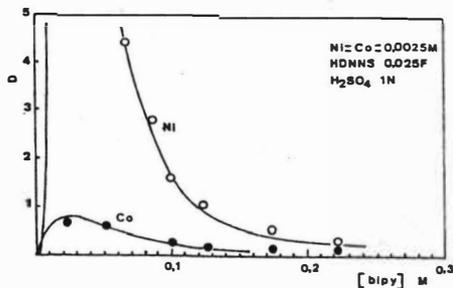
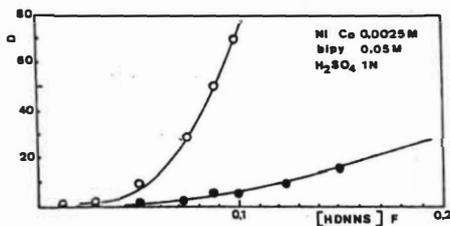


Fig. 4 . Nickel/cobalt separation from sulfuric acid media

Bibliography

1. X. VITART , C. MUSIKAS// Proc. Int. Solv. Extr. Conf. 1986, Munchen RFA, II-79 (1986).
2. R.R. GINSTEAD , A.L. TSANG// Proc. Int. Solv. Extr. Conf. 1983, Denver USA,
3. A.K. PYARTMAN , M.V. SOF'IN , V.E. MIRONOV//Russ. J. Inorg. Chem. 28(8). (1983).
4. A.K. PYARTMAN , M.V. SOF'IN . V.E. MIRONOV//Russ. J. Inorg. Chem. 29(6). (1984).
5. E.G. KARMANOVA , A.K. PYARTMAN// Russ. J. Inorg. Chem. 28(2). 298-291 (1983).
6. V.E. PYARTMAN , M.V. SOF'IN , Y.B. SOLO'EV//Russ. J. Inorg. Chem. 23(8). (1978).

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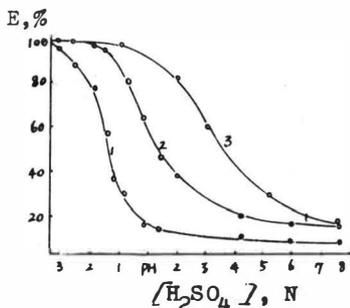
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Mono-2-hexyloctyl phosphoric acid M_2HOPA was made in Shang Hai Institute of Organic chemistry. The study on the extraction of indium with M_2HOPA has been reported at home and abroad. In order to study the effect of difference in chemical structure of a kind of acidic phosphoric acid extractant on extraction behavior of indium, in our paper we have investigated the factors of acidity, concentration of extractant etc, effect on extraction of indium with M_2HOPA , compared with (2-ethyl hexyl) phosphoric acid $[HDEHP]$ and 2-ethyl hexyl phosphoric acid mono (2-ethyl hexyl) ester $[HEH(EH)P]$. The extraction equilibrium reaction can be confirmed by slope method; extraction of Indium was made by saturation method; IR, NMR spectrum were received the mechanism of Indium extraction with M_2HOPA was studied.

At the same time, we studied the questions of M_2HOPA extraction of indium to separate it from accompanying rare metals.

1. Effect of the acidity extractant concentration on the extraction.

The extract behavior of Indium with M_2HOPA , HDEHP and HEH(EH)P in different acidity is shown in the Figure.



Relationship between hydrochloric acid concentration and extraction percentage

aqueous phase: $[In^{3+}] = 0.01M$

organic phase: 1-0.1M HEH(EH)P,

kerosene; 2-0.1M HDEHP, kerosene;

3-0.1M M_2HOPA kerosene

On the basis of the Figure, it is shown that the extraction percentage decreases with increasing acidity, the extractability of indium was found to decrease in the order: $M_2HOPA > HDEHP > HEH(EH)P$. It can be explained by two aspects that the acidic group and substitute radical of the extractant effect its acid nature. So we established that the extraction was carried in acidity lower than 0.5N, the back-extract in higher acidity extent. For back-extraction of indium we used 12N H_2SO_4 +just the right amount of TBP one-two times, or 1N HCl+just the right amount of TBP one time, and back-extraction was carried completely. After the extractant TBP was used three times, its decreasing percentage was 0.2%. HDEHP was back-extracted by 6M HCl, HEH(EH)P by 2-3N H_2SO_4 two times to back-extract completely. The acidic nature of M_2HOPA was higher therefore the extractability increased, the back-extraction was not easy.

In the same acidity extent, the extraction percentage of Indium increases as the extractant concentration increases. The extractant concentration of 0.1M was fit for our experiment.

II. Separation of In and rare metals with accompanying elements.

The extraction properties of M_2HOPA to commonly countered elements have been measured at different acidities. It resulted that Zn(II), Cu(II), Co(II), Ni(II), Cd(II), Ge(IV) as well as alkali and alkaline earth metals were not extracted except In(III), Ga(III), TI(III) and Fe(III) at extractive conditions. So before extraction making Fe(III) being reduced primarily, and if suitable back extraction agents were chosen in back extraction stage, for example, Ga was back-extracted using 1N $H_2C_2O_4$ at first, and owing to In and TI not being back-extracted Ga was separated. In organic phase In that was back-extracted by using 12N H_2SO_4 or 1N HCl+TBP (back-extraction percentage 99.5%) was parted from TI. The last of TI was back-extracted one time using 2N NaCl from organic phase.

III. Determination of the constitution of the extract complexes and the mechanisms

1. Slope ratio method

The molecular weight that was measured using VPO method at different concentration of M_2HOPA in n-hexane indicated that 0.1M M_2HOPA existed as hexamer mainly in n-hexane solvent and expression was $(H_2A)_6$. It was obtained that the line slope come close to 3 by slope ratio method experiment and calculation. So the equilibrium equation of M_2HOPA extracting In was: $In^{3+} + (H_2A)_6(o) = In(HA)_3 \cdot 3H_2A + 3H^+$. The composition of the extract complex was $In(HA)_3 \cdot 3H_2A$.

2. Saturated method and equimolar series method

The experiments indicated that the molar number ratio of M_2HOPA with In^{3+} was 3:1 in saturant organic phase. So the composition of saturant extract complex was $In(HA)_3 \cdot 3H_2A$.

3. IR and NMR ($^{31}P_{15}$ and 1H_1)

To study bonding properties of In complex its IR and NMR were measured. The IR spectrum of the extraction agent at $3500-2400\text{ cm}^{-1}$ and 1660 cm^{-1} showed strong and wide stretching and bending vibration band of P-OH bonding and it indicated that the molecule formed sexamer by hydrogen bond association. Moreover the strength of the P-OH bonding absorption band of the saturant extract complex reduced remarkably and 1660 cm^{-1} absorption peak disappeared. Separately, the characteristic peak of the P=O bond at 1180 cm^{-1} moves about 25 cm^{-1} downwards and the characteristic peak of the P-O-C bond at 1030 cm^{-1} moves 15 cm^{-1} upwards. It indicated that the H of P-OH in M_2HOPA polymer was substituted by In ion and coordination reaction of H with P=O took place and the vicinal P-O-C bond was affected by these factors.

In $^{31}P_{15}$ spectrum δ value of extract agent P nucleus moves from 1.2 ppm to 3.4 ppm of the extract complex. It indicated that the electron density of the P=O bond in extract complex went up and the shielding effect strengthened because of the intension of giving electron function after In being coordinated. So the resonance peak moved high field and value reduced. This represented that coordination function of In with P=O bond took place. 1H_1 spectra data were consonant with the results of IR and $^{31}P_{15}$ spectrum.

All results as said above indicated that M_2HOPA existed as sexamer form mainly in n-hexane solvent. H of P-OH bond in extract agent was replaced by In^{3+} and coordinated with P=O bond and was extracted to organic phase. The composition of forming saturant extract complex was $In(HA)_3 \cdot 3H_2A$. The H of three molecular P=OH bond in the sexamer molecule of M_2HOPA exchanged with In^{3+} and coordinated with P=O bond, and other three molecules existed in the extract complex as inter associate.

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The extractions from sodium hydroxide solutions of aluminium (III) by 7-(5, 5, 7, 7-tetramethyl-1-octen-3-yl)-8-hydroxyquinoline (Kelex 100) in kerosene and of vanadium(V) by trioctylmethylammonium compounds ($R_3R'NCl$ and $R_3R'NOH$) in benzene have been examined under different conditions.

Introduction

The present authors have reported the results for the extraction from sodium hydroxide solutions of zinc (II) [1,2], lead(II) [1,2], gallium(III) [1-6] and aluminium(III) [5,6] by 7-(5, 5, 7, 7-tetramethyl-1-octen-3-yl)-8-hydroxyquinoline (Kelex 100, HQ) and of chromium(VI) [7,8], molybdenum (VI) [8] and tungsten(VI) [8] by long-chain alkyl quaternary ammonium compounds. Consequently it is suggested that the metals in alkaline solutions as the species $M(OH)_n^{m-}$ are extracted by the former extractant and as the species Mo_n^{m-} by the latter one. Therefore this paper extends the work to investigate the extractions from aqueous sodium hydroxide solutions of aluminium(III) by Kelex 100 and of vanadium (V) by trioctylmethylammonium compounds in order to obtain further information on the separation of those metals by solvent extraction.

Experimental

Reagents. Aqueous solutions of aluminium [8] and vanadium were prepared by dissolving aluminium (99.85 %) and sodium metavanadate ($NaVO_3$) in sodium hydroxide solutions of selected concentrations, respectively, and generally the metal concentrations were 0.01 mol·dm⁻³ for aluminium(III) and 0.005 mol·dm⁻³ for vanadium(V).

Kelex 100 (Schering AG), purified by twice distillations at 147-159°C under 0.25 mm Hg and at 159-161°C under 0.36 mm Hg [2], was diluted with kerosene. Trioctylmethylammonium chloride ($R_3R'NCl$, TOMAC, Koei Chemical Co., Ltd.) of high purity was used without further purification and diluted with benzene. A stock solution of trioctylmethylammonium hydroxide ($R_3R'NOH$) was prepared as follows: 0.05 mol·dm⁻³ TOMAC in benzene was shaken with 2 mol·dm⁻³ sodium hydroxide; the procedure was repeated five times. Other chemicals used were of analytical reagent grade.

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Equal volumes (15 cm^3 each) of organic and aqueous phases, placed in 50 cm^3 centrifugal glass tube, were shaken with a mechanical shaker at 340 rpm for a required time at constant temperatures (24h at 30°C for Al(III); 5 min at 20°C for V(V)), except for the experiments on temperature effect. Frequency of the shaker was determined in order to avoid diffusion control of the rate. Preliminarily experiments showed that equilibration was complete in 24h for aluminium and 5 min for vanadium. After the mixture was quickly separated by centrifuge, the concentration of metal in both phases was assayed: aluminium and vanadium in the organic phases were stripped many times repeatedly with $2 \text{ mol}\cdot\text{dm}^{-3}$ HCl on addition of 2-ethylhexyl alcohol and $1 \text{ mol}\cdot\text{dm}^{-3}$ HCl, respectively; the concentrations of both metals in the aqueous solutions were determined by EDTA titration using Xylenol Orange (XO) as indicator [9]. The concentration of sodium extracted into organic phase was measured by atomic absorption spectrophotometry using Hitachi Ltd., Model 170-50-A after stripping it into aqueous phase with $2 \text{ mol}\cdot\text{dm}^{-3}$ HCl or $2 \text{ mol}\cdot\text{dm}^{-3}$ HNO_3 . The concentration of chloride and the water content in the organic phase were examined by Volhard's and Karl-Fisher's methods. The distribution coefficients, E_a^0 , were calculated with the data at equilibria as the ratio of metal concentration in organic phase to that in aqueous phase.

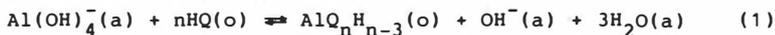
Infrared and Raman spectrophotometries. The infrared spectra of the organic extracts prepared by evaporation in vacuo of solvents (n-hexane for aluminium extraction; benzene for vanadium one) used as diluent were measured on Japan Spectroscopic Co., Ltd. grating models IRA-1 ($4000\text{--}650 \text{ cm}^{-1}$) and IR-F ($700\text{--}200 \text{ cm}^{-1}$) using a capillary film between thallium halide plates or polyethylene films. The Raman spectra of the organic extracts were measured on a JASCO Laser Raman Spectrophotometer Model R-300 using a source of Ar-laser.

Results and discussion

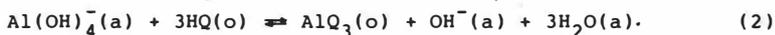
Extraction of aluminium(III) by Kelex 100. The extraction of aluminium(III) from sodium hydroxide solutions by Kelex 100 in kerosene at 30°C was examined in comparison with the extraction from mixed solutions of sodium hydroxide and sodium perchlorate with $0.025 \text{ mol}\cdot\text{dm}^{-3}$ in kerosene. The distribution coefficient decreases with increasing the concentration of sodium hydroxide solution, and is not affected when a part of sodium hydroxide is replaced by sodium perchlorate, indicating that the extraction of aluminium proceeds through ion exchange in which hydroxide ion is liberated.

The log-log plots of E_a^o vs [NaOH] at the constant concentrations of Kelex 100 in kerosene give straight lines with slopes of -0.55, -0.62, -0.72 and -0.83 for 0.025, 0.05, 0.1 and 0.2 mol·dm⁻³ Kelex 100, respectively. However, as it is observed that at a constant total sodium concentration the distribution coefficient is inversely proportional to the hydroxide concentration, those slopes are expected to approach unity, taking the mean activity of sodium hydroxide in aqueous solution into consideration. Further the Raman spectra of aqueous solutions of aluminium(III) in sodium hydroxide exhibit the absorption at 621 cm⁻¹, suggesting that the species of aluminium(III) exists in a point group of Td as Al(OH)₄⁻ [10].

Since Kelex 100 exists as HQ at sodium concentration below 6 mol·dm⁻³ [2], it is presumed that the extraction of aluminium(III) from sodium hydroxide solutions by Kelex 100 proceeds by the following cation-exchange reaction



in which (a) and (o) denote the aqueous and organic phases, respectively. The Log-log plots of E_a^o vs [Kelex 100] give straight lines with a slope of 3. Accordingly, it can be inferred that n=3 and extraction equilibrium can be formulated as



This is supported by continuous variation experiments: in the continuous variation of aluminium concentration in the organic phase as a function of initial concentration of Kelex 100, using fixed total concentrations of initial aluminium and Kelex 100 of 0.05 mol·dm⁻³ each at a constant concentration of sodium hydroxide in 0.6 or 6 mol·dm⁻³ at 30°C, the organic aluminium concentration exhibits a maximum at a mole fraction of 0.75([HQ]_{init} = 3[Al]_{init aq}). In the extraction of aluminium with 0.05 mol·dm⁻³ Kelex 100 in kerosene at a constant concentration of sodium hydroxide in 6 mol·dm⁻³, the loading test of aluminium to the organic phase suggests that the molar ratio [Al] : [Kelex 100] : [Na] : [H₂O] in the organic phase approaches a limiting value of 1 : 3 : 0 : 0 with increasing initial concentration of aluminium in the aqueous phase, consistent with the formation of the species AlQ₃, although the organic phase is not yet saturated by aluminium loading even at the initial aqueous aluminium concentration in 1 mol·dm⁻³. The formation of the species AlQ₃ is also confirmed by infrared spectral result of the organic extracts: the Al-O and Al-O stretching bands appear at 665 and 360 cm⁻¹, respectively; the C=N and C-O stretching absorptions which appear at 1580 and 1405 cm⁻¹, respectively, for free extractant shift to lower frequencies; the OH stretching and bending bands at 3360 and 1280 cm⁻¹, respectively, decrease in in-

tensities in comparison with those for free extractant. From this it is considered that the species formed in the organic phase possesses the structure in which oxine group coordinates to aluminium through oxygen and nitrogen.

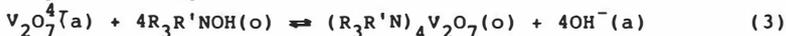
Extraction of vanadium(V) by TOMAC. In the extraction of vanadium (V) from sodium hydroxide solutions by TOMAC in benzene at 20°C, the distribution coefficient decreases with increasing the hydroxide ion concentration in aqueous phase and then its decrease becomes gently at $[\text{NaOH}] > 3 \text{ mol}\cdot\text{dm}^{-3}$. In the extraction by TOMAC, however, from the variation of chloride concentration in the organic phase the formation of the species $\text{R}_3\text{R}'\text{NOH}$ cannot be neglected during the extraction process, although the chloride form is more stable than the hydroxide one as expected from the energies of hydration of chloride and hydroxide ions [11].

On the one hand, the distribution isotherm of vanadium by $\text{R}_3\text{R}'\text{NOH}$ in benzene reveals an enhancement of the extraction of vanadium by $\text{R}_3\text{R}'\text{NOH}$ in comparison with that by $\text{R}_3\text{R}'\text{NCl}$, corresponding to the order of substitution of anion [12]. In the extraction of vanadium(V) at $[\text{NaOH}] < 6 \text{ mol}\cdot\text{dm}^{-3}$, the dependence of distribution coefficient on sodium hydroxide concentration indicates a typical extraction behaviour through anion-exchange reaction which shows the monotonous decrease in the distribution coefficient with increasing the concentration of hydroxide ion in aqueous phase. In contrast, a slight increase of the distribution coefficient is observed at higher sodium hydroxide concentrations, but this anomalous rise does not occur in the extraction from potassium hydroxide solutions. In addition, when the extractions from aqueous vanadium (V) solutions ranging from 0.001 to 0.02 $\text{mol}\cdot\text{dm}^{-3}$ at the concentration of sodium hydroxide in 10 $\text{mol}\cdot\text{dm}^{-1}$ are carried with 0.05 $\text{mol}\cdot\text{dm}^{-3}$ $\text{R}_3\text{R}'\text{NOH}$ in benzene 20°C, only a little amount of sodium ($5.5\text{--}7.0 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$) is extracted into the organic solution. As the organic vanadium concentration increases from 2.17×10^{-4} to $8.97 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, the molar ratio of the concentration of sodium to that of vanadium in the organic phase decreases with increasing the concentration of vanadium(V) extracted. This means that sodium ion is not a constituent of the species formed in the extraction from aqueous solutions of sodium hydroxide above $6 \text{ mol}\cdot\text{dm}^{-3}$. These facts, however, suggest that the sodium cation in aqueous phase affects the chemical potential of vanadium ion in aqueous phase, and accordingly that the existence of vanadium(V) in potassium hydroxide solutions is more stable than that in sodium hydroxide ones.

Furthermore three times repeated extractions of vanadium(V) from fresh aqueous solutions containing $0.005 \text{ mol}\cdot\text{dm}^{-3}$ sodium

metavanadate with $0.01 \text{ mol}\cdot\text{dm}^{-3}$ $\text{R}_3\text{R}'\text{NOH}$ at a constant sodium hydroxide concentration in $0.2 \text{ mol}\cdot\text{dm}^{-3}$ give the limiting molar ratio $[\text{R}_3\text{R}'\text{N}]/[\text{V}]$ in the organic phase of two. Additionally the infrared spectral data of the metal-saturated organic extracts exhibit the V-O stretching band at 930, 860, 815 and 780 cm^{-1} , the V-O bending band at 335 cm^{-1} and V-O-V stretching absorption at 640 cm^{-1} . According to Newman et al [13], the species of vanadium in sodium hydroxide solutions exists as VO_3^- , VO_3^{3-} and $\text{V}_2\text{O}_7^{4-}$. However, since the infrared results suggest the presence of the extracted organic species $\text{V}_2\text{O}_7^{4-}$, it is deduced from the loading test that the species $(\text{R}_3\text{R}'\text{N})_4\text{V}_2\text{O}_7$ is formed in the extraction of vanadium(V) from sodium hydroxide solutions by $\text{R}_3\text{R}'\text{NOH}$.

Hence it is postulated that vanadium(V) is extracted into the organic phase through the reaction



In contrast, for the extraction of vanadium from aqueous alkaline solutions by tetraoctylammonium chloride, Ivanov et al [14] have reported that the species $\text{H}_4\text{V}_{10}\text{O}_{28}^{4-}$, $\text{V}_3\text{O}_9^{3-}$ and $\text{V}_2\text{O}_7^{4-}$ are extracted at pH 1 - 8.5, 8.5 - 10 and 10, respectively.

Effect of anion on quaternary ammonium salts. When the extraction of vanadium(V) from aqueous solutions containing $0.005 \text{ mol dm}^{-3}$ sodium metavanadate in 0.2 mol dm^{-3} trioctylmethylammonium salts, replaced by anions such as NO_3^- , SCN_4^- , HSO_4^- and ClO_4^- , in benzene at 20°C , it is seen that the extraction efficiency of quaternary ammonium compounds for vanadium(VI) is the order $\text{OH}^- > \text{Cl}^- > \text{HSO}_4^- > \text{NO}_3^- > \text{ClO}_4^- > \text{SCN}^-$, corresponding to dimension of equilibrium constant [17].

Temperature effect. The extractions from aqueous solutions containing sodium aluminate in $1 \text{ mol}\cdot\text{dm}^{-3}$ sodium hydroxide of aluminium(III) with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ Kelex 100 in kerosene and sodium metavanadate in $0.5 \text{ mol}\cdot\text{dm}^{-3}$ sodium hydroxide of vanadium(V) with $0.05 \text{ mol}\cdot\text{dm}^{-3}$ $\text{R}_3\text{R}'\text{NOH}$ in benzene were carried out at temperatures between 10 and 40°C . These gave the results that the distribution coefficients decrease with rising temperature in both extraction systems. Thus the values of heat of reactions (change in enthalpy, $-\Delta H$) in Eqns. (2) and (3) are estimated as 43.4 and 44.1 KJ mol^{-1} for aluminium(III) and vanadium(V), respectively.

Extraction rate. As the extraction of aluminium(III) from sodium hydroxide solutions by Kelex 100 is relative slow to attain to the equilibrium state, a kinetic investigation is carried out under non-equilibrium conditions in order to elucidate the mechanism of

reaction in this extraction system. As the result, it is presumed that for the extraction of aluminium(III) from sodium hydroxide solutions by Kelex 100 in kerosene the slow rate is mainly attributable to the formation of action of activated species such as $\text{Na}^+[\text{Al}(\text{OH})_3]$, OH^- and $\text{Na}^+\cdot\text{Na}^+[\text{Al}(\text{OH})_3]$.

Acknowledgement

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References

1. Sato T., Nakamura T., Oishi H.//Proc, Int. Solvent Extr. Conf. ISEC'83. Denver, 1983. P.274.
2. Sato T., Nakamura T., Oishi H.//Solvent Extr. Ion Exch. 1984. Vol.2. P.45.
3. Sato T., Nakamura T., Yabuta M., Oishi H.//Chem. Lett. 1982. P.591.
4. Sato T., Oishi H.//Hydrometallurgy.1986. Vol.16. P.315.
5. Sato T.//Chemical Separations, 1 st Int. Conf. Separations Sci. Technol., Ed. King. C. J., Navratil J. D., Litarvan Literature, Denver, 1986. Vol.1. P.285.
6. Sato T.//J. Jpn. Inst. Light Met. 1986. Vol.36. P.137.
7. Sato T., Nakamura T., Takeuchi Y.//Solvent Extr. Ion. Exch. 1984. Vol.2. P.1033.
8. Sato T., Takeuchi Y., Sato K.//Proc. Int. Solvent Extr. Conf. ISEC'86. Munich, 1986. P.153.
9. Kinnunen J., Wennerstrand B.//Chemist-Analyst 1957. Vol.46. P.92.
10. Lippincott E.R., Psellos J. A., Tobium M.C.//J. Chem. Phys. 1952. Vol.20. P.536.
11. Schmidt V.S., Rubakov K.A.//Zh. Neorg. Khim. 1981. Vol.26. P.723.
12. Vandegrift G.F., Lewry S.M., Dyrkaca G.R., Horwitz E.P.//J. Inorg. Nucl. Chem. 1980. Vol.42. P.127.
13. Newman L., Lafleuer W., Brausides F., Ross A.//J. Amer. Chem. Soc. 1958. Vol.80. P.4491.
14. Ivanov I.M., Grimbati N.I., Girden L.M., Fisher K., Paul P.//Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk. 1977. P.52

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One of the problems of acidic processing of the aluminium containing raw material is the purification of solutions from iron which passes into the solution with aluminium during the process of leaching.

The effective extraction separation of iron (III) and aluminium is possible in the systems with monocarboxylic acids, α -ramified acids (VIC) having some advantages in comparison with the acids with normal structure. In the VIC systems coefficients of separation and solubility of forming of carboxylates of iron in the organic phase are relatively higher

Fig.1 shows the results obtained in extracting of iron from the solutions of nitrate, chloride and aluminium sulphate. As one can see in the Figure the extraction considerably depends on the nature of anion of aluminium salt. The decrease of the distribution coefficients of nitrate solutions to chloride and sulphate solutions and the corresponding shift of the dependences $\lg D_{Fe}$ on pH corresponds to the increase of the constants of complexation of iron (III) in aqueous solutions in the anion series $NO_3^- < Cl^- < SO_4^{2-}$. At the same period the separation coefficients of iron and aluminium diminish, which can be explained by the lesser influence of complexation on the aluminium extraction because of lesser stability of the corresponding complexes. For the nitrate solutions the separation coefficient of iron and aluminium amounts $\sim 3 \cdot 10^5$, for chloride $\sim 7 \cdot 10^3$, for sulphate $\sim 2 \cdot 10^3$. The comparison of the data, obtained in the process of iron extraction from $FeCl_3$ solution of 0,12M (curve 3) and in the presence of 2M $AlCl_3$ (2) shows that the aluminium salt contributes to the considerable growth of the distribution coefficients of iron in spite of considerable increase of the concentration of chloride-ion and increase of complexation Fe in aqueous solution. Probably, in this case the predominant influence is caused by the increase of the activity coefficient of cation Fe owing to the lowering of water activity in adding greatly hydrated aluminium salts (salting out action). The considerable shift of dependences $\lg D_{Fe}$ on pH to the lesser pH when extracting from aluminium solutions, and also the development of the leaching conditions under which the solution practically doesn't contain the excess of mineral acid creates the conditions for the effec-

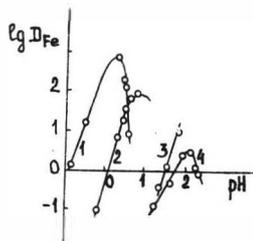


Fig. 1. Extraction of iron by 2 M solution of α, α -dialkylmonocarboxylic acids (C_9-C_{19}) in decane from nitrate (1), chloride (2) and sulphate (4) solutions, containing 2g-ion/l Al, 0.12 g-ion/l Fe; 3- chloride solution without aluminium

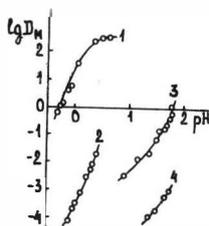
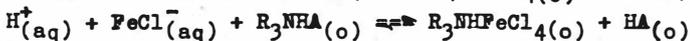
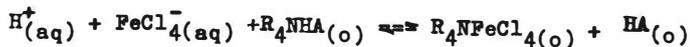


Fig. 2. Extraction of iron (1, 3) and aluminium (2,4) by VIC of the fraction C_5-C_9 at temperature $80^\circ C$ from nitrate (1, 2) and sulphate (3,4) solutions (2.0g-ion/l Al; 0.16g-ion/l Fe)

tive purification from iron by monocarboxylic acids without adding alkali into the system. The usage of monocarboxylic acids without any diluents allows to extract at high temperature ($40-80^\circ C$) without coloring leaching solutions. When the extracting with VIC fraction C_5-C_9 (Fig. 2) under these conditions the value of the separation coefficients Fe-Al practically doesn't change, and the phases decompose considerably better. Verification of purifying solutions of leaching sinter of nephelin sienits from iron by extraction was successful. The special interest represents the hydrochloric-acid way of processing of aluminium containing raw material in connection with heightened reactional ability of alumina which is got according to this method. For the purification of chloride solutions from iron it is advisable to use binary extractants - the salts of organic acids and amines (or the quaternary bases).

The study of extraction power of binary extractants of different composition (on the base of monocarboxylic acids of normal and α -ramified structure and also alkylphenols of different structure) showed that these extractants efficiently extract iron from chloride aluminium solutions in accordance with the reactions:



The distribution coefficients D_{Fe} ranged from 60 to 300 (see the table)

When studying the stripping of Fe from the organic phase by the water it was indicated, that in the systems with binary extractants the stripping considerably improves and the distribution coefficients decrease when using trialkylamine salts ($R=C_7-C_9$) in comparison with quaternary ammonium salts (Fig. 3,4), when using alkylphenolates of va-

Extraction of iron by 0,3M solutions of organic salts of trialkylamine from chloride solution

54g/l Al, 3.5g/l,Fe, pH 0,18,0:Aq= 1:1

Amine salt	$C_{Fe(aq)}$ g/l	$C_{Fe(o)}$ g/l	D_{Fe}	pH eq.
Chloride	<0.01	3.44	>340	0.29
α -monocarboxylate	<0.01	3.55	>340	0.31
Caprylate	<0.01	3.41	>340	0.29
α -monocarboxylate ^x	0.0116	3.33	287	0.27
2,6-di-tret.butylphenolate	<0.01	3.43	>340	0,27
4-tret.butylphenolate	0.0572	3.39	59,2	0.28
4-isooctylphenolate	0.057	5.7	132	-
2-cumylphenolate	0.0124	3.45	287	0.29

^xthe solution in VIC

rious structure as binary extractants in comparison with carboxylates (Fig.4) and also when adding of the excess of monocarboxylic acid or alkylphenol (Fig.4,5). The stripping in the systems with binary extractants on the base of p-alkylphenol is more effective in comparison with sterically hindered ortho-substituted phenolates. Owing to the great stability of the amine salt R_3NHA in systems with binary ext-

tractants, more concentrated reextracts in comparison with amines were obtained. When using the monocarboxylic acids as the solvent the extraction can be held at high temperature. In this case the energetic expenditures are decreased, the cooling of the solutions after the leaching doesn't need. The extraction isotherms of Fe under the optimal conditions are shown in Fig.6. For the purification of solutions from 12 g/l to 0,01 g/l Fe it is quite enough 2 stages of the extraction.

On the basis of the carried out researches two variants of technological schemes of extraction purification of aluminium solutions from

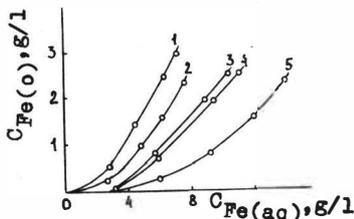


Fig.3. Stripping of Fe in the systems with 0.3M trialkylbenzylammonium chloride (1) and binary extractants: 2,6-tret.butylphenolate (2), α -monoalkylcarboxylate (3), caprylate (4), 4-tret.butylphenolate (5) in gasoline

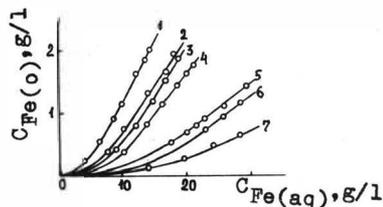


Fig.4. Stripping of Fe in the systems with 0.3M trialkylamine (1) and binary extractants: 2,6-tret.butylphenolate (2), α -monoalkylcarboxylate (3), caprylate (4), p-cumylphenolate (5), 4-tret.butylphenolate (7) in gasoline, α -monoalkylcarboxylate in the VIC (6)

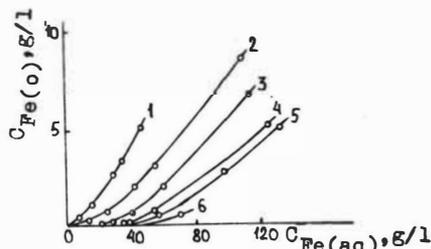


Fig. 5. Stripping of Fe in the systems with 0.3M trialkylamine (1) in gasoline, with trialkylamine phenolate (2), in presence of excess 4-octylphenol: 0.3M(3), 0.5M (4), 0.6M (5), 1.2M (6)

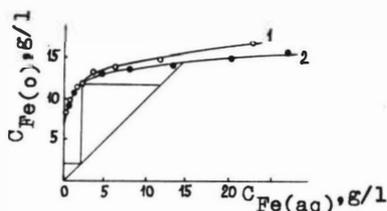


Fig. 6. Extraction isotherms of Fe by 0.3M solutions of L-monoalkylcarboxylate TAA in VIC, $t=80^{\circ}C$ (1), p-isooctylphenolate TAA in gasoline, $t=25^{\circ}C$ (2). Content of Al - 54g/l, HCl- 40g/l

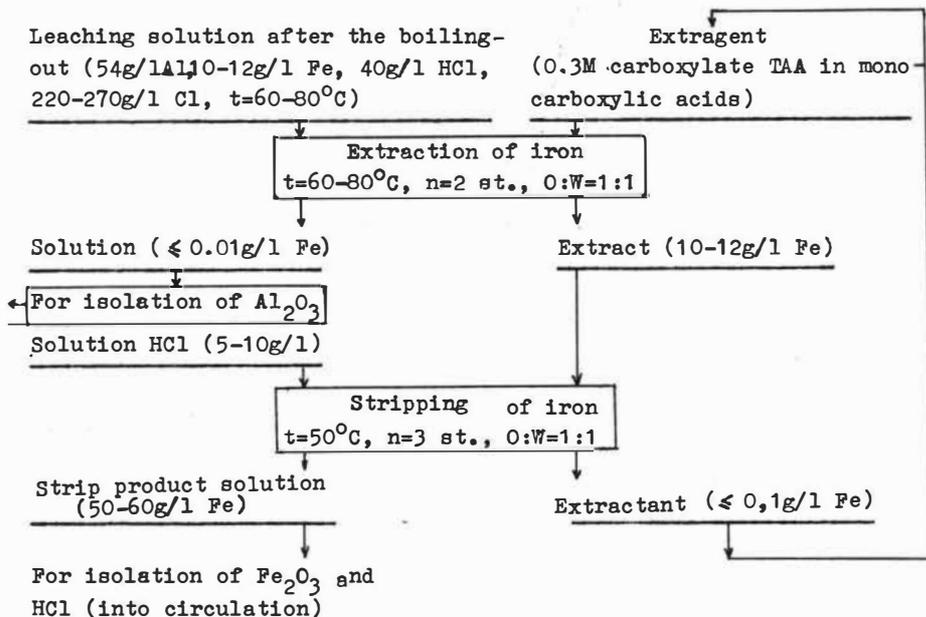


Fig. 7. Principle technological scheme of purification of aluminium chloride solutions from iron by the solution of binary extractant in monocarboxylic acids

iron with the help of binary extractants were worked out. Under low temperature (20-30 °C) as extragent 0.3-0.5 M solution of p-alkylphenolate in gasoline was used, and under high temperature (50-80°C) 0.3-0.5 M solution of trialkylamine in monocarboxylic acids was used.

The technological scheme of iron purification is represented according to the second variant at the Fig. 7.

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The problem of finding alternative raw material sources for aluminium production can be solved by way of waste products of some metal treating processes such as hydrometallurgical treating as well as by way of aluminium-containing wastes reprocessing, e.g. slags and ashes. Solvent extraction is a much promising method for this.

Methods of aluminium extraction from sulfate solutions by alkyl phosphoric acids have been described in some papers (1). Some other authors (2,3) established that aluminium sulfate was not extracted by tri-n-octylamine, TOA from sulfuric solutions, though in the presence of uranium aluminium was extracted in the form of a mixed complex (3). When aluminium is extracted from its sulfate solution in nitric acid with fluoride addition it is only the fluoride complex AlF_6^{3-} that passes into the organic phase.

During the experiments carried out according to a joint program developed by the Mendeleev Institute of Chemical Technology and Prague Institute of Chemical Technology it was established that neither tertiary nor secondary amines extracted aluminium sulfate from aqueous solutions. Primary aromatic amines (paradodecylaniline, alkylanilin, dimethylanilin, benzyaniline) don't extract aluminium from these solutions as well. Long-chain aliphatic primary amines (Primene JMT) behaved well enough as extractants. The use of aliphatic amines with shorter chains resulted in the formation of stable unseparated dispersions, which could be prevented by introducing considerable amounts of octanol (up to 25%).

In connection with the results mentioned above the extraction of aluminium sulfate with Primene JMT was studied in detail.

Sulfate aluminium solutions in water and sulfuric acid were prepared by dissolution of the exact amount of $Al_2(SO_4)_3 \cdot 18 H_2O$. The aluminium concentration was determined by back complexometric titration using 0,01 M solution of plumbous nitrate with xylenol orange as indicator. For determining the water concentration on extracts Fisher method was applied. Primene JMT manufactured by Lachema, Brno was used without any additional purification. Benzene was used as diluent.

The IR-spectra were recorded on Perkin-Elmer 325 midel in the wave length range $400-4000 \text{ cm}^{-1}$ using $AsCl_3$ glasses. The extraction was carried out by shaking test-tubes plugged with ground-in stoppers for 30 min. at room temperature and the phase ratio 1:1.

The effect of water phase acidity. The results of extraction at various sulfuric acid concentrations are given in Table 1. It can be easily seen that the highest concentration of aluminium in extract is obtained when it is extracted from water solution. The addition of excess H_2SO_4 leads to the elimination of aluminium extraction. The same results were observed in the case of extracting ammonium alums from water and acidic solutions. This indicates that the nature of the initial aluminium compound doesn't exercise any appreciable influence on the extraction, the acidity of the aqueous phase being the determining factor.

Table 1. The influence of acidity of aqueous solution on the extraction of aluminium sulfate using 0,24 M solution of Primene JMT
 $[Al]_{initial} = 0,145 \text{ gr-ion/l}$

$[H_2SO_4]_M$	Balanced concentr., g-ion/l	
	$[Al]_{aq}$	$[Al]_{org}$
0*	0.043	0.102
0.5	0.136	0.009
1.0	0.140	0.005
2.0	0.143	0,002

* - Sulfuric acid was not added into solution.

The effect of aluminium and amine concentrations. The data obtained when amine solutions of different concentration (in the form of free base) were brought into contact with aqueous solutions of aluminium sulfate are shown in Fig.1.

The initial aluminium concentration in the aqueous phase is given on the x-coordinate since the equilibrium aqueous concentration in some initial points approaches zero due to the practically complete extraction. In all cases the maxima points correspond to the formation of compounds in the organic phase which contain from 2 to 3 amine moles per one metal mole. The shape of the curves can be accounted for by the following. It is known that aluminium sulfate in aqueous solutions undergoes hydrolysis with formation of complex hydroxosulfates and sulfuric acid. Assuming that the ave-

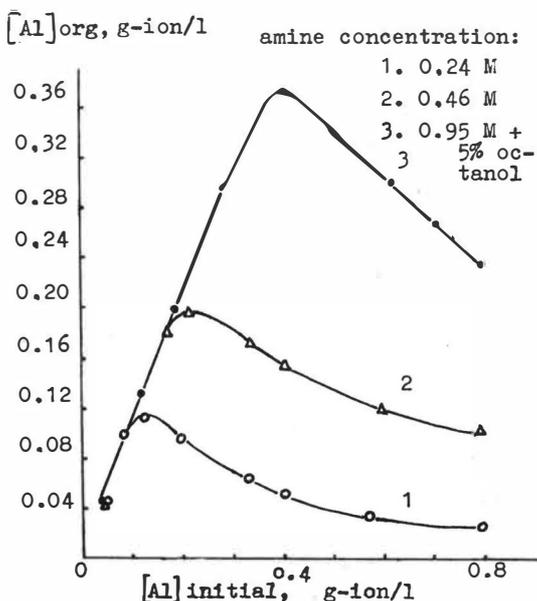


Fig.1. The influence of Al and amine concentration on aluminium sulfate extraction

range extent of hydrolysis remains approximately constant in the studied range of concentration, the amine: aluminium proportion in saturated extracts (approximately 2-3 amine per 1 aluminium) can be accounted for by the fact that the amount of H_2SO_4 yielded as the result of sulfate hydrolysis is sufficient for the complete transfer of the free base into the form of amine sulfate which acts as the extractant. The increase of the sulfate aluminium concentration should result in the appearance of free sulfuric acid in the system which can force out the metal from the organic phase due to competition extraction. Besides the presence of H_2SO_4 excess in the aqueous phase should decrease the extent of aluminium sulfate hydrolysis, which can prevent the extraction of aluminium.

The results of the sulfate aluminium extraction by a free base and amine which was initially brought into contact with H_2SO_4 of various concentrations confirm the assumptions concerning the extraction mechanism. The introduction of H_2SO_4 into the amine sharply reduces the extraction of aluminium (Fig.2). It has to be mentioned that the transfer of the hydrolysis forms of aluminium sulfate into the organic phase is accompanied by coextraction of considerable amounts of water. The water concentration in the organic phase changes equally with the aluminium concentration. No unextracted forms of aluminium sulfate are obtained in the aqueous phase and the extent of aqueous phase exhausting depends only on the number of contacts with the extractant.

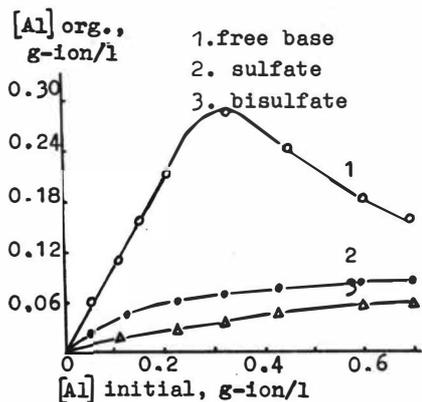


Fig.2. The influence of extractant composition on the extraction of Al; 0.5 M solution of amine

The Effect of the Solution Initial Characteristics. When extracting the elements with the pattern of behaviour complicated by hydrolysis the initial characteristics of the solutions

often play an important role, viz retention time, temperature, the initial compound nature, etc. (in other words all the factors which influence the hydrolysis equilibrium). To this end the initial solutions were subjected to ageing through prolonged retention as well as to heating, crystallizing the saturated aluminium sulfate solutions by means of slow evaporation in vacuum and multicrystallizing at elevated temperatures. As it turned out it was impossible to shift the stable hydrolysis equilibrium in water solutions by means of the above factors. In spite of the fact that the IR-spectra and x-ray phase analysis show-

ed a difference between the reactive aluminium sulfate and the compounds obtained after crystallization in vacuum, we could not find the difference between their solutions - there was no change in aluminium extractability. At the same time our experiments in the Lewis cell showed a difference in the behaviour of fresh and aged solutions and different samples of the reactive sulfate.

In the Lewis cell the extraction of aluminium was first characterized by turbidity of the organic phase, after that a thick interphase film appeared in the interface and crystalline sediment settled in the organic phase. The sediment was dissolved as the kinetic curve was reaching the plateau. The increase of aluminium concentration in the organic phase can be achieved by raising pH of the initial solution up to 3.5-3.6 as a result of introducing an appropriate amount of Na_2CO_3 (Fig.3). It can be seen that the curves are practically similar. The character of the curve for the solution with a higher pH confirms the existence of some range of aluminium sulfate concentration with the mechanism of extraction suggested in this paper.

All the above results were obtained for the amine of technical grade. At the same time it was found that the high boiling fraction formed during vacuum distillation was characterized by a higher ability for extrac-

tion. According to our point of view the difference is associated with the presence of alcohols in the technical amine, which have, as a rule, lower boiling points than amines.

References

1. Cattrall R.W.//Austral.J.Chem. 14 (1).1961. P.163.
2. Coleman C.F.//Proc.II Intern.Conf.on Peaceful Using of Atomic Energy. Geneva, 1958.
3. Medvedeva E., Gromov B.V.//Trans.of Mendeleev Inst.of Chemical Technology. Moscow, 1964. № 47. P.140.
4. Shevchuk J.A., Skripnik N.A.//Ukr.Chem.J.(USSR).1968.V.34,№10. P.1086.

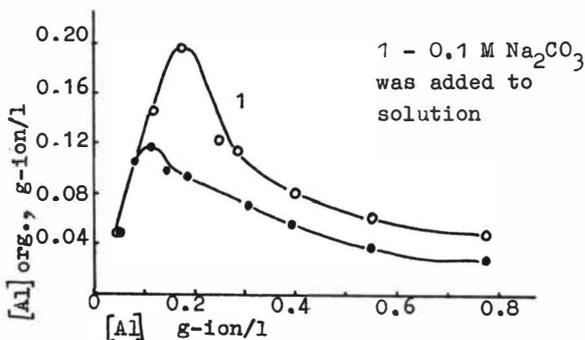


Fig.3. 0.1 M Na_2CO_3 adding influence on aluminium extraction by 0,23 M amine solution

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During processing of some intermediate products of chemical industry and non-ferrous metallurgy acidic solutions containing gallium are formed. Solvent extraction is the effective method of its recovery [1].

The most interesting for the extraction are halogenous complexes of gallium especially $[GaCl_4]^-$ anion, which can effectively be extracted with neutral organophosphorous and anion-exchange extractants [1,2].

Kinetics and mechanism of extraction processes of micro- and macro-quantities of gallium in the systems Ga-HCl-TBP and Ga-HCl-TOA in kerosene (decanol as modifier) taking into account interphase phenomena at work were studied.

Lewis diffusion cell (specific interface (a) equal 0.125 sm^{-1}) was selected as the study technique. The plateau on the graph of the extraction rate dependence R_0 ($\text{mol} \cdot \text{sm}^{-2} \cdot \text{sec}^{-1}$) on stirrer's Reynolds number and linear character of function $R_0=f(a)$ indicates either the presence of microheterogeneity zones and automodel regime of the process, or the fact that the extraction rate is limited by the chemical reaction at work at the interface or by masstransfer with a quick reaction [3]. Extractants concentration increase on the boundary with $4 \text{ mol} \cdot \text{dm}^{-3}$

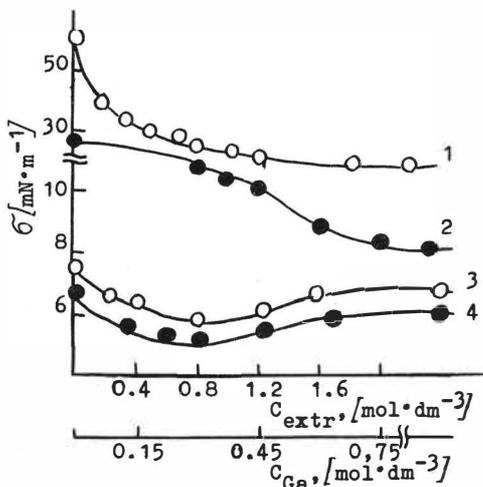


Fig.1. Dependence of σ on the boundary of interface: TBP(1), TOA(2)-HCl on extractant concentration; TBP(3), TOA(4)-HCl-Ga on gallium concentration

solution of HCl (Fig.1) results in marked lowering of interface tension (σ) which evidences about its surface activity conditioned by bifilar character of TBP and TOA molecules. Dependence of σ on metal concentration (C_{Ga}) in aqueous phase has more complex character. Adsorption isotherm calculation (G) according Gibbs equation: $G = -(1/RT)(\partial \sigma / \partial \ln C)$ has showed that in that region of concentration where lowering of σ was observed gallium complexes adsorption on interface was taking place. Further increase of metal concentration in original solutions brings to the increase of interphase tension, that seems to be caused

by the formation of ion associates of gallium complexes[4].

Because of formation of higher surface concentrations of extractant and metal in the systems studied phase status of adsorption layer, orientation character of molecules in it influence on the gallium extraction kinetics[3].

We can get some idea about the contribution of the chemical reaction rate into the overall extraction rate taking account of the change of energy activation (E_A) values. So, in case of TBP, E_A values for micro- ($1.6 \cdot 10^{-3}$) and macroconcentrations ($573 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) of gallium, equal to 30.6 and $34.8 \text{ kJ} \cdot \text{mol}^{-1}$ respectively, can probably be attributed to the decisive role of the chemical reaction rate of the formation of the complex being extracted. In case of TOA with the decrease of metal concentration (E_A values decrease from 23.01 to $16.17 \text{ kJ} \cdot \text{mol}^{-1}$) the contribution of mass transfer rate of the complex forming in the diffuse layer into the overall process rate seems to increase.

Independently from the type of extractant used chemical reactions going in the systems studied are of the first order with respect to gallium. The values of K_s (rate constant of surface chemical reaction of formation of extractable complex) received during transition from micro- ($K_s \cdot 10^{-3} \text{ sm} \cdot \text{sec}^{-1}$ for TBP and TOA respectively 2.50 ± 0.19 and 1.68 ± 0.08) to macroconcentrations (1.86 ± 0.04 and 0.86 ± 0.08) of the extracted metal have a tendency to decrease. This seems to be caused by the formation of larger associates of gallium complexes hindering mass transfer across the interface. S-like character of emulsion stratification curves inherent to the systems with the structural-mechanical properties serves as the convincing evidence. Increase of E_A and entropy values together with metal concentration increase evidences to this. This is connected with the expenditures of additional energy for the activated complex formation. In this case extract electroconductivity increase is observed evidencing that different ionic associates are current-conducting particles apart from single ions[4].

Dependences of process rate on concentration of hydrogen ions and extractant are given on the Fig. 2,3.

The orders of proceeding chemical reactions according to acid for the systems with TBP and TOA at $C_{\text{HCl}} > 2 \text{ mol} \cdot \text{dm}^{-3}$ are equal to unity. Absence of R_0 dependance on C_{HCl} evidences about zero order of reaction according to hydrogen ions, at more lower meanings of HCl concentration in the system with TBP. This is an indication of the gallium extraction mechanism change by TBP connected with the participation of $[\text{GaCl}_4]^-$ or GaCl_3 in the formation of extractable complex. At the same time besides indicated molecules protonated form of extractant consisting from three molecules of TBP is taking part in elemental act of chemical interaction (Fig.3).

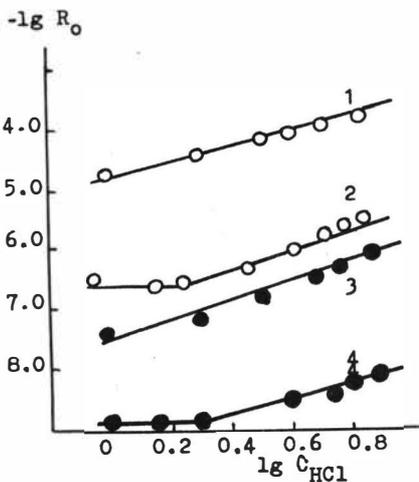


Fig. 2. Effect of HCl concentration on the initial extraction rate: TOA (1,3) and TBP (2,4) when $C_{Ga} \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$:
 ○ -573 and ● -1,6

On extraction with TOA change of the mechanism is observed during transition from micro- to macroconcentrations of gallium about which the orders of extractant equal to 0,5 and 1, respectively, are evidenced. Substitution of diluent for nitrobenzene confirms the results received (Fig.3).

Considering strong tendency of amine salts to association [5] it is possible to suggest that in complex formation reaction are taking part in the case of macroconcentrations of metal dimer molecules of TOA adsorbed on interface and at microconcentrations of metal - monomeric molecule of TOA.

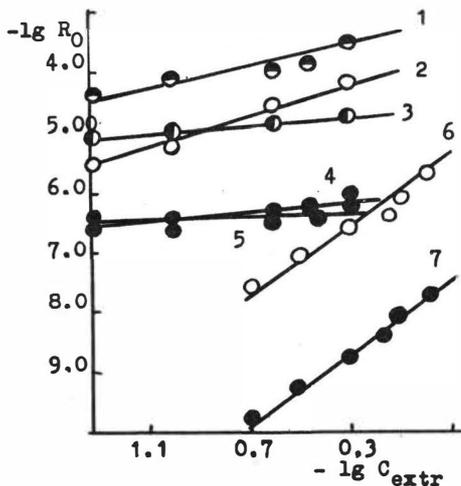


Fig. 3. Effect of extractant concentration on the initial extraction rate: TOA-nitrobenzene (1,4), TOA-kerosene-decanol (2,3,5), TBP (6,7) when $C_{Ga} \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$:
 ● -203; ○ -573; ● -84; ○ -1,6

On the basis of the research done the following suggestions about the step-by-step mechanism of the gallium extraction process from chloride solutions with TBP and TOA were made: adsorption of extractant molecules, oriented by nucleophilic groups to the aqueous phase on interface; formation of the protonated forms of extractants; slow step - formation of the extracted gallium complex on interface; its mass transfer into the organic phase volume. The reaction of the extracted complex formation TOA with gallium microquantities seems to be shifted to the diffusion layer adjoining aqueous phase.

Kinetic equations of gallium extraction process from hydrochloric acid solutions by TBP and TOA can be represented in the following way: for the Ga microconcentrations

$$R_0 = 0.741 e^{-16170/RT} [H^+][GaCl_4^-][R_3N]^{0,5},$$

$$R_0 = 83.07 e^{-30600/RT} [H^+][GaCl_4^-][TBP]^3,$$

for the Ga macroconcentration

$$R_0 = 15.082 e^{-23010/RT} [H^+][GaCl_4^-][R_3N],$$

$$R_0 = 278.5 e^{-34820/RT} [H^+][GaCl_4^-][TBP]^3.$$

From the point of view of practice the extractants studied are characterized by a high selectivity and capacity, and the surface character of processes established gives an opportunity for their intensification.

References

1. Reznik A.M., Ponomareva E.I., Silaev Yu.N., Abisheva Z.S., Bukin V.I. *Protsessy ekstraktsii i sorbtsii v khimicheskoi tekhnologii galliya*. Alma-Ata: Nauka, 1985.
2. Zolotov Yu.A., Ioffa B.Z., Chuchalin L.K. *Ekstraktsiya halogenidnykh kompleksov metallov*. M.: Nauka, 1973.
3. Tarasov V.V., Yagodin G.A., Pichugin A.A. // *Itogi nauki i tekhniki. Neorganicheskaya khimiya*. T.11. Kinetika ekstraktsii neorganicheskikh veshchestv. M.: VINITI, 1984.
4. Fialkov Yu.Ya., Grishchenko V.F. *Elektrovydelenie metallov iz nevodnykh rastvorov*. Kiev: Naukova dumka, 1985.
5. Shmidt V.S. *Ekstraktsiya aminami*. M.: Atomizdat, 1980.

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Primary amine N₁₉₂₃ (R_1CHNH_2 , hereafter referred to as RNH_2) is an excellent extractant for extraction separation of thorium(IV), cerium(IV), rare earth elements(III), and iron(III) [1,2]. The present article is the results on the extraction mechanism of Fe(III) and Al(III) from phosphate solutions by primary amine N₁₉₂₃.

Extraction mechanism of iron(III)

The partition equilibria of Fe(III) between phosphate and RNH_3NO_3 in benzene were investigated. Figure.1 shows the effect of phosphate concentration on Fe(III) extraction by RNH_3NO_3 . The data of Fig.1 determine a straight line having a slope of 2.0, which suggests that the species of $\text{Fe}(\text{PO}_4)_2^{3-}$ in the aqueous solution has been extracted into the organic phase. Figure 2 shows the LogD as a function of the equilibrium concentration of free RNH_3NO_3 in benzene. The slope of the plot of Fig.2 is 1.0. The results on the determination of molecular weight of RNH_3NO_3 in benzene prove that the polymerization degree of RNH_3NO_3 in benzene is 3. Thus, the extraction reaction of Fe(III) in the phosphate system by RNH_3NO_3 could be written as follows:

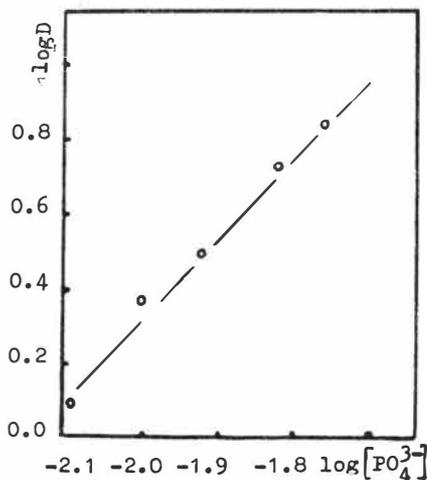


Fig.1. Effect of PO_4^{3-} concentration on Fe(III) extraction by RNH_3NO_3
 organic phase: 0.10M RNH_3NO_3
 aqueous phase: 0.1M HNO_3 ,
 $3.7 \times 10^{-3}\text{M}$ Fe(III)

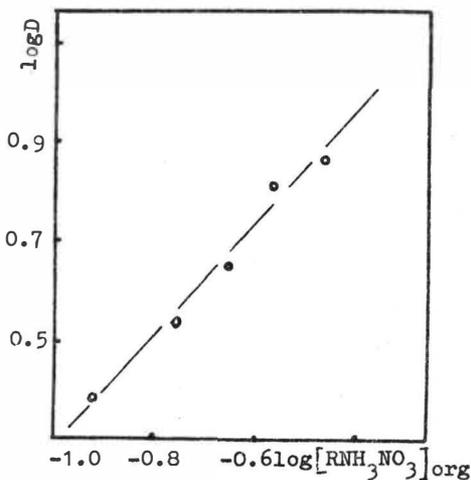


Fig.2. Effect of RNH_3NO_3 concentration on Fe(III) extraction
 aqueous phase: 0.05M HNO_3 ,
 0.24M PO_4^{3-} , $2.9 \times 10^{-3}\text{M}$ Fe(III)

Extraction mechanism of aluminium(III)

The extraction equilibrium data of aluminium(III) from phosphate solutions were obtained by RNH_3NO_3 in heptane as a function of PH, PO_4^{3-} , metal and extractant concentrations. The composition of the extracted complex and extraction mechanism have been determined with the methods of slope, IR and NMR spectra. The relationship between LogD and PH was investigated (see Fig.3). It may be seen from Fig.3 that LogD increases as increasing of aqueous PH. Plots given in Fig.4 represent the relationship between LogD and $\text{Log}[\text{RNH}_3\text{NO}_3]_{\text{org}}$ at different Al(III) concentration. As seen from Fig.4 the slopes of the plot are 1.0. Thus, the extraction reaction of Al(III) in the phosphate system by RNH_3NO_3 can be represented by

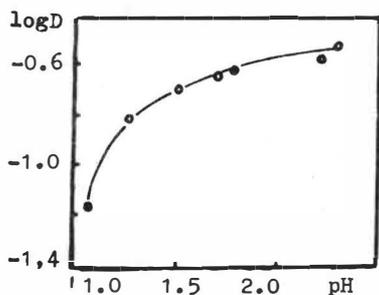
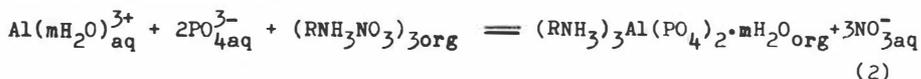


Fig.3. Relationship between LogD and PH
 organic phase: 0.24M RNH_3NO_3
 aqueous phase: 0.021M Al(III),
 0.11M PO_4^{3-}

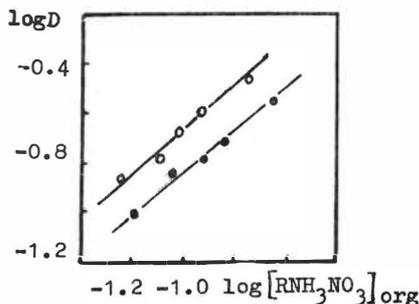


Fig.4. LogD against $\text{Log}[\text{RNH}_3\text{NO}_3]_{\text{org}}$ at different Al(III) concentrations
 O: 0.011M Al(III)
 O: 0.021M Al(III)

The results of IR and NMR spectra show that the extracted complex of Al(III) with phosphate of primary amine is ionized. These data are in satisfactory agreement with the extraction mechanism of Al(III) by RNH_3NO_3 .

References

1. Li Deqian, Ji Enrui, Xu Wen et al.//Chinese Journal of Applied Chemistry. 1987. Vol.4. N 2. P.36.
2. Li Deqian, Wang Zhonghua, Zeng Guangfu //He Huaxue Yu Fangshe Huaxue. 1984. Vol.6. N 3. P.153.

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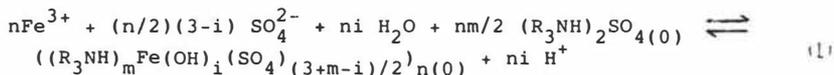
Work have been carried out rather extensively on the removal of Fe(III) in sulfate solutions by extraction with amines as solvent. Primary and secondary amines have often been used while practically no work has been done with tertiary amine as solvent⁽¹⁻⁵⁾. In our work, we have found that tertiary amine can be used to extract Fe(III) very effectively in the pH range resulting partial hydrolysis of ferric ions. In addition, the iron extracted into the organic phase can be stripped rather easily with dilute sulfuric acid or even with water. Mechanism of extraction of Fe(III) by tertiary amine from sulfate solutions is presented in this paper.

The method of saturation capacity was used first to determine the empirical formula of the extraction species. Solutions of 0.1066 M tri-n-octyl amine (TOA) in benzene were used to contact a number of times with fresh ferric sulfate solutions of different pH to saturate the organic phase with iron. The concentrations of Fe(III) and SO_4^{2-} in the organic phase are listed in Table 1. It can be considered that the mole ratios of TOA: Fe(III): SO_4^{2-} are 2:1:2. Based on the aqueous solution chemistry of ferric iron and electric neutrality principle, the extraction species can be represented as $(\text{TOAH})_2 \text{Fe}(\text{OH})(\text{SO}_4)_2$.

Table 1. Experimental results of concentrations of Fe(III) and SO_4^{2-} in the saturated organic phase
 $\sim 15^\circ\text{C}$, 0.1066 M TOA in benzene

pH	1.75	1.91	2.09	2.13	2.48	2.53
Fe(III), M	0.0521	0.0451	0.0462	0.0503	0.0519	0.0473
SO_4^{2-} , M	0.1060	0.1052	0.1021	0.1104	0.1146	0.1063
(TOA)/(Fe)	2.05	2.36	2.31	2.12	2.05	2.25
(TOA)/(SO_4^{2-})	1.01	1.01	1.04	0.97	0.93	1.00
(SO_4^{2-})/(Fe)	2.03	2.33	2.21	2.19	2.21	2.25

With the consideration of hydrolysis, complexes formation and polymerization of Fe(III) in sulfate solution, the extraction of Fe(III) into the organic phase can be expressed as:



* Patent Applied for, China Patent Office.

The equilibrium constant K_{ex} of the above reaction can be expressed

$$K_{ex} = \frac{((R_3NH)_m Fe(OH)_i (SO_4)_{(3+m-i)/2})_n(o) \cdot (H^+)^{ni}}{(Fe^{3+})^n (SO_4^{2-})^{n(3-i)/2} ((R_3NH)_2 SO_4)_{(o)}^{nm/2}} \quad (2)$$

where n = degree of polymerization of iron,

m = number of R_3N molecules associated with Fe^{3+} ,

i = number of OH groups in the extracted species associated with Fe,

o stands for organic phase in subscripts.

The coefficient of distribution of Fe(III) D is defined as:

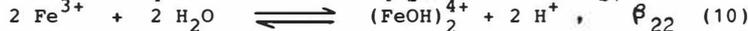
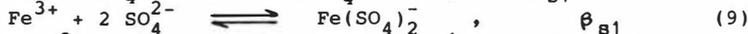
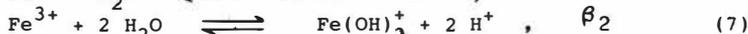
$$D = C_{Fe(III)(o)} / C_{Fe(III)} \quad (3)$$

Assume there is only one extraction species in the organic phase, then:

$$C_{Fe(o)} = n ((R_3NH)_m Fe(OH)_i (SO_4)_{(3+m-i)/2})_n(o) \quad (4)$$

$$C_{Fe} = (Fe^{3+}) (1 + \beta_1 / (H^+) + \beta_2 / (H^+)^2 + \beta_{S1} / (SO_4^{2-}) + \beta_{S2} / (SO_4^{2-})^2 + \beta_{22} / (Fe^{3+})(H^+)^2) \quad (5)$$

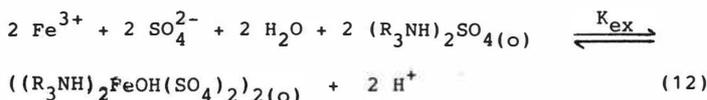
where $\beta_1, \beta_2 \dots$ are equilibrium constants of hydrolysis and complex formation reactions as given below and their values can be found in the literature⁽⁶⁻⁸⁾:



By substituting Equations 3 and 4 into Eq. 2 and taking logarithm, we obtain:

$$\log(C_{Fe(o)}) = \log(D C_{Fe(III)}) = \log(n K_{ex}) + n \log(Fe^{3+}) + (n/2)(3-i) \log(SO_4^{2-}) + ni \text{ pH} + nm/2 \log((R_3NH)_2 SO_4(o)) \quad (11)$$

If equation 1 represents the reaction involved in the extraction of Fe, coefficients n, m and i can be determined by carrying out a series of experiments. Fig. 1 and 2 represent some of the experimental results. From the slopes of the straight lines in these figures, Values of n, m and i are obtained as 1.85, 1.82 and 0.97 respectively. Equation 1 can be written as:



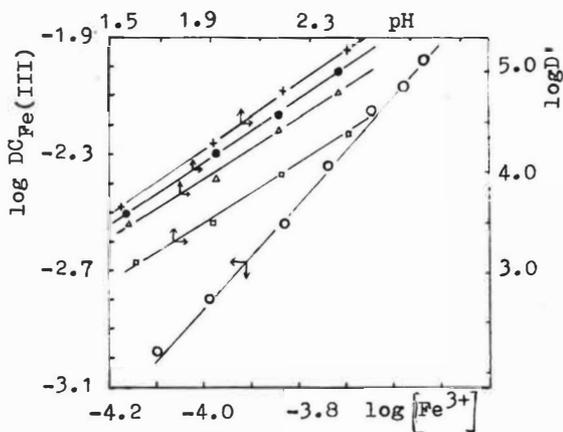


Fig.1. Effect of Fe^{3+} & pH on D_{Fe}

○ pH 2.09, 0.1066 M TOA, 0.25 M SO_4^{2-} , $\sim 18^\circ C$.
 (TOAH) $_2SO_4$: □ 0.032 M
 △ 0.059 M
 ● 0.080 M
 + 0.107 M
 0.25 M SO_4^{2-} , $\sim 13^\circ C$.
 $log D' = \log(DC_{Fe}) - n \cdot \log(Fe^{3+})$

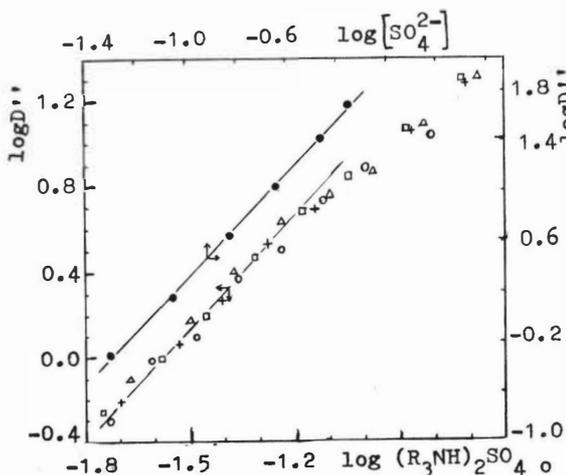
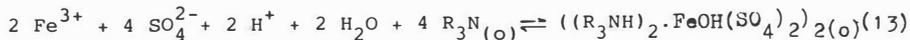


Fig.2. Effect of conc.

of (TOAH) $_2SO_4$ & SO_4^{2-} on D_{Fe}
 0.25 M SO_4^{2-} , $\sim 13^\circ C$.
 pH: △ 1.57, ○ 1.93
 + 2.20, □ 2.44.
 ● 0.1066 M (TOAH) $_2SO_4$
 $\sim 17^\circ C$, $C_{Fe} = 0.02990 M$
 $log D'' = \log(DC_{Fe}) - ni \text{ pH} - n \log(Fe^{3+})$

It can be seen that the composition of extraction species is the same as that obtained by the method of saturated capacity.

Effect of temperature on equilibrium of the following reaction was studied and it was found it is an exothermic reaction.



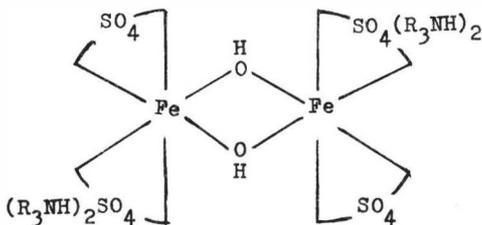
The heat of reaction was found to be -93.4 kJ/mol (pH 1.76), -99.6 kJ/mol (pH 1.13) and -102.1 kJ/mol (pH 1.76) respectively ($10-50^\circ C$).

From the UV spectroscopy, the extracted species has been found to have a strong absorption peak at ~ 295 nm and a broad shoulder type absorption peak at ~ 335 nm. These peaks are consistent with the

reported absorption characteristics of Fe-OH and Fe(OH)₂Fe respectively (3-7). It has also been found that the presence of excess amount of amine sulfate has no influence on the spectroscopy of ferric iron extraction species. Using primary and secondary amines as solvent, the presence of excess amount of amine salt has a strong influence on the spectroscopy of extracted species⁽³⁾. It can be considered that the extraction mechanism of tertiary amine toward Fe is different from that of primary and secondary amines. The tertiary amine can extract the partially hydrolyzed species of Fe³⁺ by adduct formation while the primary and secondary amines can extract both the hydrolyzed species and the unhydrolyzed iron.

As only the hydrolyzed form of ferric iron can be extracted by tertiary amine, the iron extracted into the organic phase can be easily stripped by solution with acidity higher than that required for partial hydrolysis of ferric iron. In contrast, the iron in the organic phase with primary and secondary amines as solvent is very difficult to strip. It was reported⁽³⁾ that when the UV spectra of secondary amine loaded with ferric iron sulfate in the presence of excess amount of amine sulfate was studied, the absorption peak of hydroxy-ferric complexes was disappeared with the appearance of the absorption peak of FeSO₄⁺ and Fe(SO₄)₂⁻⁽³⁾.

The infrared spectroscopy indicated that the sulfate ions are a bidentate ligand to the iron atoms. It also indicated that the species contain bridge forming hydroxyl groups⁽¹⁰⁾. Based on these studies, the structure of the extracture species can be represented as shown in the following figure.



References

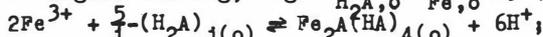
1. Good M.L. et al. Inorg. Chem. 2, 963 (1963).
2. Seeley F.G. et al. // J. Inorg. Nucl. Chem. 43, 375 (1981).
3. Cattrall R.W. et al. // Ibid. 28, 3035 (1966).
4. Cattrall R.W. et al. // Ibid. 32, 663 (1970).
5. Alquacil F.J. et al. // Hydrometallurgy, 15, 337 (1986).
6. Sylva R.N. // Rev. Pure Appl. Chem. 22, 115 (1972).
7. Sylva R.N. et al. // J. Inorg. Nucl. Chem. 37, 779 (1975).
8. Hogfeldt E. Stability Constants of Metal-Ion Complexes, Part A Pergamon Press (1982).
9. Nakamoto K. Infrared & Raman Spectra of Inorganic & Coordination Compounds, 3rd Ed. John Wiley & Sons (1978).
10. Ferraro J.R. et al. // Inorg. Chem. 4, 1382 (1965).

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P538(ROP(O)(OH), R = C₁₂ - C₁₈), behaves a strong extraction ability for iron(III) and has been used to remove iron(III) existing as an impurity in production of H₂O₂. The extraction of iron(III) from nitrate solution with P538 in kerosene has been studied at 25°C in this paper. The experimental results were drawn in Fig.1 and 2. The extraction equilibria are proposed as follows:

1) at higher loading, e.g. C_{H₂A,0}/C_{Fe,0} < 3 (Fig.1):



2) at lower loading, e.g. C_{H₂A,0}/C_{Fe,0} > 3 (Fig.2)



where C_{H₂A,0} and C_{Fe,0} denote total concentration of P538 and Fe(III) in organic phase, respectively.

From these experimental results, the apparent extraction equilibrium constants were calculated to be 10^{11.16} for equilibria 1 and 10^{6.84} for 2, and the apparent polymerization number (j) of extractant (P538) can also be estimated as 1.5-1.7 when its formality is less than 3·10⁻³.

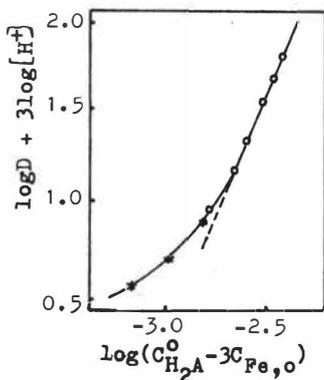


Fig.1. The experimental results at lower loading (C_{H₂A}^o/C_{Fe,0} > 3)

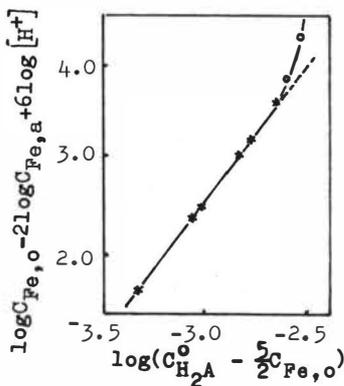


Fig.2. The experimental results at higher loading (C_{H₂A}^o/C_{Fe,0} < 3)

Note: 1.*denotes the experimental points at higher loading

(C_{H₂A}^o/C_{Fe,0} < 3);

2. C_{Fe,a} denotes the total concentration of Fe(III) in equilibrium aqueous phase; C_{H₂A}^o and C_{Fe,0} the total concentration of P538 and Fe(III) in equilibrium organic phase, respectively.

THE STUDY OF EXTRACTION OF Cr(III), Mn(II) AND Fe(III)
IONS WITH ALIPHATIC CARBOXYLIC ACIDS IN SULPHATE SYSTEMS
USING COMPUTER TECHNIQUES

7-47

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The extraction of Cr(III), Mn(II) and Fe(III) with capronic, caprylic and caprynic acids into n-heptane from sulphate solutions has been studied.

On the grounds of the partition data compositions of the complexes of the ions investigated in the organic phase were calculated and the applied calculation methods discussed. It was found that the composition of the complexes of extracted metals is independent of the kind of carboxylic acid and is equal: $(CrR_3 \cdot 2HR)_2$, $(MnR_2 \cdot 2HR)_2$, $(FeR_3)_3$ (Table). It was pointed out that the discrepancies in the interpretation of the results obtained by different authors are often due to different assumptions or disregard of the characteristics of the functions describing the extraction process.

The EKSTRAKTOR computer program in Pascal language was applied to analyse experimental data. The composition of the complexes was determined using a method based on the dependence of $pH_{0.5}$ on phase composition. It was proved that the method can apply to any division coefficient values, i.e. when $D \neq 1$ and $pH \neq pH_{0.5}$. Calculation for same different values of partition coefficients and their corresponding pH values was carried out. The determined composition of the complexes was checked using the KEX-TORT simulation programme in Pascal based on the law of mass action. A new way of collecting experimental data in cation-exchange extraction with carboxylic acids based on the KEX-TORT simulation program was proposed.

Extraction of metals with carboxylic acids in sulphate systems

Metal	Carboxylic acid	Complex	K_{ex}
Mn(II)	n-Hexanoic	$(MnR_2 \cdot 2HR)_2$	$3.18 \cdot 10^{-22}$
	n-Octanoic		$2.54 \cdot 10^{-20}$
	n-Decanoic		$3.43 \cdot 10^{-20}$
Cr(III)	n-Hexanoic	$(CrR_3 \cdot 2HR)_2$	$2.56 \cdot 10^{-18}$
	n-Octanoic		$3.56 \cdot 10^{-16}$
	n-Decanoic		$2.60 \cdot 10^{-15}$
Fe(III)	n-Hexanoic	$(FeR_3)_3$	$2.95 \cdot 10^{-16}$
	n-Octanoic		$2.25 \cdot 10^{-11}$
	n-Decanoic		$1.11 \cdot 10^{-10}$

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The partition equilibria of sodium between chloride or sulfate aqueous solution and P538 (monoalkylphosphoric acid)-kerosine have been investigated by using sodium ion selective electrode. The experimental results (Fig.1 to 4) show that the extraction mechanism of both systems is as follows:

$$\text{Na}^+ + 4(\text{H}_2\text{A})_j(\text{o}) \rightleftharpoons (\text{NaHA} \cdot (4j-1)\text{H}_2\text{A})(\text{o}) + \text{H}^+$$
 and the equilibrium constants determined are $10^{-1.24}$ and $10^{-1.48}$, respectively.

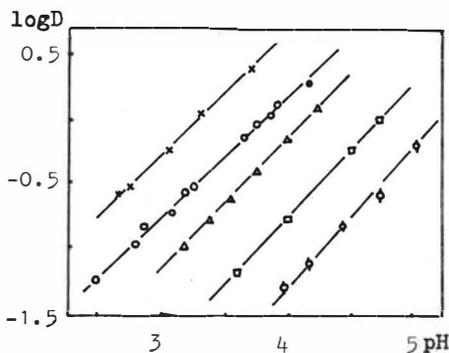


Fig. 1. The curves of D vs. pH in NaCl system

$C_{\text{Cl}^-}^{\circ} = 1.00 \cdot 10^{-2} \text{ M}$; $C_{\text{H}_2\text{A}}^{\circ} (\text{M}) \times 0.316$; \circ 0.218; Δ 0.170; \square 0.127; \diamond 0.0797

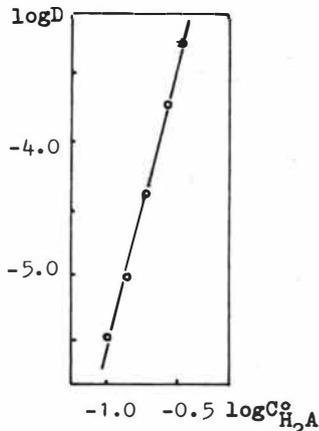


Fig. 2. The curves of D vs. $C_{\text{H}_2\text{A}}^{\circ}$ in NaCl system

$C_{\text{H}_2\text{A}}^{\circ} = 1.00 \cdot 10^{-2}$; $\text{pH } 0^{\circ}$

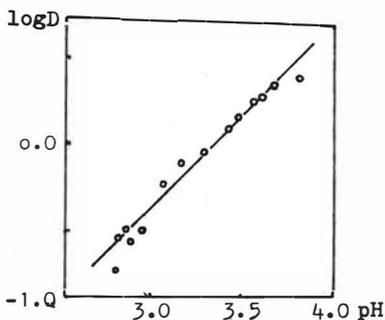


Fig. 3. The curve of D vs. pH in Na_2SO_4 system.

$C_{\text{Na}_2\text{SO}_4}^{\circ} = 5 \cdot 10^{-3} \text{ M}$; $C_{\text{H}_2\text{A}}^{\circ} = 0.316 \text{ M}$

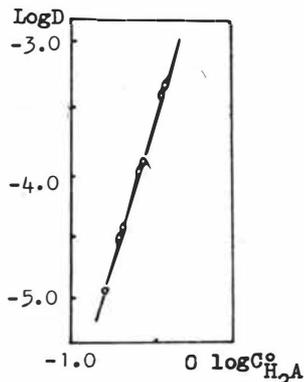


Fig. 4. The curve of D vs. $C_{\text{H}_2\text{A}}^{\circ}$ in Na_2SO_4 system. $C_{\text{Na}_2\text{SO}_4}^{\circ} = 5.00 \cdot 10^{-3}$

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For extractive separation of cations with the same electronic structure and different sizes it is preferable to use of steric effects at forming of extracted compounds. Thus, the phenol derivatives with ortho-substituents are the most effective for the separation of Cs, Rb and other alkali metals [1]. Effective separation of alkali, alkaline-earth and other metal salts is also obtained in the systems with crown-ethers and the selectivity of these extractants is determined mainly by conformity of the extracted salt cation size to the macrocycle cavity diameter [2].

The results of the researching of the extraction of alkali metals with alkylphenols and their mixtures with crown-ethers are presented in the paper. The systems with p-alkylphenols are studied to compare them with the systems with ortho-substituted phenols that have been studied previously [1].

The composition of extracted compounds. The state of extractant has been studied previously for the studying of extracted phenolate solvation in organic phase. The activity coefficients of p-tretbutylphenol in CCl_4 have been determined by the infrared spectroscopy method (Fig.1). The obtained data point out considerable self-association of the extractant in organic solutions and pronounced interaction of water, phenol it must be taken into account at determining the solvation extent by metal distribution data at different extractant concentrations. Fig.2 shows that the determining of solvation numbers without taking phenol

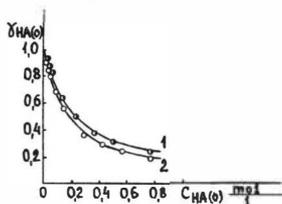


Fig.1. $\gamma_{HA(o)}$ as a function of p-tretbutylphenol concentration in CCl_4 (1), the same in the presence of H_2O (2)

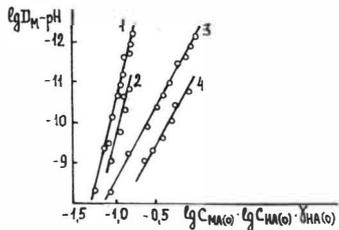


Fig.2. $(lg D_M - pH)$ as a function of $lg C_{HA(o)}$ (1,2) and of $lg C_{HA(o)} \cdot \gamma_{HA(o)}$ (3,4) at the extraction of Rb(1,3), Cs(2,4) with p-tretbutylphenol solution in CCl_4

selfassociation in organic phase into account (which is often in the literature) leads to wrong results. The solvation numbers, obtained by $(\lg D_M - pH)$ as a function of extractant activity logarithm, are close to 7, that is remarkably higher than for the systems with steric hindered phenols.

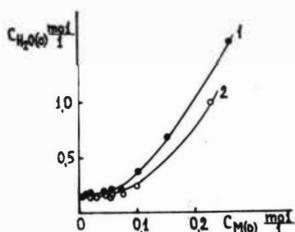


Fig.3. Water distribution at the extraction of Rb (1) and Cs (2) with 0,8M solution of p-tretbutylphenol in CCl_4

The hydration numbers of approximately 3 and 2 are obtained at the studying of water behaviour at low concentrations of Rb and Cs phenolates respectively (Fig.3). Significant increasing of water concentration takes place at increasing of phenolate concentration (and at decreasing of phenol concentration). Abnormally high metal distribution coefficients are observed in the same region. The micelle formation of phenolates and the water solubilization in inner micelle cavity occur evidently under these conditions.

Phenolates dissociation in organic phase is possible at the use of polar solvents. As it can be seen in Fig.4, the character of $\lg D_{Na}$ as a function of pH at the extraction of Na with 1M thymol solution

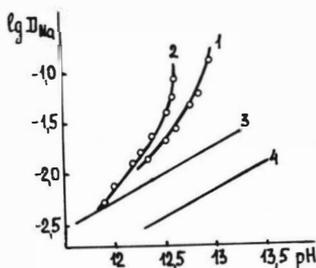


Fig.4. The extraction of Na with 1M thymol solution in isoamyl alcohol from 0,5M (1) and 3,0M (2) $NaCl$ solutions. 3, 4 - are calculated for 0,5M and 3,0M $NaCl$ respectively without taking ion association into account

in isoamyl alcohol points out extracted compounds dissociation in organic phase (1). The calculated values of activity coefficients are shown in Fig.5, the dependences are typical for 1-1 electrolytes in non-aqueous solvents.

The effect of phenol nature.

Two factors can be marked qualitatively, which affect the substituted phenol extractability: the value of constant of phenol dissociation (the presence of electrophilic substituents) and the steric effects in forming of phenolates and their solvation (volumetric ortho-substituents). Thus

o-bromphenol ($K_a = 3,6 \cdot 10^{-10}$), *L*-naphtol ($1,4 \cdot 10^{-10}$) and β -naphtol ($2,3 \cdot 10^{-10}$) have higher extractability of Cs, Rb, K in comparison with *p*-alkylphenols ($5 \cdot 10^{-11}$).

The highest separation coefficients of alkali metals are observed in the systems with volumetric radicals in ortho-position, e.g. with 4-tretbutyl-2-benzylphenol and 4-tretbutyl-2-allylphenol (see the table). However, the distribution coefficients of Cs and Rb for ortho-allylphenol are very low, it hindered the use of ortho-allylphenol.

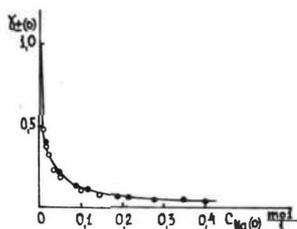


Fig.5. The activity coefficients of Na phenolate in organic phase at $C_{Na}(init)=0,5$ mol/l and 3,0 mol/l (solid points)

The calculated separation coefficients of Cs and Rb in the systems with phenols of various structure

Extractant	pH range	$-\lg D_{CS}$	$\beta_{CS/Rb}$
4-tretundecyl-2-bromphenol	11,0-12,0	1,5-1,3	4,0-1,8
3-phenyl-1-naphtol	11,8-12,5	1,4-1,3	6,6-2,7
4-phenyl-2-naphtol	11,0-12,0	1,6-1,4	3,5-1,5
4-tretnon ₉ decylphenol	12,2-13,2	1,6-1,4	2,5-1,6
4-tretbutyl-2-benzylphenol	12,0-13,0	1,6-1,4	6,5-2,6
4-(tricyclo-4,3,0 ^{2,9} non-8-yl)phenol	12,0-12,8	1,8-1,5	3,2-1,4
4-tret butyl-2-allylphenol	12,5-13,5	2,8-2,2	6,5

The extraction of alkali metals with mixtures of alkylphenols and organic acids. Synergistic effects were observed at the extraction of Cs with the mixtures of n-caprylic acid, α -monoalkylmonocarbonic acid, D2EHFA and dialkyldithiophosphoric acid with steric hindered phenols due to the solvation of extracted salts with phenol molecules. Synergistic and antagonistic effects take place at the extraction of Rb depending on the acid nature and pH water phase.

The systems with the mixtures of crown-ethers and alkylphenols are characterized by significant interaction of extracted ML_yB complexes with alkylphenol and by formation of MA phenolate and its complex with crown-ether ML_yA , it leads to the increasing of metal distribution coefficients; interaction of extragents causes the value of D_M to decrease. It's hard to predict the total effect. The composition of extracted compounds corresponds to $KLCl \cdot S_4HA$ and $CsL_2Cl \cdot S_2HA$ at the extraction of K and Cs chlorides with the mixture of p-tretbutylphenol and dibenzo-18-crown-6 (DVS-18) in chloroform from solutions with low pH-values, when alkali metal phenolates don't form. Earlier [2]

it's shown that sandwich compounds are formed in the cases when cation sizes are higher than crown-ether cavity diameter. Data obtained under the conditions of saturation are shown in Fig.6. The solvation of extracted complexes with non-dissociated phenol molecules is significant

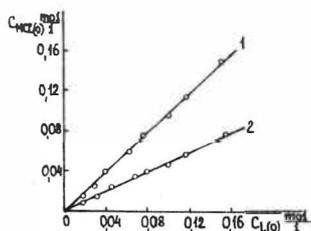


Fig.6. The extraction of KCl (1) and CsCl (2) with the mixtures of p-tretbutylphenol (1 mol/l) and DVS-18 with various concentration in chloroform

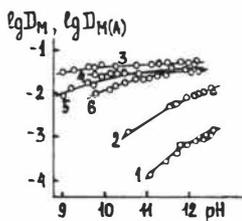


Fig.7. The extraction of K (1,3,5) and Cs (2,4,6) with 0,35 M p-tretbutylphenol (1,2), the mixture of 0,35 p-tretbutylphenol and 0,21 M DVS-18M in chloroform (3,4) from chloride aqueous solutions; 5,6-calculated $\lg D_M$ as functions of pH

and leads to synergistic effect inspite of strong interaction of phenol and crown-ether in the system.

At using of mixtures of crown-ethers and alkylphenols at comparatively high pH of water phase, the conditions are realized under which metal phenolates are formed. It can be seen in Fig.7 that the presence of crown-ether leads to significant growth of distribution coefficients in comparison with the system containing only alkylphenol. With increasing pH values of D_K and D_{CS} are also increase 4-5 times, it points to phenolate formation. The fraction of metal chlorides and phenolates in complex with crown-ether in organic phase is determined. As it's seen in Fig.7 with the formation of phenolates the values D_M are much higher than in the systems without crown-ether, and K is extracted better than Cs. The hydration of phenolates occurs at transition from the systems with p-alkylphenols to the systems with their mixtures with crown-ethers.

Thus, phenolate-ion forming in the systems with the mixtures of alkylphenols and crown-ethers provides the increasing of metal distribution coefficients, and crown- ether - the selectivity at extraction.

References

1. Kholkin A.I., Gindin L.M., Markova L.S., Shtilman I.S. Ekstraktsiya metallov fenolami. Novosibirsk; Nauka, 1976.
2. Kholkin A.I., Gindin L.M., Luboshnikova K.S. et al.// Tezisy dokladov XVI Vsesoyuznogo Chugaevskogo soveshaniya po khimii kompleksnykh soyedineniy. Krasnoyarsk, 1987. S.660.

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Mercury(II) is on the one hand a dangerously toxic element and on the other hand a very useful metal indispensable for industry. Therefore separation techniques for the recovery of mercury(II) from various kinds of wastes are necessary. Liquid-liquid extraction is a very effective and energy-saving separation method for this purpose.

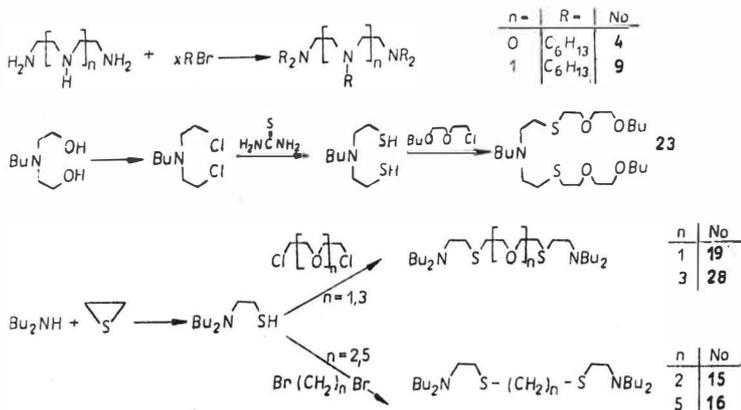
Another scope of our interest is the search of ligand structure - extraction power - relations for lipophilic multidentate neutral ligands [1-7].

The present paper reports on the influence of the structure of several oxathiaaza alkanes and related compounds 3 - 29 on the extraction of mercury(II)chloride.

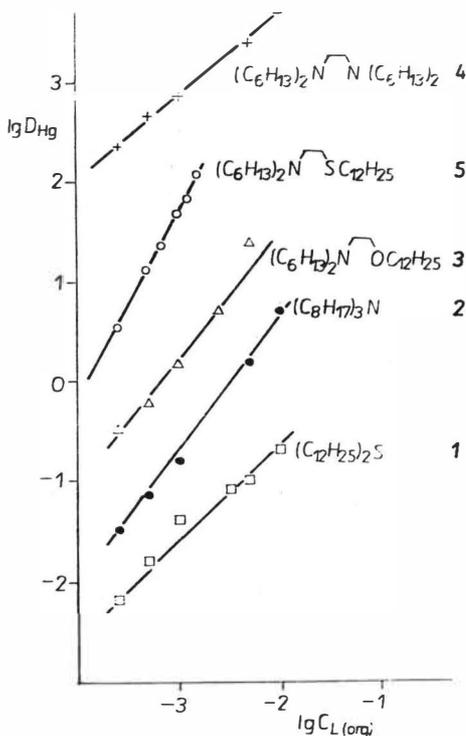
The investigated extractants are summarized together with their physical data in Table.

Some selected examples of their syntheses are given in the formula schema. In most cases the synthesis consists of a set of nucleophilic reactions.

Examples for ligand syntheses



All distribution experiments have been carried out under the same conditions and are demonstrated in the figure for mono- and bivalent extractants 1 - 5: $c_{\text{HgCl}_2} = 1 \cdot 10^{-4} \text{ M} \cdot \text{dm}^{-3}$; $c_{\text{extractant}} = 5 \cdot 10^{-4} - 1 \cdot 10^{-2} \text{ M} \cdot \text{dm}^{-3}$; pH 5.2 (buffer system NaOAc/HCl); shaking time 30 min; CHCl_3 as diluent.



Summary of the results¹:

- Even simple tertiary amines and sulfides (see fig., substances No. 1 and 2) extract HgCl_2 from aqueous solution with low extent.

- A strong increase of extraction ability results if a second ligator atom is included into the extractant molecule (see Fig.1).

$\text{NN}(4) > \text{NS}(5) > \text{NO}(3) > \text{N}(2) > \text{S}(1)$
 $\log D: 2.85 \ 1.70 \ 0.13 \ -0.80 \ -1.53$
 These mentioned extractants have equal lipophily ($\Sigma C_{\text{alkyl}} = 24$).

- The interruption of NN or NS sequence by oxygen sharply decreases the extraction ability.

$\text{NN}(4) > \text{NS}(5) > \text{NOOON}(17) > \text{NOOOS}(18)$
 and also: $\text{SS}(7) > \text{SOS}(14)$ - $\log D: 2.85, 1.70, 0.25$; $\log D: -0.50 \ -0.70$.
 This demonstrates an only low coordination action of the oxygen atoms. Otherwise the presence of an (or several) oxygen atoms also influences the extraction power.

$\text{SOS}(14) > \text{S}(\text{CH}_2)_5\text{S}(8) > (\text{C}_6\text{H}_{13})_2\text{S}(29)$

$\log D: -0.70 \ -1.90 \ -2.30$

- The neighbourhood of N and S is significant for high distribution ratios with oxathiaza alkanes. In this cases further oxygen atoms have no influence on the extraction.

$\text{SNS}(13) \approx \text{OOSNSO}(23) > \text{SONOS}(20-22) \approx \text{SOONOOS}(25-27) \approx \text{OSONOSO}(24)$

$\log D: 1.10 \ 1.10 \ 0.40 \ - \ 0.65$

- It seems, that no more than two coordinated ligator atoms are necessary $\text{NN}(4) \approx \text{NNN}(9) \gg \text{NS}(6) \approx \text{NSSN}(15) \approx \text{NSOSN}(19)$

$\approx \text{NSOOSN}(28) \approx \text{NS}(\text{CH}_2)_5\text{SN}(16)$

$\log D: 2.85 \ 2.85 \ 1.12 \ - \ 1.37$

¹ Given $\log D$ -values are at a concentration of $1 \times 10^{-3} \text{ M} \cdot \text{dm}^{-3}$.

Compound No	Ligand atoms No order	Extractant a) Formula	B.p. °C/Pa	n_D^{20}
3	2 NO	$(C_6)_2N \curvearrowright OC_{12}$	185-190/80	1,4522
4	NN	$(C_6)_2N \curvearrowright N(C_6)_2$	171-172/65	1,4517
5		$(C_6)_2N \curvearrowright SC_{12}$	210/13	1,4675
6	NS	$(C_4)_2N \curvearrowright SC_8$	148-152/25	1,4675
7	SS	$C_6S \curvearrowright SC_6$	127/33	1,4851
8		$C_6S-(CH_2)_5-SC_6$	165/27	1,4872
9	3 NNN	$(C_6)_2N \curvearrowright N \curvearrowright N(C_6)_2$ C_6	204-207/13	1,4592 ^{b)}
10		$(C_6)_2N \curvearrowright N \curvearrowright N(C_6)_2$ C_6	230/13	1,4625 ^{b)}
11	NSN	$(C_6)_2N \curvearrowright S \curvearrowright N(C_6)_2$	218/20	1,4723
12		$(C_6)_2N \curvearrowright S \curvearrowright N(C_6)_2$	221-223/27	1,4706
13	SNS	$C_4S \curvearrowright N \curvearrowright SC_4$ C_{12}	220-224/40	1,4828
14	SOS	$C_6S \curvearrowright O \curvearrowright SC_6$	145-149/27	1,4870
15	4 NSSN	$(C_4)_2N \curvearrowright S \curvearrowright S \curvearrowright N(C_4)_2$	213-217/80	1,4909
16		$(C_4)_2N \curvearrowright S-(CH_2)_5-S \curvearrowright N(C_4)_2$	235-237/33	1,4888
17	5 NOOON	$(C_6)_2N \curvearrowright O \curvearrowright O \curvearrowright O \curvearrowright N(C_6)_2$	195-200/25	1,6568
18	NOOOS	$(C_6)_2N \curvearrowright O \curvearrowright O \curvearrowright O \curvearrowright SC_{12}$	285-290/65	1,4692
19	NSOSN	$(C_4)_2N \curvearrowright S \curvearrowright O \curvearrowright S \curvearrowright N(C_4)_2$	233-238/65	1,4863
20	SONOS	$C_4S \curvearrowright O \curvearrowright N \curvearrowright O \curvearrowright SC_4$ R: C_4	165-167/13	1,4851
21		C_8	189-198/20	1,4801
22		C_{12}	190-200/12	1,4770
23	7 OOSNSOO	$C_4O \curvearrowright O \curvearrowright S \curvearrowright N \curvearrowright S \curvearrowright O \curvearrowright OC_4$ C_4	209/13	1,4835
24	OSOWOSO	$C_4O \curvearrowright S \curvearrowright O \curvearrowright N \curvearrowright O \curvearrowright S \curvearrowright OC_4$ C_4	215-216/33	1,4816
25	SOONOOS	$C_4S \curvearrowright O \curvearrowright O \curvearrowright N \curvearrowright O \curvearrowright O \curvearrowright SC_4$ R: C_4	200/65	1,4820
26		C_8	220-225/90	1,4812
27		C_{12}	252-260/27	1,4800
28	NSOOOSN	$(C_4)_2N \curvearrowright S \curvearrowright O \curvearrowright O \curvearrowright O \curvearrowright S \curvearrowright N(C_4)_2$	258/40	1,4838

a) C_n always mean nonbranched saturated chain $C_{nH_{2n+1}}$.

b) at 25°C.

\curvearrowright is a $-CH_2-CH_2-$ unit.

- Optimum distance between the ligator atoms is given by two methylene groups. $NNN(9) > NNN(10)$ and $NSN(11) > NSN(12)$

log D: 2.85 1.15 1.61 0.85

All results lead to the conclusion, that derivatives of ethylene diamine are the most powerful extractants for $HgCl_2$, according to the high stability constant of the extracted complex.

Nevertheless specific feed compositions or extraction and stripping conditions can lead to a preferred use of other quoted extractants in practice.

References

1. Schiefser H., Quaißer M., Beger J., Gloe K., Mühl P.//Z.Chem. 1982.Bd.22.S.426.
2. Fritsch F., Gorski B., Beer M., Beger J., Jacobi R.//Z.Chem. 1983.Bd.23.S.193.
3. Beger J., Jacobi R., Merkwitz H., Gloe K., Mühl P.//Z.Chem. 1984.Bd.24.S.230.
4. Gloe K., Mühl P., Beger J., Jacobi R., Urban A.//Z.Chem.1985.Bd. 25.S.99.
5. Merkwitz H., Jacobi R., Beger J., Gloe K., Mühl P.//Z.Chem.1985. Bd.25.S.231.
6. Gloe K., Merkwitz H., Mühl P., Beger J.//Z.Chem.1987. Bd.27.S.376.
7. Gloe K., Rüstig H., Mühl P., Beger J.//Solvent Extraction and Ion Exchange, in press.

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The extraction of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions with benzoic or o-toluic acid into benzene as well as with mixtures containing benzoic or o-toluic acid and 3,4-dimethylaniline into benzene from sulphate solutions has been studied. It has been found that benzoic or o-toluic acid in benzene do not separate Co(II) and Ni(II) ions, whereas the other ions are separated in the order of increasing pH values: Fe(III) < Cu(II) < Zn(II) < Mn(II) (Fig.1). The intro-

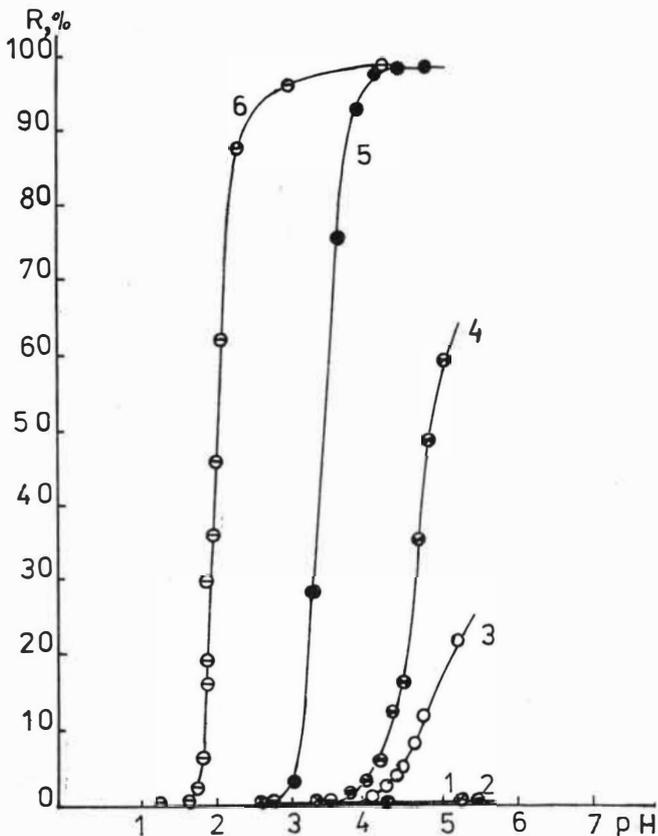


Fig. 1. Extraction of 1 - Co(II), 2 - Ni(II), 3 - Mn(II), 4 - Zn(II), 5 - Cu(II), 6 - Fe(III) with benzoic acid (HAr) in benzene

$$C_{\text{HAr}} = 0.5 \text{ M}, C_{\text{metal}} = 2.5 \cdot 10^{-2} \text{ M}$$

duction of 3,4-dimethylaniline into simple extraction solvents improves their extraction characteristics and brings about a synergic effect in the systems studied. Complex extraction solvents enable the separation of all the studied metal ions over a large pH range of aqueous phase in the order of increasing pH values: Fe(III) < Cu(II) < Zn(II) < Ni(II) < Co(II) < Mn(II) (Fig.2).

On the grounds of the extraction data the compositions of metal complexes in the organic phase for extraction with simple and complex extraction solvents were determined [1,2]. Complexes: MnR_2 , $(FeR_3)_3$, $(CuR_2 \cdot HR)_2$ [3], $ZnR_2 \cdot 2HR$ were found in the organic phase in case of

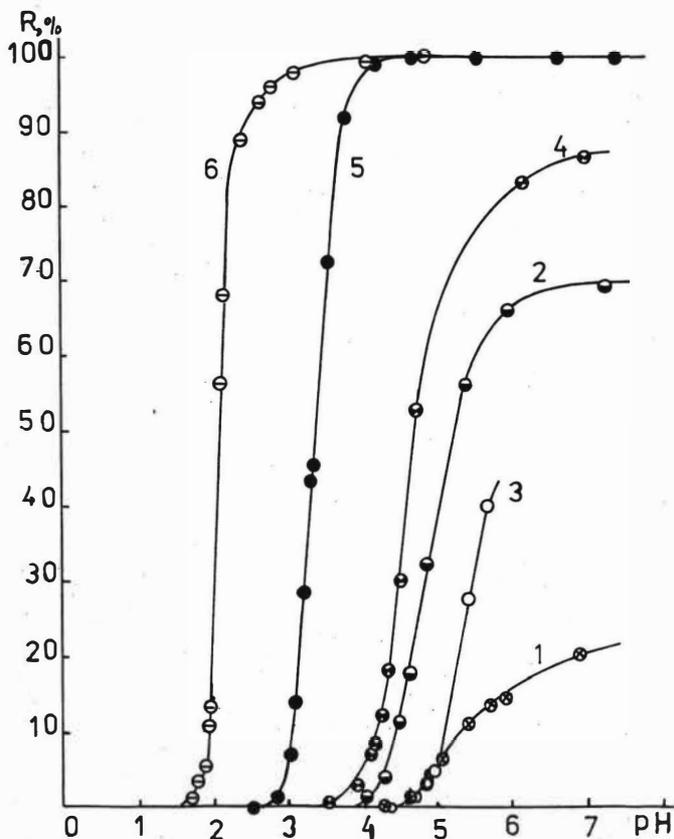


Fig.2. Extraction of 1 - Co(II), 2 - Ni(II), 3 - Mn(II), 4 - Zn(II), 5 - Cu(II), 6 - Fe(III) with mixtures of benzoic acid (HAr) and 3,4-dimethylaniline (Am) in benzene $C_{HAr} = 0.5 M$, $C_{Am} = 0.25 M$, $C_{metal} = 2.5 \cdot 10^{-2} M$

simple extraction solvents containing benzoic or o-toluic acid in benzene (under those conditions Ni(II) and Co(II) ions do not pass into organic phase).

For complex extraction solvents containing benzoic or o-toluic acid mixed with 3,4-dimethylaniline in benzene, the complex: $\text{CoAr}_2 \cdot 2\text{HAr} \cdot 2\text{Am}$ [4], $\text{NiAr}_2 \cdot 2\text{Am}$ [5], $(\text{CuAr}_2 \cdot \text{Am})_2$ [5], $\text{ZnAr}_2 \cdot \text{HAr} \cdot \text{Am}$ were determined in the organic phase (HAr - carboxylic acid, Am - 3,4-dimethylaniline).

The synergic effect observed in the systems studied is due to the formation of mixed complexes of metal ions in the organic phase the participation of 3,4-dimethylaniline in all the cases analyzed. The results arrived at indicate a direct influence of 3,4-dimethylaniline as an extraction reactant on the synergic effect.

The extraction mechanism of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions with simple and complex extraction solvents was described by appropriate chemical equations and the concentration constants of the extraction were calculated.

References

1. Korenman I.M. // Ekstrakciya v analize organicheskikh vechestv. Moskva: Khimiya, 1977. P.57.
2. Kopacz S. // Hornicka Pribram ve Vede a Technice. Pribram. 1984. Sekce N. P. 347.
3. Kopacz S., Kalembekevich J. // Zhurn. Neorg.Khim.1986. Vol.31. N 3. P. 730.
4. Kopacz S., Kalembekevich J. // Chemia Anal. 1986. Vol. 31. P. 645.
5. Kopacz S., Kalembekevich J. // Zhurn. Neorg.Khim. 1986. Vol.31. N 3. P. 747.

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Components in the organic phase interact differently, making quantitative description of systems with monocarboxylic acids difficult. One to the same reason experimental dependence have complicated character, and the obtained data are very difficult to interpret. The literature data on determining the composition of extracted species are of numerous contradictious.

Extractant condition. Taking n-caprylic acid (HA) as the example, using the distribution method it has been shown (see Table), that distribution constants of the monomeric form increase, and dimerization in the solvents series decreases: n-decane, benzene, isoamylacetate, diisopropylketone, isoamyl alcohol, that is connected with the increasing interaction of monomers with the solvents in the given series.

Distribution and dimerization constants of n-caprylic acid

Solvent	\bar{K}_{HA}	\bar{K}_d
Decane	23 \pm 6	990 \pm 390
Benzene	103 \pm 21	146 \pm 33
Isoamylacetate	700 \pm 140	2,6 \pm 1,1
Diisopropylketone	740 \pm 50	3,0 \pm 0,4
Isoamyl alcohol	3100 \pm 280	0,0 \pm 0,2

Extracted compounds composition. Formation of bi- and polynuclear extracted complexes in organic phase is a widespread phenomenon for the monocarboxylic acids. For example, in extracting iron with the solutions of n-caprylic acid in decane in organic phase over a wide range of

the component concentrations and pH of aqueous solutions the composition of complexes is $Fe_2A_9 \cdot 3 H_2O$. In the range of high pH with lack of solvent there form hydrolyzed complexes, which precipitate. In systems with benzene we managed to saturate the extractant in these conditions too, and the composition of the extracted complex was $Fe_3(OH)_3A_6$ (water wasn't determined). When extracted from the nitrate solutions in the range of low pH, iron is well extracted in the form of $Fe(NO_3)_2A$ complex, probably solvated by excessive extractant. It should be stressed that the formation bi- and polynuclear complexes essentially affects the distribution character, specifically the tangent of the slope angle of dependence of $lg D_M$ on pH increases at low pH, distribution coefficients are essentially dependent on the concentration of metal (see Fig.1).

Carboxylates forming in extracting cobalt and nickel by monocarboxylic acids are partially dimerized in organic phase. Nickel caprylate dimerization constants somewhat decrease in series: n-decane, benzene, CCl_4 , 1,2,4-trichlorobenzene.

The literature data on cobalt and nickel extracted complexes solvation in organic phase are contradictory. According to the data on nickel extraction with solutions of the n-caprylic acid in decane and benzene (Fig.2), the concentrations of the monomers and dimers of nickel caprylate were calculated. By processing these data, it has been obtained, that the process of extracting nickel with solutions of caprylic acid in decane is characterized by

the formation of monomeric forms of the nickel caprylate of the composition NiA_2 and $\text{NiA}_2 \cdot 6\text{HA}$ and also dimers - Ni_2A_4 and $\text{Ni}_2\text{A}_4 \cdot 8\text{HA}$. Extracted species NiA_2 , $\text{NiA}_2 \cdot 4\text{HA}$ and $\text{NiA}_2 \cdot 6\text{HA}$ as well as $\text{Ni}_2\text{A}_4 \cdot 4\text{HA}$ and $\text{Ni}_2\text{A}_4 \cdot 8\text{HA}$ are likely for the systems with benzene. At the same time the form $\text{NiA}_2 \cdot 4\text{HA}$ is realized in the systems with benzene over broad range of concentrations of HA, but in the systems with decane the form $\text{NiA}_2 \cdot 2\text{HA}$, with the smaller solvation number, is realized, in spite of the great activity coefficients of the caprylic acid in decane. Such behaviour is probably connected with possible solvation of caprylates both by caprylic acid monomers and dimers, and these or solvates are stable in the organic solvents, for which the corresponding extractant form is the most stable.

The influence of solvents on the extraction of metals with monocarboxylic acids is determined by the differences in interactions of solvents with the extractant and solvents with the extracted compounds, and especially shows in the cases, when the extracted compound isn't solvated by the extractant. The data on the extraction of iron with 1M caprylic acid solutions in different solvents are given in Fig.3. Essential decrease of distribution coefficients of iron with the increase

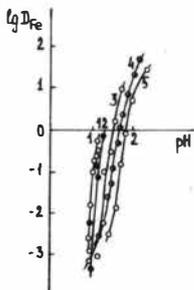


Fig.1. Extraction of iron with n-caprylic acid from nitrate solutions. $C_{\text{Fe}}(\text{init.})$, g-ion/l: 1- $1 \cdot 10^{-1}$, 2- $5 \cdot 10^{-2}$, 3- $8 \cdot 10^{-3}$, 4- $1 \cdot 10^{-3}$, 5- $5 \cdot 10^{-4}$

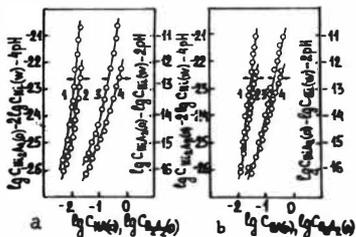


Fig.2. Defining of solvation numbers of monomers (2,4) and dimers (1,3) of nickel caprylate in the system with decane (a) and benzene (b)

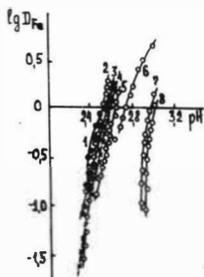


Fig.3. Extraction of iron with 1M caprylic acid solution in decane (1), benzene(2), mixture nitrobenzene + CCl₄(5:1)(3), CCl₄(4) and nickel in the systems with isoamylalcohol, 1,2,4-trichlorobenzene (5), isoamylalcohol(6) essential influence of extracted compounds dissociation on the character of dependence lgD_M from pH is displayed in the extraction of sodium (Fig.5). The activity coefficients, calculated according to the experimental data are given in Fig.6.

of electronodonor solvent properties indicates the predominant influence of the extractant - solvent interaction in these systems.

Correlation of the metal-hydrogen exchange constants with the activity coefficients of the organic acid in the various solvents is presented in Fig.4. The slope of the straight line corresponds to the theoretical value $\text{tg } \alpha = 9$.

The interaction with extracted compound, resulting in partial destruction of tri-nuclear compound, is essential in isoamyl alcohol. By analogy, the caprylates in organic phase are not dimerized in the extraction of cobalt their marked dissociation is observed. Essential influence of extracted compounds dissociation on the character of dependence lgD_M from pH is displayed in the extraction of sodium (Fig.5). The activity coefficients, calculated according to the experimental data are given in Fig.6.

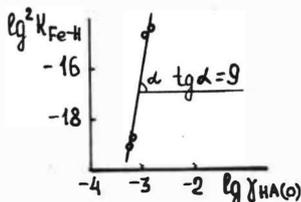


Fig.4. Correlation of $\lg K_{\text{Fe-H}}$ and $\lg \gamma_{\text{HA}(o)}$ for the systems with decane (1), benzene(2), isoamylacetate(3) and diisopropylketone(4)

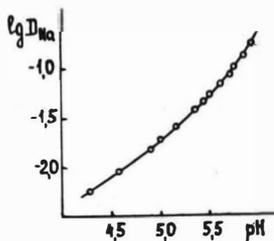


Fig.5. Dependence of $\lg D_{\text{Na}}$ on pH at the extraction of sodium with 2M caprylic acid solution in isoamyl alcohol

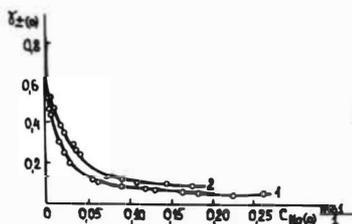


Fig.6. Activity coefficients of sodium caprylate in organic phase at $a_{\text{H}_2\text{O}}=1(1)$ and 0,967 mol/l(2)

Formation of heteronuclear carboxylates is rather specific for the systems with monocarboxylic acids of some metals in their combined presence. For example, the data obtained for extraction of iron(III) and copper are presented in Fig.7, the data on extraction of iron(III) and nickel are shown in Fig.8. The relationship Fe:Ni in the composition of heteronuclear complex is obtained according to the spectrophotometrical and extraction data as 3:1. The heterobinuclear complex of CoNiA_4 composition forms in the combined extraction of cobalt and nickel in organic phase, that essentially decreases these metals separation coefficients (Fig.9).

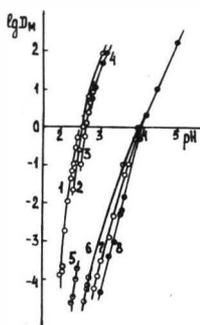


Fig.7. Extraction of iron(4) and copper (8) separately and in their combined presence(1-3,5-7) with 1M HA solution in decane. $C_{\text{Cu}}(\text{init.}) = 0,05 \text{ mol/l}$, $C_{\text{Fe}}(\text{init.}), \text{mol/l}$: 0,01(4,7); 0,03(3,6); 0,05(2); 0,1(1,5)

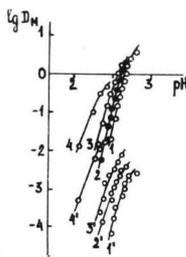
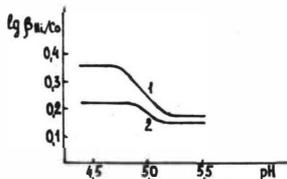


Fig.8. Extraction of iron (1-4) and nickel (1'-4') at combined presence with 1M HA solution in decane from the solutions, containing 0,02g-ion/l Ni and Fe, g-ion/l: 0,02(1); 0,05(2); 0,10(3); 0,45(4)

Fig.9. Dependences of $\lg \beta_{\text{Ni/Co}}$ on pH, calculated according to the data for simple systems (1), obtained in combined presence (2)



Thus, the systems with monocarboxylic acids are characterized by the processes of association of extractant hydro-solvates of various composition, and also polynuclear and heteronuclear extracted compounds because of the carboxylate-ion bidentance, four-members cycles tension and unstability at carboxylate-ions and cations interaction and because of H-bonds formation.

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In a process producing glyoxal from acetaldehyde by oxidation with nitric acid, the resulting aqueous glyoxal solution contains 1-3% residual nitric acid, 12% acetic acid and small amounts of glyoxalic, glycolic and oxalic acids. These acids have to be removed before further processing in order to obtain a satisfactory commercial product.

Many methods have been suggested for accomplished this purpose [1-3], but efforts to find better and more economical process remains unabated. The ultimate aim of the present investigation is to develop a commercial solvent extraction process to remove the undesired acids and to obtain a qualified glyoxal product.

Experimental. Feed solutions are (1) solutions prepared from C.P. chemicals and deionized water and (2) solutions supplied by commercial works.

Solvents used are (1) Alamine 336 or tributylphosphate purchased from Shanghai market dissolved in odorless kerosene supplied by Shanghai Refinery used as single extractant solvent and (2) both Alamine 336 and tributylphosphate were dissolved in odorless kerosene to form mixed extractant - kerosene solvents.

Method of Analysis - acid content was determined by acid-base titration; and glyoxal content was analyzed by adding an excess of potassium hydroxide to react with glyoxal and the unreacted potassium hydroxide was determined by back titration with standard hydrochloric acid solution.

Determination of Distribution Coefficient - equal volumes of the organic and glyoxal aqueous solution were shaken for 180 seconds at room temperature, as preliminary experiments shew that 60 seconds are sufficient to attain equilibrium. The volume changes of both phases were measured before and after equilibration.

Results and Discussion

Equilibrium Relationships

1. Extraction of individual acid by a single extractant in diluent

The distribution coefficients of HNO_3 and HAc between Alamine 336 and aqueous solution are shown in Figs. 1 and 2. The curves show that the extraction of HNO_3 is more efficient than that of HAc and the distribution coefficient of HNO_3 decreases but that of HAc increases with increasing concentration of the respective acid in solution.

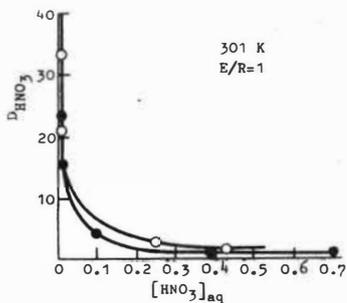


Fig. 1. $[\text{HNO}_3]_{\text{aq}}$ vs. D_{HNO_3}

- Alamine 336:Kerosene=3:7(v/v)
- Alamine 336:Kerosene=2:8(v/v)

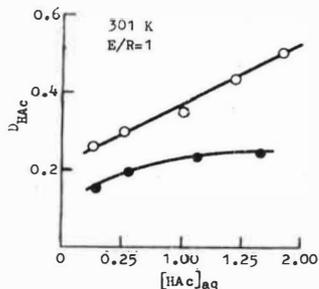


Fig. 2. $[\text{HAc}]_{\text{aq}}$ vs. D_{HAc}

- Alamine 336:Kerosene=3:7(v/v)
- Alamine 336:Kerosene=2:8(v/v)

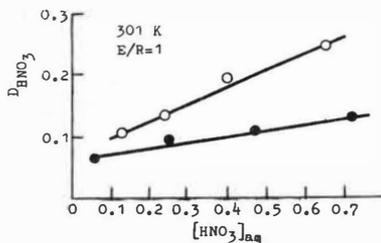


Fig. 3. $[\text{HNO}_3]_{\text{aq}}$ vs. D_{HNO_3}

- TBP:Kerosene=5:5(v/v)
- TBP:Kerosene=3:7(v/v)

When TBP-kerosene mixture is used, the extraction efficiency is reversed, i.e. HAc is more extracted than HNO_3 , but distribution coefficients for both acids are always below unity (see Figs. 3 and 4).

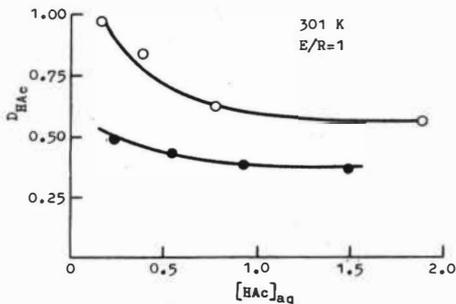


Fig. 4. $[\text{HAc}]_{\text{aq}}$ vs. D_{HAc}

- TBP:Kerosene=5:5(v/v)
- TBP:Kerosene=3:7(v/v)

2. Extraction of mixed acids from aqueous synthetic solution by a single extractant

Curves 1 and 2 indicated in Fig. 5 show the influence of total acidity on the distribution coefficient when either Alamine 336 or TBP is used. It was discovered that extraction is inefficient even at low acid concentrations.

3. Synergistic extraction of mixed acids by mixed extractants

Synergistic extraction of HAc and HNO_3 by Alamine 336 and TBP is observed (see curve 3 in Fig.5). The distribution coefficient is 2-4 times the value measured when Alamine 336 or TBP alone is used at low acid concentration. It also maintains quite high values at high concentrations.

Extraction of Mixed Acids by a Solvent Consisting of Mixed Extractants

By using a solvent consisting of Alamine 336 and TBP in kerosene, HNO_3 and HAc can be very effectively removed from the aqueous glyoxal solution.

1. Effect of extractant concentration

Experimental data show that the distribution coefficient of total acidity increases with increasing concentrations of both extractants. In order to avoid entrainment and emulsification, proper concentrations of Alamine 336 and TBP together with a modifier and odorless kerosene should be used. The optimal concentrations of Alamine 336 and TBP were found empirically to be 20% and 50% by volume respectively.

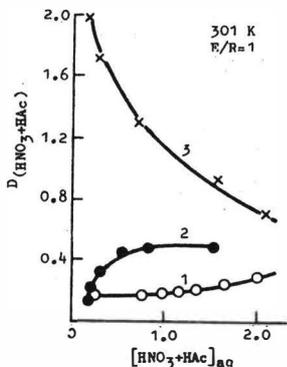


Fig. 5. $[\text{HNO}_3+\text{HAc}]_{\text{aq}}$ vs. $D(\text{HNO}_3+\text{HAc})$
 1. Alamine 336:Kerosene=2:8(v/v)
 2. TBP:Kerosene=5:5(v/v)
 3. Alamine 336:TBP:Kerosene=2:5:3

2. Effect of temperature

The preliminary test was done and results are illustrated in Table 1.

TABLE 1. Effect of temperature on distribution coefficient

Temperature, K	301	315	324	333
Distribution coefficient, D	1.395	1.310	1.123	1.051

Glyoxal in aqueous solution, 1.57 Kmol/m^3 ; Total acidity, 1.75 Kmol/m^3 ; Solvent, Alamine 336 : TBP : Mixed Alcohol : Kerosene = 20 : 50 : 3 : 27; E/R, 1

From the data of Table 1 the overall heat effect of extraction which involves complex formation and mass transfer steps can be estimated. By assuming all steps as a pseudo-macroscopic process, the relation between distribution coefficient and temperature may be written as

$$\ln D = \ln D_0 + (\Delta H_p/R)(1/T),$$

where T - temperature; R - gas constant; ΔH_p - total enthalpy change;

$$\Delta H_p = -2.2 \times 10^4 \text{ KJ/Kmol},$$

McCabe-Thiele Diagram for the Extraction of Mixed Acids

The X-Y diagram at 301K and the operating line are shown in Fig.6. The number of theoretical stages required can be found to be about four.

Using NaOH or Na_2CO_3 as the stripping solution the solvent can be easily recovered in a single stage.

Mixer-Settler Test

Extraction was carried out in a battery of mixer-settlers which were made of stainless steel, the volumes of each mixer and settler being 1.2 and 3 liters respectively. The design of the mixer-settler was provided by Z.J. Shen et al with a large triangle agitator and special phase flow compartment [4].

Operating conditions:

Aqueous solution, glyoxal = 1.66 Kmol/m^3 ,
 $[\text{H}^+] = 2.00 \text{ Kmol/m}^3$;

Solvent, Alamine 336 : TBP : mixed

alcohol : kerosene = 20 : 50 : 3 : 27;

Temperature, 301K; E/R, 1.5/1;

Residence time, 300 seconds.

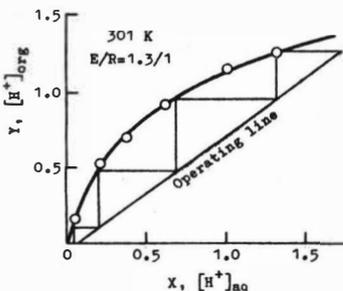


Fig. 6. X-Y diagram for glyoxal solution
 Alamine 336:TBP:Mixed Alcohol:Kerosene,
 =20:50:3:27
 Glyoxal in aqueous solution, 1.57 Kmol/m^3 .

After continuous countercurrent extraction in mixer-settlers of four stages and stripping in a single stage, the overall acid removal is about 97% and glyoxal loss about 3%. The solvent loss is about 5 ppm.

The process has been also carried out commercially in a mixer-settler battery with success and a qualified glyoxal solution was produced.

ACKNOWLEDGEMENT. Thanks are indebted to Li Jian, Song Ke-Gang, Wu Gou-Wei, Ling Han-Lin and Chen Zi-Wei who offered kind support and assistance to the completion of this work.

REFERENCES

1. C. Judson King // Proceedings of International Solvent Extraction Conference, ISEC'80. P.66.
2. Wessendorf et al. // U.S. Patent 4,065,506 (1977).
3. McCain, Jr. et al. // U.S. Patent 3,860,656 (1975).
4. Z.J. Shen, Q.Y. Zhang, B.Y. Sun, J. Li and Y.F. Su // Proceedings of International Solvent Extraction Conference, 1983, 24-25.

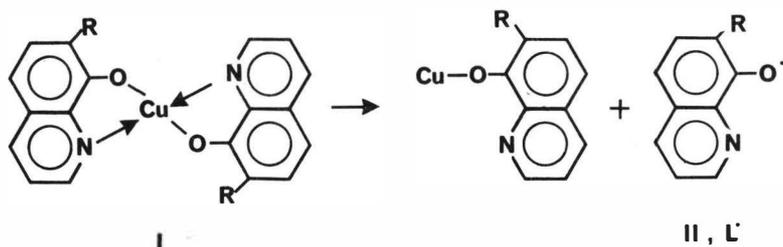
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Introduction: It has been well documented now that in certain metal extraction systems of commercial importance, the extracted metal is oxidized by atmospheric oxygen. Examples of metals oxidized are: Co(II)/Co(III) loaded in *o*-hydroxyoxime (1), 8-hydroxyquinoline (2,3) or β -diketone (4) and Mn(II)/Mn(III) in β -diketone (4). In addition to the extracted metal the extractant itself (e.g. TiBPS (5)) or the diluent (6) can be oxidized as well by atmospheric oxygen. In reference to the latter the cobalt (II)-catalysed oxidation of commercial aromatic diluents by atmospheric oxygen was described in an ISEC'86 paper by Flettand West (6). It is the object of this paper to report a new kind of redox reaction involving solely the metal ion and the organic ligand forming the extractable complex. This type of redox reaction does not involve oxygen and thus differs completely from the previous redox reactions reported in metal solvent extraction.

Inner-Sphere Complexes: Some years ago during the course of an investigation involving the interaction of loaded organic solvents with hydrogen under pressure for direct metal precipitation (7) it was observed that upon heating the Cu-loaded Kelex* 100, I, under nitrogen atmosphere (180-244°C, 12 hours) copper powder would precipitate. A zero-order dependence on copper (II) concentration was observed. The precipitated copper particles were extremely fine exhibiting a relatively narrow size distribution (70% -2 + 1 μm). An infra-red spectroscopic examination of the thermally treated organic revealed a reduction in the size of the peak 3400 cm^{-1} (representing the phenolic OH group (8)) and the simultaneous appearance of a new strong peak at 1720 cm^{-1} (representing a keto $>\text{C}=\text{O}$ group).

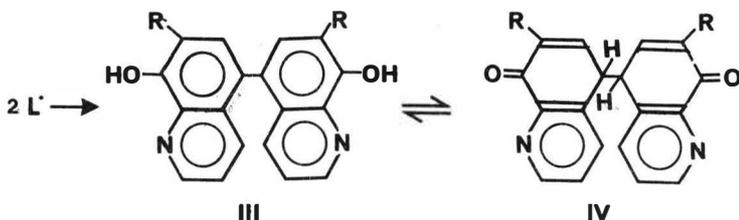
The observed changes were grossly interpreted on the basis of oxidation of the phenolic substrate of the extractant molecule by Cu(II). Here further elucidation of the proposed mechanism (7) is attempted. Phenols are known to be oxidized with relative ease in non-aqueous systems yielding reactive initial products which undergo rapid polymerization (9,10). Thus upon heating, the Cu-Kelex 100 complex, I, presumably undergoes the following intramolecular reactive changes:

- a) one-electron transfer yielding the neutral radical, II, and Cu(I) L'



* Kelex 100, an alkylated derivative of 8-hydroxyquinoline, is an extractant supplied by Sherex Chemical Co.

b) dimerization of II to give tautomers III and IV



and c) disproportionation of $\overline{\text{Cu(I)L}}$



The latter reaction is responsible for the production of very fine copper particles.

The complexes of Co(II)-Kelex 100 and Ni(II)-Kelex 100 in contrast to Cu(II)-Kelex 100 complex were found not to undergo any intramolecular reaction even at temperatures as high as 325°C. This is attributed to the lack of operation of appropriate oxidizing couples for the metals in question (i.e. Co(II)/Co(I) and Ni(II)/Ni(I) (11).

A similar intramolecular redox reaction has also been observed in the extraction of Fe(III) from strong H_2SO_4 solutions with mixtures (2:1 molar ratio) of D2EHPA and Kelex 100 (12). The exact composition of the organometallic complex was not directly determined but it is postulated to be $\overline{\text{FeR}_2\text{L}\cdot 2\text{HR}}$ where HR: D2EHPA and HL: Kelex 100. To effect stripping of iron, from the loaded organic phase, the latter had to be subjected first to hydrogen reduction at temperatures 135 to 165°C up to 4 hours to reduce Fe(III) to Fe(II) and then contact it with a dilute mineral acid solution. During the course of this investigation it was observed that 10 to 15% of the Fe(III) loaded in the organic phase was reduced to Fe(II) upon heating under N_2 atmosphere for one hour. Apart from the phenolic substrate of Kelex 100 (same as in the case of Cu(II)-Kelex 100) the anion of the di-2-ethylhexyl phosphoric acid is also believed to have been oxidized to some extent (10). Again in this case one electron transfer is observed



It is of interest to note here that Doyle-Garner and Monhemius in their work on hydrolytic stripping of metal-loaded Versatic acid solutions (13) reported that Mn(III), Co(III) and Cu(II) species were reduced to Mn(II), Co(II), and Cu(I) respectively during hydrolytic stripping (200°C; 3 hours). These results could again be considered as manifestations of the intramolecular oxidation of the organic moiety (carboxylic acid anion) by the multi-valence metal ion (10); all three couples (one electron transfer) Mn(III)/Mn(II), Co(III)/Co(II) and Cu(II)/Cu(I) having oxidizing properties (i.e. $e^0 > 0$). Considering for example the potential of the couple $\text{M}^{(z+1)+}/\text{M}^{z+}$ we obtain

$$M^{(z+1)} + e^- \rightarrow M^{z+}$$

$$e = e^0 - \frac{RT}{F} \ln \frac{\alpha_{M^{z+}}}{\alpha_{M^{(z+1)+}}}$$

where the activities of M^{z+} and $M^{(z+1)+}$ will depend on the stability constants of the metal-organic complexes,

$$M^{z+} + zR^- = \overline{MR_z} \quad , \quad K_z \quad \text{where } R^-, \text{ the organic ligand moiety}$$

$$M^{(z+1)+} + (z+1)R^- = \overline{MR_{(z+1)}} \quad , \quad K_{z+1}$$

if $\alpha_{M^{z+}} < \alpha_{M^{(z+1)+}}$ or equivalently

$$K_z > K_{z+1} \text{ then } e > e^0.$$

Thus considering the couple Co(III)/Co(II), its potential in Versatic acid solutions (O-ligators) is expected to be high ($e_0 \rightarrow 1.84$ V) while in Kelex 100 (O,N ligators) is expected to be very low ($e_0 \rightarrow 0.1$ V) (14). Consequently oxidation of the carboxylic acid would be favoured while the oxidation of Kelex 100 would not. It is understood of course that the nature of the organic moiety of the complex (i.e. phenol, ketone, acid etc.) would equally influence the extend of the redox coupling reaction.

Outer-Sphere Complexes: All the systems considered so far involved one-electron transfer in inner sphere complexes (i.e. chelates and salts). Electron transfer has, however, been observed in outer-sphere complexes as well. This is the case of gold and platinum group metal extraction with Lix*26 (15). During the course of this work it was found out that upon long standing of Au(III)- loaded organic samples (complex $H_2L^+ \cdot AuCl_4^-$, where HL: Lix 26) or upon heating (60-90°C; 4 hours) the loaded organic phase under N_2 overpressure, precipitation of Au crystals took place. Electrochemical and spectroscopic measurements (16) revealed that the observed precipitation of gold was the result of an outer-sphere electron exchange process. Gold(III) as a strong oxidant would oxidize the phenolic part of the Lix 26 substrate to a keto form while simultaneously the same would be reduced to Gold (I). Mechanistically the reduction of

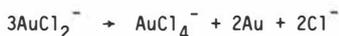


gold (III) to gold (I) is envisaged to proceed in two consecutive one-electron steps via the intermediate formation of Au(II) (17) due to its non complementary nature (18). The two neutral radicals, L^{\cdot} , (Structure II) form eventually a dimer species (III,IV) same as that produced in the Cu(II)-Kelex 100 system. The difference between the oxidation of the 8-hydroxyquinoline nucleus by Cu(II) and Au(III) is the dependence of the latter on pH. This effect is examined in more detail elsewhere (16). It is of interest to note that in addition to Lix 26, isodecanoil was also found to

* Lix 26, an alkylated derivative of 8-hydroxyquinoline, is an extractant supplied by Henkel Corporation.

get oxidized (but to a lesser degree) by Au(III) into aldehyde (16).

Finally AuCl_2^- via the following thermodynamically favoured disproportionation reaction ($K = 5 \times 10^7$) (17)



yields gold crystals.

Electron exchange may be associated with simultaneous ligand exchange as well (18).

Thus upon ageing (> 1 week storage, 25°C) the ion pair $(\text{H}_2\text{L}^+)_2\text{PtCl}_6^{2-} \cdot 2\text{H}_2\text{L}^+\text{Cl}^-$ (where HL: Lix 26) was found to be transformed to a non-strippable form (15). The following reaction is postulated to describe the observed transformation



In other words PtCl_6^{2-} oxidizes 2 molecules of HL (Lix 26) to form the respective radicals L[•], II, while simultaneously the reduced platinum species (PtCl_4^{2-}) - being a less inert complex - undergoes ligand exchange forming a chelate complex (PtL_2)

Summary: Various intramolecular redox reactions observed in solvent extraction systems were identified. The electrode potential of the metal couple in question and the applied temperature appear to control mainly the extent of the reaction. Catalysis of intramolecular redox reactions in conventional solvent extraction of metals is undesirable since it would result in increased extractant losses and metal lock-up. On the other hand, the exploitation of reversible intramolecular reactions could prove useful in preparing fine metal powders (e.g. Au and Cu) of high purity.

References

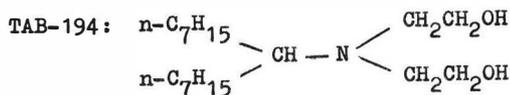
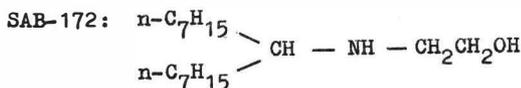
1. Merigold C.R., Sudderth R.B. // Int'l Symp. on Hydrometall., AIME, New York, 1973. P. 552.
2. Ritcey G.M., Lukas B.H. // CIM Bull, Feb. 1975. P. 105.
3. Guesnet P., Sabot J.L., Bauer D. // ISEC'80, Liege, 1980, paper 80-75.
4. Sekine, T. // ISEC'86, Munich, 1986, V. II. P. 179.
5. Pouskouleli G., CANMET, Ottawa, private communication.
6. Flett D.S., West D.N. // ISEC'86, Munich, 1986, V. II. p. 3.
7. Demopoulos G.P., Distin P.A. // J. Chem. Tech. Biotechnol. 1983, V. 33A. p. 249.
8. Demopoulos G.P., Distin P.A. // Hydrometallurgy, 1983, V. 11, P. 389.
9. Mann C.K., Barnes K.K. // Electrochemical Reactions in Non aqueous Systems, Marcel Dekker, N.Y. 1970. p. 247.
10. Denisov E.T. Liquid Phase Reaction Rate Constants, Plenum, N.Y. 1974, p. 479.
11. Bard A.J., Parsons R., Jordan J. Standard Potentials in Aqueous Solution, Marcel Dekker, N.Y., 1985.
12. Demopoulos G.P., Gefvert D.L. // Hydrometallurgy, 1984, V. 12, p. 299.
13. Doyle-Garner F.M., Monhemius A.J. // Minerals and Metall. Proces. 1985, V. 2, P. 47.
14. Uhlig E. // Coord. Chem. Rev., 1982, V. 43 P. 299.
15. Demopoulos G.P., Pouskouleli G., Ritcey G.M. // ISEC'86, Munich, 1986, V. II, P. 581.
16. Demopoulos G.P. Kelebek S., Pouskouleli G., to be published.
17. Puddphatt R.J. The Chemistry of Gold, Elsevier, N.Y., 1978.
18. Cotton F.A., Wilkinson G. Advanced Inorganic Chemistry, 4th ed. Wiley-Interscience, N.Y., 1980 p. 1213, 1216.

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In this paper, the extraction behavior of gallium from hydrochloric acid, sulphuric acid and sodium chlorid medium with self-made extractant SAB-172, TAB-194 in heptane has been studied. We investigated several factors for extraction of gallium. The mechanism of Ga extraction with SAB-172, TAB-194 was established by IR, NMR spectra.

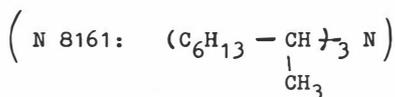
We measured interfacial tension γ of liquid/liquid extracted system, in which SAB-172, TAB-194 and TOA in heptane extracted gallium(III) from hydrochloric acid medium. By fitting a polynomial, analytic formulae of γ was gained. We calculated and discussed the special parameter of interfacial adsorption of liquid/liquid. Some regular patterns were found, for example: interfacial activity of the extracts was found to decrease in the order SAB-172 > TAB-194 > TOA, etc. The effect of organic additive, one-valence converse ion and temperature on the interfacial activity was studied. The salient feature of the extraction is probably that the actual complexation of gallium ion occurs at the interface. The thermodynamical data of micellization were calculated.

The structures of the extractants are:



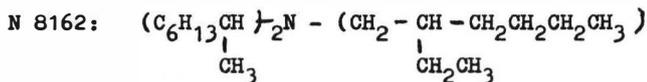
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The extraction of rhenate from hydrochloric acid, nitric acid and sulfuric acid medium by trialkylamine (N 8161) in heptane has been studied. The extraction percentage of rhenate is greater than 95% at the concentration range of acid from 0.02 N to 0.6 N. NaOH and NaClO_4 are used as back extractants. The composition of extracted species R_3NHReO_4 has been confirmed by slope method, equal molar series method and saturation method. At 10-50°C temperature, ionic strength $i=0.5$, enthalpy change of N 8161 extracting HReO_4 is 77.82 kJ/mol. At 25°C, $I=0.5$ the concentration equilibrium constants for HReO_4 , HNO_3 , HCl and H_2SO_4 were determined to be $3.98 \cdot 10^6$, $2.32 \cdot 10^5$, $3.31 \cdot 10^4$ and $2.21 \cdot 10^4$, respectively. The bonding properties between R_3NH and HReO_4 were studied by means of EHM method, and the results showed that ionic bond existed for R_3NHReO_4 , that is $(\text{R}_3\text{NH})^+(\text{ReO}_4)^-$.



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The extraction of rhenate from hydrochloric acid, nitric acid and sulfuric acid medium by trialkylamine (N 8162) in heptane has been studied. The extraction percentage is greater than 95% at the concentration range of acid from 1N to 0.05N. NaOH and NaClO₄ are used as back extractants. The composition of extracted species R₃NHReO₄ has been confirmed by slope method, equal molar series method, saturation capacity method and element analysis. At 10-50°C temperature, ionic strength I=0.5, enthalpy change of N 8162 extracting HReO₄ is 77.94 kJ/mol. At 25°C, I=0.5 the concentration equilibrium constants that HReO₄, HNO₃, HCl and H₂SO₄ are extracted were determined to be 2.82·10⁵, 4.53·10⁴, 4.76·10³, respectively. N 8162 and its extracted species show high thermal stability.



**ORGANIC
AND BIOORGANIC
PROCESSES**

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Liquid-liquid extraction technology for the recovery, separation and purification of organic compounds has been known for at least 70 years. In most cases the application of the technology was, and to a good measure still is, limited to the production of bulk chemicals. As none of these extraction processes involves chemical reactions, there was until recently little interest in the chemistry of the extraction process as applied to the usually low market-value organic products.

For the last decade or so there appears to be a renewed interest in the extractive technology as applied to organic compounds in general, and organic nonelectrolytes in particular. Examples are the separation and purification of speciality pharmaceuticals recovered from natural sources; the recovery of ethanol from biomass; the production of organic acids and other fermentation chemicals formed by bioconversion of glucose via metabolic intermediates; the fractionation among chemically similar solutes such as isomers, and others. In these and similar processes, liquid extraction is proposed as an alternative to existing separation processes such as distillation, esterification or precipitation. With the possible exception of the pharmaceutical industry, no extractive technology for organic chemicals based on chemical interaction appears to have been carried through to major industrial implementation.

It is our considered opinion that the development of a technologically viable cost-effective and energy-efficient process, the extractive recovery of organic chemicals must be based more on chemical sophistication than considerations of design and other engineering parameters. The experience accumulated for the last three decades on the application of solvent extraction to the inorganic field of hydrometallurgy and nuclear technology demonstrates the all-important role chemistry must play in the development of modern and efficient separation processes. For the extraction technology to penetrate the organic chemical industry, substantial improvements in the existing recovery and purification technology are needed.

The existing information on the chemistry and thermodynamics of

the transfer process of organic compounds and nonelectrolytes from water into an organic solvent or mixtures of a diluent and an extractant is rather limited both in scope and depth. Two earlier monographs, one on the extraction of organic compounds in general [1] and another restricted to phenols and their derivatives [2], cover the Soviet literature comprehensively. An extensive compilation of partition data of organic compounds covering the literature up to 1975 is included in a monograph [3] on correlation and semi-empirical prediction of distribution ratios in water - n-octanol systems. Our, more recent, reviews on the extraction of fermentation product carboxylic acids [4] and low-molecular weight aliphatic alcohols [5] summarize the state-of-the-art, and emphasize the need for a large body of reliable chemical and thermodynamic data. We submit that for a successful application of solvent extraction to the recovery and separation of organic compounds, the level of knowledge and understanding of the fundamental chemistry involved has to reach that on inorganic salts and complexes. A systematic collection of fundamental factual and numerical data is thus the order of the day.

The chemistry of extraction of most organic compounds and nonelectrolytes, but especially those which are liquid at room temperature, is complex and differs from that of inorganic salts and complexes in many respects. Most differences are associated with one or more of the following characteristics:

(i) State of the solute in the aqueous phase. While most ionic equilibria of dissociation, association, ion-pair and complex formation are reactions well understood in aqueous solutions and quantitatively expressed in terms of mass-action equilibria, the state of nonelectrolyte solutes in water and aqueous solutions is still far from being described quantitatively in terms of chemical reactions involving hydration, dissociation, aggregation or simple dimerization. Carboxylic acid semielectrolytes are the possible exception as for most their ionization constants are known.

As an example of the complexities involved is the state of alcohol solutes in water in general, and those water-miscible alcohols in particular. In spite of such simple solubility behavior, aqueous solutions of ethanol, for example, show abnormalities both in physical and thermodynamic properties. In descriptive terms, of course, the peculiarities of such solutions can be attributed to the dual character of the alcohol and to the simultaneously occurring competing reactions of hydrogen bonding. In the water-rich region, the ethanol-water mixture is characterized by a strong exothermic

enthalpy of mixing. Exothermicity reflects the "structure-breaking" effect of ethanol on the three-dimensional water structure. None of these effects are known well enough, certainly not to the extent that numerical values can be attached to the equilibrium constants of the assumed reactions.

(ii) State of the solute in the organic phase. In most cases the state of inorganic solutes in the organic phase composed of the extractant dissolved in a diluent is relatively simple. When the extraction is by virtue of salt or complex formation as in the case of chelating agents, phosphoric and carboxylic acids extractants, the organic phase species are mostly unhydrated and unsolvated. With the possible exception of the salts formed between simple or complex inorganic acids and alkylamine extractants, the organic phase species are nonassociated and mononuclear. The transfer process can usually be described by simple mass-action law equilibria and the relevant constants are known with good precision. In some more complicated inorganic systems in which the extraction is by virtue of solvation as in the case of neutral extractants such as ethers, ketones, or neutral phosphoric or carboxylic acid esters, the degree of solvation of the neutral and undissociated inorganic species is known in quantitative terms of solvate-formation constants.

The state of the nonelectrolyte solute in the organic phase is still only known in descriptive terms, in best of the cases. Taking again the example of alcohols, specifically that of the simple binary system of an alcohol in a normal alkane. These are the simplest conceivable systems suited for testing theories of ideally associated liquids: as the alkane is the ideally nonreacting component, any deviation from an ideal behavior must be governed by the alcoholic component alone. In spite of this apparent simplicity, the problem of alcohol selfassociation is far from being resolved. Hydrogen bonding produces varying extents of alcohol aggregates, defined in a number of different forms, and several association equilibria are superimposed upon each other. There is a stepwise formation of alcohol oligomers with small stepwise equilibrium constants -though large overall equilibrium constants-, and their quantitative determination with any degree of reliability is not trivial. In spite of many attempts [5] to identify the sizes of the oligomers and to evaluate the equilibrium constants there is little consensus regarding the state of alcohol solute, much less the numerical oligomerization constants.

(iii) Coextraction of water. In most cases the transfer of inorganic compounds via salt or complex formation, or via dipole-dipole interaction is not accompanied by water. As a matter of fact, water coex-

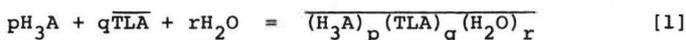
traction has no, or only marginal, effect on the chemistry of the partition process.

Not so in the extractive transfer of nonelectrolytes. As a rule, coextraction of water plays a dominant role, especially with water-soluble or water-miscible nonelectrolytes. In many cases, separation of the solute from water at the recovery end is very crucial. There is little economic incentive in an extractive separation process if it results only in a marginal enrichment of the water/solute ratio over that in the initial aqueous solution. In order to minimize the coextraction of water and to facilitate subsequent dewatering, significantly more attention is needed to understand factors affecting the transfer process of nonelectrolytes.

(iv) Overall extractability. As a very general observation, the extractability of nonelectrolytes from water is very low. A significant exception is that of carboxylic acids by alkylamines when the extracted species are the unionized, and possibly aggregated, alkylammonium salts of the acid. Taking again the example of the low-molecular weight aliphatic alcohols, typical distribution ratios into aromatic hydrocarbons are around 0.03 and less than 0.01 into aliphatic hydrocarbons. Extractability into reactive solvents, usually oxygen-bearing, such as tributylphosphate, higher aliphatic alcohols and phenol derivatives, is significantly higher, sometimes by as much as two orders of magnitude. In absolute terms, however, even that extractability is low when compared to that of inorganic compound and electrolytes. It is thus an important challenge to identify powerful extractants for nonelectrolytes.

Finally, we will discuss briefly a few examples to demonstrate the way in which distribution data for nonelectrolytes can be treated quantitatively. The first is that of extraction of carboxylic acids by long-chain trialkylamines dissolved in a diluent, and the other example discusses distribution data of lower alcohols between water and m-cresol extractant dissolved in hydrocarbon diluents.

Extraction of carboxylic acids. Citric acid, 2-hydroxypropane-1,2,3-tricarboxylic acid, with pK values of 3.13, 4.76 and 6.40 at 25°C is extracted from its aqueous solutions of constant ionic strength by tri-n-dodecylamine, TLA, dissolved in toluene. Vanura and Kuca [6] have measured distribution ratios of high precision as a function both of the acid concentration in the initial aqueous solution and that of the amine extractant in toluene in a wide concentration range. The extraction process



taken to represent the interaction between the components, has the equilibrium constant

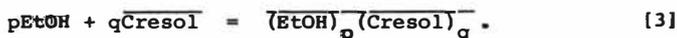
$$K_{p,q,r} = \frac{[(H_3A)_p(TLA)_q(H_2O)_r]}{[H_3A]^p [TLA]^q [H_2O]^r} \quad [2]$$

The stoichiometry of the extracted complex is determined from functions of the $\bar{q} = f(\bar{p})$ type, where \bar{q} and \bar{p} are the average values of the stoichiometric indexes q and p , using a suitable, rather simple, computer program. The experimental distribution data were best explained by the formation of five predominating complexes in equilibrium having the following p,q,r stoichiometries and equilibrium constants

$$\begin{aligned} \log K_{1,2,1} &= 1.17 \pm 0.22, \\ \log K_{2,3,2} &= 3.17, \\ \log K_{5,6,4} &= 8.39 \pm 0.05, \\ \log K_{5,6,5} &= 8.49, \\ \log K_{13,13,8} &= 19.14 \pm 0.013. \end{aligned}$$

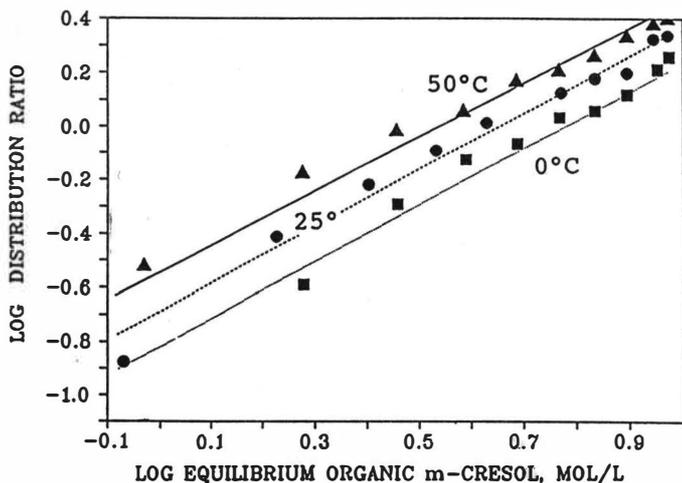
Along similar lines, the extraction of succinic acid, ethane 1,2-dicarboxylic acid, with dissociation constants 4.20 and 5.64 at 25°C, from its aqueous solutions into chloroform and methyl-isobutyl ketone solutions of Alamine 336, a C₈-C₁₀ trialkylamine, was recently studied [7]. A similar calculation procedure, though more restricted in the number of set of complexes taken into account, suggests that in chloroform the predominating complex is $p=q=1$ with the equilibrium constant of $\log K_{1,1} = 2.39$ at 25°C. In methyl-isobutyl ketone the best fit was obtained by assuming two complexes existing in equilibrium, one with the composition and constant of $\log K_{1,1} = 1.26$, and the other $\log K_{2,1} = 1.93$.

Extraction of alcohols. Quantitative information on the extraction of alcohols is very limited [5], their overall low extractability making it difficult to obtain experimental data with sufficient precision for quantitative treatment. Arenson [8] has measured the distribution ratio of ethanol from water to toluene solution of *m*-cresol as the extractant. The relative high distribution ratios were attributed to the formation of ethanol-cresol adduct according to the equilibrium



The straight line plots of the conventional slope-analysis method drawn with a unit slope, shown in Figure , indicate the stoichiometry

of $p=q=1$ of the extracted adduct. Very similar treatment has been recently reported for the extraction of four butanol isomers with *m*-cresol [9].



Distribution ratio of ethanol from 1 mol/L solution into toluene as a function of the extractant concentration at various temperatures

References

1. Korenman I.M.//Ekstraktsiya organicheskikh veshstv (Extraction of organic compounds). Gorkii, 1973.
2. Korenman Ya.I.//Ekstraktsiya Fenolov (Extraction of phenols). Gorkii, 1973.
3. Hansch C., Leo A.//Substituent constants for correlation analysis in chemistry and biology. New York: Wiley, 1979.
4. Kertes A.S., King C.J.//Biotechnol. Bioeng. 1986. Vol.28. P.269.
5. Kertes A.S., King C.J.//Chem. Rev. 1987. Vol. 87. P.687.
6. Vanura P., Kuca L.//Collec. Czech. Chem. Commun. 1976. Vol. 41. P.2857.
7. Tamada J.A.// Ph.D. Thesis, University of California, Berkeley.
8. Arenson D.R.// Ph.D. Thesis, University of California, Berkeley.
9. Arenson D.R., Kertes A.S., King C.J.// Submitted for publication.

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Fermentation processes for the production of carboxylic acids produce multi-component, aqueous solutions with product acid concentrations typically 10% w/w or less. Extraction of these acids from such aqueous solutions by long-chain, alkylamine extractants dissolved in organic solvents has been shown to be an effective separation process on the laboratory scale [1].

An industrial extraction process for recovery of low-volatility carboxylic acids would involve two main stages. The first is the extraction of the acid into the solvent to produce an acid-loaded extract and a relatively acid-free aqueous raffinate. The second stage transfers the acid from the solvent into the aqueous product and regenerates the solvent to be recycled to the extractor (see Fig. 1a).

A McCabe-Thiele diagram (Fig. 1b) outlines the process [2]. During the extraction stage, the equilibrium curve must lie above the operating relationship. A low solvent flow rate corresponds to a

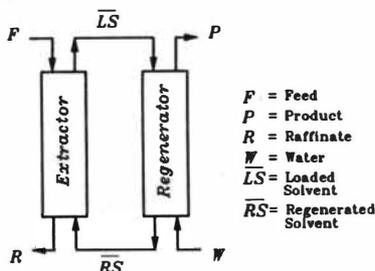


Fig 1a. Extraction-Regeneration Scheme for Recovery of Non-Volatile Carboxylic Acids into an Aqueous Product

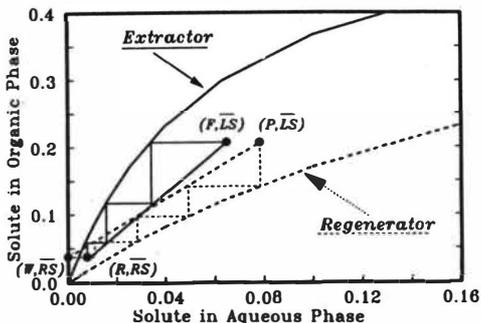


Fig 1b. McCabe-Thiele Diagram for an Extractor-Regenerator System

relatively large slope of the operating relationship. Thus high equilibrium distribution of acid into the solvent phase is necessary in order to achieve good product recovery at reasonable solvent flow rates. During regeneration, the situation is reversed--the equilibrium curve must lie below the operating relationship. The slope of the regenerator operating curve must be relatively small in order to achieve a reasonable product concentration. The equilibrium distribution of the acid into the organic phase must be low so that most the solute can be recovered from the solvent into an aqueous product of reasonable product concentration. Therefore, for a practical process, it is important to effect a downward shift in the equilibrium line between the extraction and regeneration stages.

Equilibrium Studies. Sets of batch experiments have been performed in which aqueous solutions of succinic acid of known concentration are equilibrated with organic solutions of Alamine 336 of known concentration. The experiments were carried out at various temperatures and in various diluents (organic solvents which dissolve the extractant). These systems have been characterized by a chemical modeling approach, in which p molecules of acid and q molecules of amine are assumed to react to form one or more acid-amine complexes:



Values of p, q, and the overall formation constant, A_{pq} , are obtained by fitting various stoichiometric models to experimental data. Previous experiments [3,4,5] have shown that the choice of diluent greatly affects both the stoichiometry and equilibrium constants of the reaction. Solvents designated as active diluents interact strongly with the complex and enhance extraction. Examples of these are hydrogen-bonding solvents such as chloroform or 2-ethyl-1-hexanol. Ketone diluents also enhance extraction and seem to promote the formation of complexes with a 2:1 acid:amine stoichiometry. Inert diluents, such as aliphatic hydrocarbons, are poor solvating agents for the complex and result in low distribution coefficients and possibly aggregate formation.

Temperature Swing Back-Extraction. Equilibrium experiments indicate that an increase in temperature decreases the loading of the extractant for carboxylic acid-amine systems. Miles Laboratories has developed a process for citric acid extraction based on this principle [6]. The acid is extracted at a low temperature, and regenerated at a higher temperature, with a change in temperature on the order of 60 C°.

Data showing the effect of temperature on the extraction of succinic acid by Alamine 336, a tertiary amine extractant, in methyl iso-butyl ketone (MIBK) and in chloroform are given in Figs. 2a and 2b, respectively. The equilibrium curves are significantly lowered by the temperature increase. However, a tangent pinch occurs midway along the operating curve for regeneration, due to the concavity of the equilibrium curve. This factor complicates design and limits the effectiveness of temperature swing.

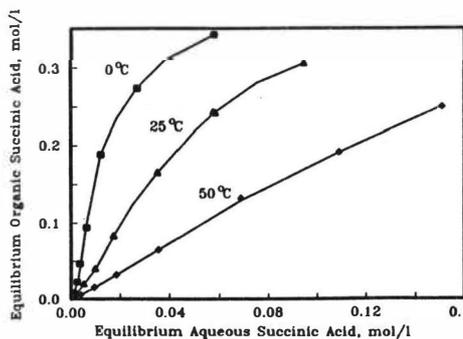


Fig 2a. Effect of Temperature on the Extraction of Succinic Acid by 0.3 mol/l Alamine 336 in MIBK

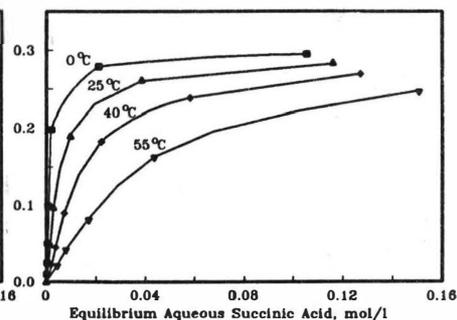


Fig 2b. Effect of Temperature on the Extraction of Succinic Acid by 0.3 mol/l Alamine 336 in Chloroform

Diluent Swing Back-Extraction. Another approach for shifting the equilibrium relationship between extraction and regeneration involves removal or addition of solvent prior to the extraction and regeneration stages [7]. The primary extraction is performed with high active diluent content in the solvent, so as to promote large distribution coefficients. The regeneration is performed with low active diluent content and relatively high inert diluent content in the solvent, so as to facilitate back-extraction of the solute into an aqueous product. In an example scheme (Fig. 3), the active diluent is distilled from the extract leaving the primary extractor, and is recycled to join the regenerated solvent leaving the regenerator.

Data for succinic acid extracted by Alamine 336 in a diluent composed of in varying ratios of chloroform (active) to n-heptane (inert) diluent are shown in Fig. 4. Removal of active diluent has a very strong effect on the equilibrium distribution of acid. The equilibrium line for regeneration is no longer concave downward. Thus the tangent pinch for the regeneration process is removed, or at least ameliorated.

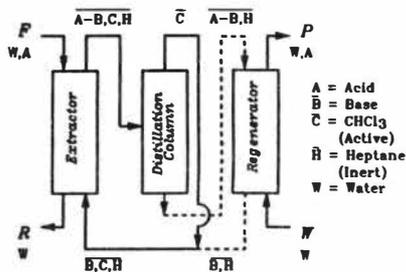


Fig 3. Diluent-Swing Process for Extraction-Regeneration of a Non-Volatile Acid. Dashed line indicates solvent with low active diluent concentration

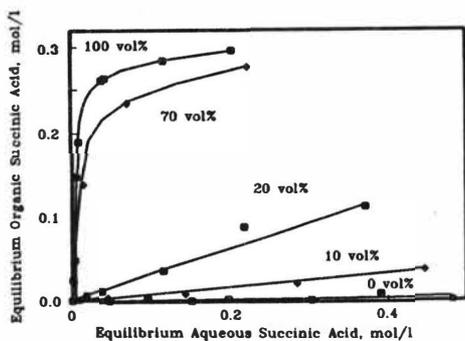


Fig 4. Effect of Active-Inert Diluent Ratio on the Extraction of Succinic Acid by 0.3 mol/l Alamine 336 in Chloroform-Heptane Mixtures. Volume percent of active diluent is indicated

Diluent change can be used in combination with temperature swing to compound the effects of both.

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References

1. Kertes A.S., King C.J.//Biotechnol. Bioeng. 1986. Vol.28. P.269.
2. King C.J.//Separation Processes. 2nd ed. New York; McGraw-Hill, 1980.
3. Vanura P., Kuca L.//Collection Czech. Chem. Commun. 1976. Vol.52. 1979. P.2857.
4. Manenok G.S., Korobanova V.I., Yudina T.N., Soldatov V.S.//Russ. J. Appl. Chem. 1979. Vol.52. P.156.
5. Tamada J.A., Kertes A.S., King C.J.//Preprints of ISEC '86. Vol.3. P.631.
6. Baniel A., Blumberg R., Hajdu K.//U.S. Patent 4,275,234. Jun.23, 1981.
7. Tamada J.A.//Ph.D. Dissertation in Chemical Engineering, University of California, Berkeley, 1988.

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Production of alcohols by fermentation results in dilute aqueous solutions from which the alcohol must be removed and concentrated. The cost of this separation process can be a substantial fraction of the value of the final product. In order for extraction to become attractive for the purification and concentration of ethanol, a solvent of sufficient capacity must be found. The solvent extraction chemistry of the lower aliphatic alcohols has recently been reviewed[1]. Equilibrium distribution ratios for ethanol are generally low. Some example values are listed in Table 1. The phenolic, m-cresol, provides a distribution ratio over twice as large as any other solvent listed, including the nonaromatic alcohols and the carboxylic acids. There is little chemical information concerning the interactions occurring in systems where lower alcohols are extracted by a polar solvent. However it is possible to use distribution data to determine some attributes of these systems, which may then be used to search for better solvents or conditions for extraction.

Table 1
Distribution ratios for ethanol, 25°C

<u>solvent</u>	<u>D</u>	<u>ref.</u>
m-cresol	2.17	*
quinoline	1.00	[2]
2-ethyl hexanoic acid	0.52	[3]
tributyl phosphate	0.54	[4]
2-ethyl hexanol	0.58	[4]
methyl i-butyl ketone	0.50	[3]
n-butyl acetate	0.34	[4]
chloroform	0.13	*
toluene	0.08	*

* - this work

In this work, phenols were investigated as extractants giving higher capacity for ethanol. m-Cresol was used in investigating some properties of the complex formed between the alcohol and the phenolic extractant.

Figure 1 shows typical data for extraction of ethanol from dilute aqueous solutions at 25°C, by various phenols with toluene as the diluent. Other diluents (xylene, dibutyl ether) were used in two cases, as indicated. Distribution ratios are reported in concentration

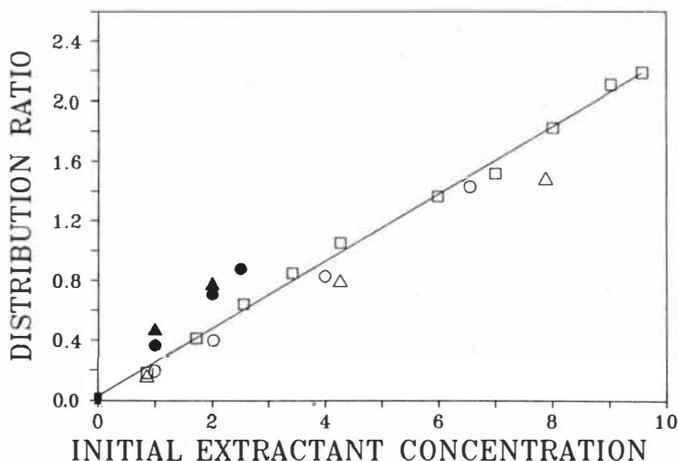


Fig. 1. Ethanol distribution ratio vs. initial organic extractant concentration in mol/l for various different phenols in toluene except where noted, at 25°C; m-cresol (□), 4-t-butyl catechol/dibutyl ether (▲), 2,4-xlenol/xylene (○), cumyl phenol (△), 4-n-hexyl resorcino¹ (●)

units. There is little effect of additional substituent groups onto the aromatic ring of the monohydroxy phenolic extractants. The extra hydroxy group of the catechol and resorcinol provides some additional capacity. The distribution ratio appears to be a nearly linear function of the extractant concentration. With other diluents, the relationship between distribution ratio and extractant concentration changes as shown in Figure 2. This difference is a result of several

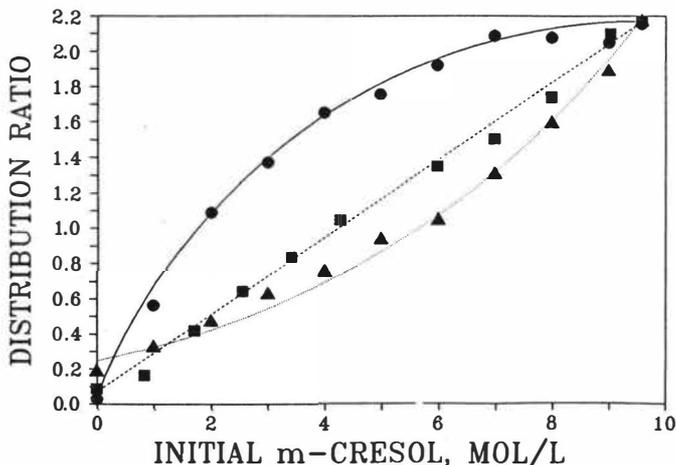


Fig. 2. Measured distribution ratios for ethanol vs. initial organic m-cresol concentration for different diluents, at 25°C; in toluene (■), in chloroform (●), in n-butyl acetate (▲)

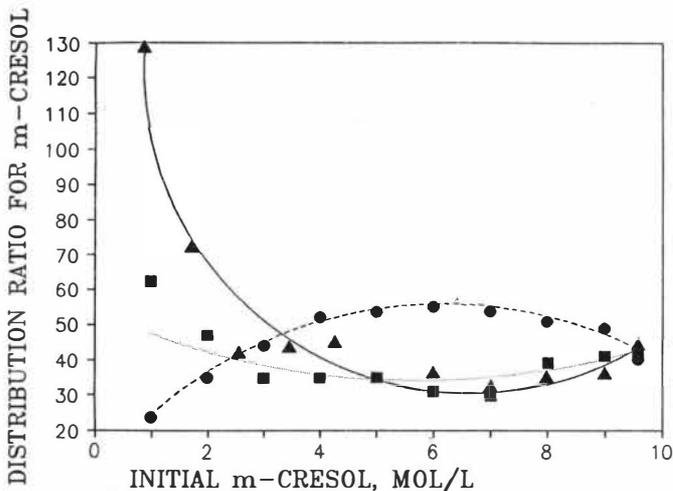


Fig. 3. Distribution ratio for m-cresol during ethanol extraction vs. initial organic m-cresol concentration for different diluents, at 25°C; in toluene(■), in chloroform(●), in n-butyl acetate(▲)

competing interactions between the diluent, solute and solvent. Among these are: competition between the diluent and the solute for the solvent, change in dimerization constant in different diluents and solvation of the ethanol-cresol complex. A complimentary effect is seen on the distribution ratio of m-cresol for the same systems in Figure 3. Previous investigations[3] have shown that high distribution ratios are accompanied by low separation factors for ethanol versus water. A similar inverse relationship is seen for the mixed solvents.

From the distribution data in Figure 4 at various temperatures in toluene, estimates can be made of the stoichiometry and stability of the complex. The interaction between ethanol and m-cresol can be expressed as a heterogeneous complexation equilibrium:



$$K_{n,m} = \frac{[E_m C_n]_o}{[E]_a^m [C]_o^n} = D [C]_o^{-n} \quad (2)$$

in which $K_{n,m}$ is the heterogeneous complexation constant; $[E]_a$, $[C]_o$ and $[E_m C_n]_o$ are the concentrations in mol/l of the aqueous ethanol, organic m-cresol and ethanol/m-cresol complex respectively; and D is the distribution ratio, with concentrations in mol/l. The stoichiometry of the complex can be ascertained by the slope-analysis method. Alternately, the complexation constant for a homogeneous

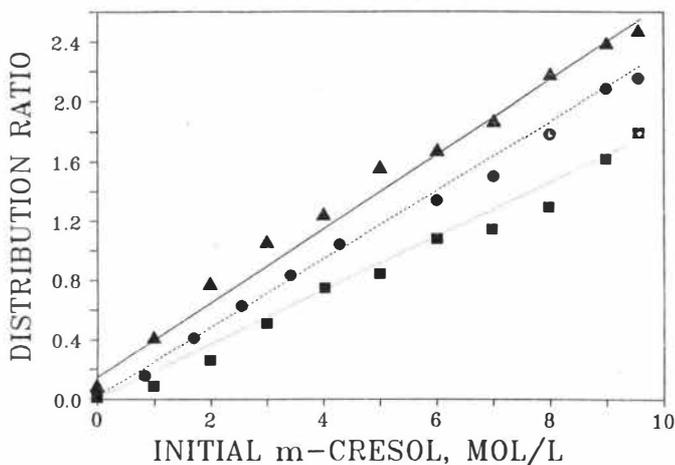


Fig.4. Ethanol distribution ratio vs. initial organic m-cresol concentration at different temperatures; 0°C(■), 25°C(●), 50°C(▲)

equilibrium can be calculated using the activity coefficients of ethanol in addition to the distribution data:



$$K = \frac{[EC]_o}{[E]_{o,free}[C]_o}, \quad (4)$$

where K differs from $K_{n,m}$ in that $[E]_a$ is replaced by $[E]_{o,free}$, the concentration of non-complexed ethanol in the organic phase (i.e. $K_{n,m} = K * K_e$ where K_e is the distribution ratio between aqueous ethanol and non-complexed organic ethanol). This assumes a 1:1 complex between ethanol and m-cresol and that the m-cresol in the aqueous phase does not affect the aqueous activity coefficient of ethanol. From these two sets of complexation constants, enthalpies of interaction can be calculated. The calculated enthalpies are all of the same magnitude as those measured for the dimerization of alcohols[5].

References

1. Kertes A.S., King C.J.//Biotechnol. Bioeng. 1986. Vol.28. P.269.
2. Feldman J.//U.S. Patent N 4,346,241. 1982.
3. Munson C.L., King C.J.// Ind. Eng. Chem. Proc. Des. Dev. 1984. Vol.23. P.109.
4. Roddy J.W.//Ind. Eng. Chem. Proc. Des. Dev. 1981. Vol.20. P.104.
5. Joesten M.D., Schaad L.J.//Hydrogen Bonding. 1974. Marcell Dekker. New York.

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In many important processes nonelectrolytic organic solutes distribute between water and either polar or nonpolar organic solvents that are essentially immiscible with water. Such processes include industrial processes for the recovery, separation, or purification of such organic solutes as drugs, pesticides, other pollutants, etc. But also natural processes that involve the transfer of certain chemicals through lipid membranes, as occur in anesthesia or toxicity phenomena, are based on such distributions. Finally, very efficient HPLC processes for the separation and analysis of organic substances are also based on their distribution between aqueous phases and organic phases.

It would therefore be of great value if a general method were available to predict the distribution ratios of organic solutes between water and organic solvents. Such predictions are now feasible, based on a multivariable approach, that has been developed in recent years, and has been applied very successfully to such quantities as the solubility of organic solutes in water [1,2], or their distribution between a typical organic solvent, 1-octanol, and water [3].

An extensive set of distribution ratios K_{OW} of organic solutes has been collected by Leo and Hansch [4], involving both small organic solutes, with up to 10 carbon atoms, and larger ones, such as certain drugs, and both nonpolar and polar organic solvents. The predictive method described above requires independent knowledge or valid estimates of certain parameters for properties of the solutes, as detailed below. These parameters are known or can be estimated so far for hundreds of monofunctional aliphatic and up to bifunctional aromatic solutes with up to 10 carbon atoms. Thus a data base of about 1500 distribution ratio data, that involves 25 water-immiscible essentially 'dry' solvents and 7 'wet' solvents (that have water contents at a mole fraction >0.13) has been obtained from this compilation and analyzed as follows. The data are valid for 25 °C and infinite dilution of the solute in the two-phase system.

The data for the dry solvents involving the solutes (subscript 2) and solvents (subscript 1) were fitted to the following equations:

$$\log K_{OW} = A_V \cdot (V_2/100) \cdot \Delta \delta_{H1}^2 + A_\pi \cdot \pi_2 \cdot \Delta \pi_1 + A_\alpha \cdot \alpha_{m2} \cdot \Delta \beta_1 + A_\beta \cdot \beta_{m2} \cdot \Delta \alpha_1$$

$$\log K_{OW} = A_V' \cdot (V_1/100) \cdot \Delta \delta_{H1}^2 + A_\pi' \cdot \pi_2 \cdot \Delta \pi_1 + A_\alpha' \cdot \alpha_{m2} \cdot \Delta \beta_1 + A_\beta' \cdot \beta_{m2} \cdot \Delta \alpha_1$$

The A's are fitting coefficients, V and V_I are the molar and intrinsic volumes, δ_H is the Hildebrand solubility parameter, π^* and π are the ^{13}C NMR and solvatochromic polarity/ polarizability parameters, α is the solvatochromic hydrogen bond donating ability, β is the corresponding hydrogen bond accepting ability (or electron pair donating ability), and subscript m denotes the monomeric solute, in the case that the solute is self-associating. The differences Δ pertain to the parameter for the solvent minus that for water.

Table 1. The fitting coefficients A_π for 'dry' solvents

Solvent	A_π Solvent	A_π Solvent	A_π
cyclohexane	0.36 benzene	-1.62 chloroform	-1.23
n-hexane	-0.14 toluene	-1.38 bromoform	-1.17
n-heptane	-0.44 xylene	-0.42 nitrobenzene	*
n-octane	0.03 CCl_4	-0.12 diethylether	-0.41
trimethylpentane	0.20 dichloroethane	-4.13 diisopropylether	-0.80
n-decane	0.17 chlorobenzene	-1.62 hexone	-3.00
n-dodecane	* bromobenzene	-2.78 ethylacetate	-1.97
n-hexadecane	-0.13 o-dichlorobenzene	3.25 butylacetate	-1.75
		isopentylacetate	-1.44

* Too few data for these solvents to give meaningful A_π values.

These expressions yielded sets of coefficients A_V , A_α , and A_β or A_V' , A_α' and A_β' that were independent of the solvents, including aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, ethers and esters, and nitrobenzene. In the cases of the ethers and esters, the differences $\Delta\beta_1$ are essentially zero, hence the term in α_{m2} was omitted. The A_π coefficients differed for the various solvents (see below), but the A_π' coefficients were nearly independent of them. No independent terms were included in the regressions, in order to have the minimal number of fitting constants. The average values found for the coefficients were $A_V = -1.79 \pm 0.15 \text{ (J/mol)}^{-1}$, $A_\alpha = 7.07 \pm 0.61$, and $A_\beta = 4.96 \pm 0.36$, for 1040 data points, ranging in $\log K_{ow}$ from -2.5 to +3.5, with an average standard deviation of the fit of 0.17 and an average correlation coefficient of 0.992. The values of A_π are listed in Table 1. The second expression yielded $A_V' = 3.32 \pm 0.21 \text{ (J/mol)}^{-1}$, $A_\pi' = 2.3 \pm 0.4$, $A_\alpha' = 4.6 \pm 0.2$ and $A_\beta' = 7.3 \pm 0.3$ for 738 data points tested for 17 solvents, with an average standard deviation of 0.13 and an average correlation coefficient of 0.995. Predictions for 'dry' solvents can be made with known values of their parameters δ_{H1} , π^*_1 , β_1 , and α_1 , the above listed coefficients.

A sufficient amount of data have been found in the compilation [4] for the distribution of solutes between water and certain 'wet' solvents: tri-n-butyl phosphate and alcohols from butanol to decanol. For these solvents, that have water mole fractions >0.13 in their water-saturated states, the values of the solvent parameters are not known, since they are expected to differ from those of the solvents in the neat state. Therefore the alternative equation:

$$\log K_{ow} = A_v' \cdot V_2 / 100 + A_\pi' \cdot \pi^* \cdot 2 + A_a' \cdot \alpha_{m2} + A_\beta' \cdot \beta_{m2}$$

was used for correlations, again with correlation coefficients >0.99 , average standard deviations of the fit of 0.11 for 320 data points in the above-mentioned range of $\log K_{ow}$. The A coefficients are shown in table 2. For the higher alcohols, the A_v' do yield nearly the average

Table 2. The fitting coefficients A for 'wet' solvents

Solvent	A_v'	A_π'	A_a'	A_β'
tri-n-butyl phosphate	2.62	0.40	-0.48	-2.19
1-butanol	2.47	-2.13	-0.14	-2.21
2-methyl-1-propanol	2.23	0.22	-0.12	-2.49
1-pentanol	2.79	0.03	0.21	-3.38
1-hexanol	3.00	0.09	-0.30	-3.19
1-octanol	3.15	-0.13	0.27	-4.24
1-decanol	3.22	0.16	-0.09	-4.00

A_v' value given above (-1.79) when divided by $\Delta\delta_{H1}$ for the neat solvents but not for the butanols or tri-n-butyl phosphate. The A_π' and A_a' values are hardly larger than twice their standard deviations, and are of low significance (except A_a' for tri-n-butyl phosphate). The apparent $A\beta$ values obtained by dividing the A_β' values by $\Delta\alpha_1$ of the neat solvents are not constant. They increase from 5.5 for butanol to 9.9 for octanol, and are higher than the average A_β (4.96) for the dry solvents. The effect of water in the 'wet' solvents thus seems to be to decrease their hydrogen bonding donation ability, by itself being hydrogen-bonded to them.

The coefficients for the hydrogen bonding terms (for the 'dry' solvents), A_a and A_β , can be used for the estimations of the basicity of anions and the acidity of cations on the same scale as is generally applicable to non-electrolytic organic substances. The α_2 values for

cations range from 5.5 for Cu^{2+} to 2.3 to Hg^{2+} and from 2.2 for Li^+ to 0.5 for Cs^+ , ordered roughly in the same manner as their hydrolysis constants. The β_2 values for anions range from 3.2 for fluoride to 0.1 for perchlorate, indicating their relative hydrogen bond acceptances.

References

1. Kamlet M.J., Doherty R.M., Abraham M.H., Carr P.W., Doherty R.F., Taft R.W.//J. Phys. Chem. 1987. Vol. 91. P. 1996.
2. Kamlet M.J., Doherty R.M., Taft R.W., Abraham M.H., to be published, 1987.
3. Kamlet M.J., Abraham M.H., Doherty R.M., Taft R.W.//J. Am. Chem. Soc. 1984, Vol. 106. P. 464. Further paper to be published.
4. Hansch C., Leo A. Substituent constants for correlation analysis in chemistry and biology, Wiley-Interscience, 1979, and unpublished data compilation, 1983.

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The present paper suggests a process for the extraction of citric acid from fermentation broth with N,N-disubstituted alkyl amides produced from the fusel oil. Fusel oil is composed of approximately 80% amyl alcohol, 15% butyl alcohol and 5% other alcohol.

Disubstituted amides are to be expected strong extractants.

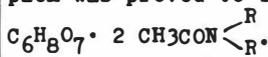


The contribution of (II) should not only weaken the carbonyl bond but should also increase the availability of the electrons of the oxygen atom for bond formation. A systematic investigation of the use of N,N-disubstituted alkyl acetamide as an extractant for the extraction of citric acid has been studied.

Table 1. Extraction of citric acid with N,N-disubstituted alkyl amides

Extractant	Distribution ratio
$\text{CH}_3\text{CON}(\text{C}_4\text{H}_9)_2$	1.85
$\text{CH}_3\text{CH}_2\text{CON}(\text{C}_3\text{H}_7)_2$	1.57
$\text{CH}_3\text{CH}_2\text{CON}(\text{C}_4\text{H}_9)_2$	1.10
$\text{CH}_3(\text{CH}_2)_2\text{CON}(\text{C}_4\text{H}_9)_2$	1.02
$\text{CH}_3\text{CON}(\text{C}_8\text{H}_{17})_2$	0.724
$\text{CH}_3\text{CON}(\text{C}_{11}\text{H}_{23})_2$	0.640
$\text{CH}_3\text{CON}(\text{C}_{13}\text{H}_{27})_2$	0.112
$\text{CH}_3(\text{CH}_2)_6\text{CON}(\text{C}_4\text{H}_9)_2$	0.106

By using logarithm plot and continued variate method, the composition of extracting complex was proved to be



Because of the requirement of low solubility in water, we selected $\text{CH}_3\text{CON}(\text{C}_5\text{H}_{11})_2$ replaced of $\text{CH}_3\text{CON}(\text{C}_4\text{H}_9)_2$, and compared its physical properties with tributylphosphate (TBP) and trialkylphosphine oxide (TRPO).

The LD 50 values of acetamides are much larger than those of neutral organophosphorus extractants, e.g. LD 50 value of acetamide is 10300 mg/kg, whereas those of TBP and TRPO are 3000 and 3370 mg/kg respectively.

Table 2. Determination of the mole ratio of DPAA to citric acid by equimolar method

$\text{C}_{\text{DPAA}}/\text{C}_{\text{H}_3\text{A}}$	1/1	2/1	3/1	4/1	5/1
$(\text{H}_3\text{A})_{\text{org}} \text{ (M)}$	0.406	0.563	0.548	0.541	0.539

Plots of $\log D$ versus $1/T$ gave a straight line. From the slope, ΔH was found to be -11.5 kJ/mol (DPAA), -15.9 kJ/mol (TRPO) and -21.4 kJ/mol (TBP) respectively. Citric acid can be conveniently recovered from the amide phase by back extraction with water. The extraction process is exothermic, so the extraction is favorably carried out at lower temperature ($10-20^{\circ}\text{C}$) and strippings at higher tem-

Table 3. The extracting power and physical properties of DPAA, TBP and TRPO

Extractant	Molecular Weight	Density d_4^{25}	Refractive Index n_D^{25}	Solubility in water	Distribution ratio (25°C)
DPAA	199	0.847	1.4495	0.032 0.322	1.71
TBP	266	0.973	1.4223	0.42	0.924
TRPO	312	0.877	1.4630	0.09	11.5

Table 4. The Comparison of Toxic Effects of extractants

LD 50 mg/kg	Acetamide	N-503	DPAA	TBP	TRPO
	10300	8200	--	3000	3370

Table 5. Diluent selection $C_{H_3A}=0.593$ M, extractant/diluent=2/1

Extractant	Distribution ratio				
	kerosene	butyl butyrate	ethyl butyrate	MIBK	n-hexane
DPAA	0.526	0.703	0.691	0.830	0.497
TBP	0.382	0.386	0.431	0.503	0.354
TRPO	2.63	2.92	2.86	2.86	2.64

perature ($60-70^{\circ}\text{C}$). Provided that a proper value of distribution ratio is adjusted by adding sweet odor diluent-butyl butyrate. The emulsification is destroyed by adding the active carbon power and suitable amounts of sodium chloride at 80°C . The extraction percentage can be attained 96.6% by five stages of counter-current extraction and back extraction required to reach high percentage recovery 99% by 60°C water at ten stages. Considering an extractant for industrial purposes, it must have a low price and high availability such as low toxicity, low solubility in water, low viscosity and high extracting power. We suggest to use N,N-disubstituted alkyl amides produced from fusil oil as an extractant and kerosene 260 as diluent for citric acid.

References

- Jing Yu-Ming, Li Dao-chen, Su Yuan-Fu.// ISEC'83, Denver, Colorado, USA, 1983. P. 517.
- Richard J. Lewis, Sr., Rodger L. Tatker. Registry of Toxic Effects of Chemical Substances. 1978. P. 3.

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The principle of linear free-energy relationship (LER) is widely applied for description of anion-exchange extraction by salts of higher quaternary ammonium bases (QAB) [1]:

$$\Delta G_{A_{st}^{A_i}}^{A_i} = a(\Delta G_h^{A_{st}} - \Delta G_h^{A_i}) \quad \log K_{A_{st}^{A_i}} = a'(\Delta G_h^{A_i} - \Delta G_h^{A_{st}}) \quad (1-2)$$

where A_i and A_{st} are the investigated and standard anions respectively; a and a' are the coefficients dependent on the solvent nature and independent of the anion nature.

As is seen from Fig.1, this dependence takes place for a number of simple mineral anions though the extractibility of SCN^- -ion is much higher than it is to be expected from its hydration energy [2]. Besides, hydration energies of this anion calculated using the LER principle appear to be different for different solvents of QAB. The main reason for such behaviour of the SCN^- -ion is a change of its position in the extractibility series, with different QAB solvents being used. Organic anions exhibit even more abrupt disturbances in the extractibility series. Fig.2.

The authors of [3] have found that diphyll anions, possessing an ionogenic group (alkylsulphates, alkylsulphonates, alkylcarboxylates) along with a hydrophobic moiety, do not obey the LER principle. This is explained by the fact that an increase of an ion size at the expense of uncharged hydrophobic groups and atoms results in a sudden increase of its extractibility and affects slightly its hydration energy. Thus, the hydration free energy of an organic anion, with a radical being increased only by one CH_2 -group, increases by 0,69 kJ/mol [4]. At the same time for the majority of solvents the free exchange energy of an anion decreases in this case by 3,64 kJ/mol, i.e. more than 5-fold decrease of the exchange energy exceeds an increase of the hydration energy.

An increase of the hydration energy with transition from Cl^- to ClO_4^- -anion due to a decrease in a charge density is rather essential and amounts to 121,3 kJ/mol [2]. But a decrease of the exchange energy, with toluene being used as a QAB solvent, equals only 30,2 kJ/mol, i.e. it is smaller by a factor of 4.

In that way contributions of ionogenic and hydrophobic groups of anions to the extraction free energy are ambiguously correlated with the hydration free energy in an aqueous phase. Therefore, application

of the LER principle to diphyl anions encounters difficulties, but separate application of the LER principle to ionogenic and hydrophobic groups of diphyl ions seems to be promising.

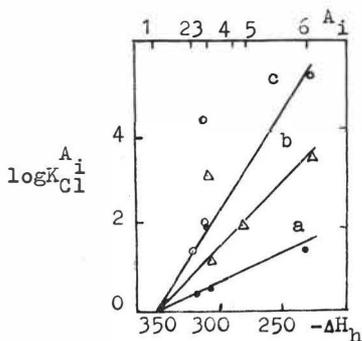


Fig. 1. Correlation $\lg K_{Cl}^{A_i} - \Delta H_h$ for mineral anions. QAB solvent: a-heptyl alcohol; b-chloroform; c-toluene. Anions: 1 - Cl^- , 2 - Br^- , 3 - SCN^-, NO_3^- ; 4 - ClO_3^- , 5 - I^- , 6 - ClO_4^-

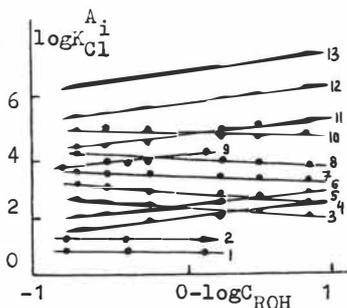


Fig. 2. The effect of heptyl alcohol concentration on $\lg K_{Cl}^{A_i}$. Anions: 1 - $CH_3OSO_3^-$, 2 - $C_2H_5OSO_3^-$, 3 - $C_6H_{13}COO^-$, 4 - $C_6H_5SO_3^-$, 5 - $C_7H_{15}COO^-$, 6 - $CH_3C_6H_4SO_3^-$, 7 - $C_8H_{17}COO^-$, 8 - $C_9H_{19}COO^-$, 9 - $(C_3H_7)_2NCH_2C_6H_4SO_3^-$, 10 - $C_{11}H_{23}COO^-$, 11 - $C_8H_{17}OSO_3^-$, 12 - $C_{10}H_{21}OSO_3^-$, 13 - $C_{12}H_{21}OSO_3^-$

One may suppose that an ionogenic group of a diphyl ion behaves like inorganic anions in the extraction system. This assumption allows simple evaluation of hydration energies of organic diphyl anions and their extractibility, using the additivity principle, by the following equations:

$$\Delta G_h^{A_i} = \Delta G_h^* + \sum I_h^i \quad (3)$$

$$\Delta G_h^* = \Delta G_h^{A_{st}} - 1/a \cdot \Delta G_{A_{st}ex}^* \quad (4)$$

$$\Delta G_{A_{st}ex}^* = \Delta G_{A_{st}ex}^{A_i} - \sum I_{ex}^i \quad (5)$$

$$\log K_{A_{st}}^{A_i} = a' (\Delta G_h^* - \Delta G_h^{A_{st}}) + \sum I_{ex}^i \quad (6)$$

where I_{ex} and I_h are the increments of groups to the extraction free energies and hydration energies, the sign (*) denotes an ionogenic group.

An advantage of the approach proposed lies in the fact that the

number of kinds of ionogenic groups at the great amount of organic anions is small. Table 1 lists their exchange constants per Cl^- -ion for QAB in toluene solutions and their appropriate hydration energies

Table 1. Increments of ionogenic groups to log exchange constants and their hydration energies for QAB in toluene solutions being used

Ionogenic group	$-\text{COO}^-$	OSO_3^-	SO_3^-
$\lg K_{\text{Cl}}^*$	-2,2	0,92	0,80
$\Delta G_h, \text{kJ/mol}$	-383	-315	-318

Application of the suggested approach is restricted to anions, the contributions to hydration energies for whose moieties are known. Predominantly, these are homologues of organic acids. For anions containing the moieties with unknown hydration energies, another approach is suggested. It has been found out that slopes of bilogarithmic dependences $\lg K_{\text{Cl}}^A - \lg K_{\text{ROH}}^A$ for non-diphyl ions and inorganic groups of organic ions have a linear correlation with their hydration energies (Fig.3). It is probably due to rather similar mechanisms of anions solvation by alcohol and their hydration.

The correlation is of the form:

$$-\Delta G_h^A = 328 + 91,2 \text{ tg} \alpha_i \quad (7)$$

Table 2. The values of $\lg K_{\text{Cl}}^A$ for QAB in toluene and hydration energies of organic anions and SCN^- -ion calculated by different methods (kJ/mol)

Anions	$\lg K_{\text{Cl}}^A$	$\text{tg} \alpha_i$	$\Delta G_h(2)$	$\Delta G_h(3)$	$\Delta G_h(7)$
$\text{CH}_3\text{OSO}_3^-$	1,89	0,17	-293	-314	-345
$\text{C}_2\text{H}_5\text{OSO}_3^-$	2,35	0,06	-283	-313	-335
$\text{C}_4\text{H}_9\text{OSO}_3^-$	3,58	-0,13	-255	-312	-317
$\text{C}_6\text{H}_{13}\text{OSO}_3^-$	4,90	-0,14	-225	-310	-316,5
$\text{C}_6\text{H}_{13}\text{COO}^-$	1,73	0,17	-297	-379	-345
$\text{C}_7\text{H}_{15}\text{COO}^-$	2,33	0,19	-283	-378	-347
$\text{C}_{17}\text{H}_{35}\text{COO}^-$	8,20	0,42	-150	-371	-368
$\text{C}_6\text{H}_5\text{SO}_3^-$	2,62	-0,37	-276	\approx -318	-296
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$	3,21	-0,36	-264	\approx -317	-296
$(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_4\text{SO}_3^-$	3,72	-0,28	-251	\approx -318	-304
$\text{C}_6\text{H}_3(\text{NO}_2)_2\text{O}^-$	6,10	-1,06	-197	\approx -247	-233
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}^-$	8,24	-1,47	-151	\approx -197	-195
Methyl red	3,32	0,30	-259	\approx -393	-357
Methyl orange	6,20	-0,30	-197	\approx -330	-302
Butyl orange	9,68	-0,50	-163	\approx -330	-284
SCN^-	4,18	-0,43	-241	-	-290

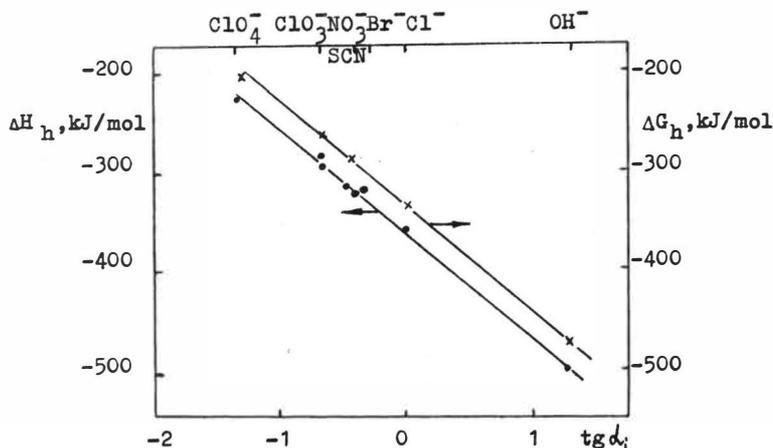


Fig.3. Correlation $\Delta G_h - \text{tg}\alpha_1$ and $\Delta H_h - \text{tg}\alpha_1$ for inorganic anions

As it is seen from Table 2, the hydration energies of anions - homologues, calculated by two suggested methods, are rather close and markedly lower than those calculated by Eq.(2). Only for anions with a delocalized charge (picrate-ions) the hydration energies calculated by all the discussed methods are close. Characteristically, the value of ΔH_h for the SCN^- -ion calculated from their correlation $\Delta H_h - \text{tg}\alpha_1$ practically coincides with available data produced by the non-extraction method [2] .

The suggested method allows to predict the extractibility of organic anions by QAB solutions in different organic solvents by their hydration energies.

References

1. Schmidth V.S. Extraction by Amines. Moscow:Atomizdat Press, 1980.
2. Izmailov N.A. // Electrochemistry of Solutions. Moscow:Khimia Press, 1976.
3. Rakhman'ko E.M., Starobinets G.L. et al. // Zh. fiz. khim. 1987. Vol.61.P.932.
4. Kakovsky M.A. // Proc. of the Institute of Mining Engineering. 1956.Vol.3.P.255.

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The studies of the salt addition effect on distribution of organic substances in water-organic solvent systems have revealed that concentrated zinc chloride and bromide solutions strongly extract lower homologs of organic electron-donating substances (alcohols, ketones, ethers, etc.). It has also been found that concentrated zinc and aluminium halide solutions in polar organic solvents form two-phase systems including aliphatic hydrocarbons with still higher extraction of electron-donating substances. Mineral salts being known to salt out organic substances [1,2], this phenomenon was thoroughly investigated.

The work is also aimed at studying the relation between the structure of concentrated zinc halide solutions comprehensively dwelt on a high level in [3,4] and the extraction power of these solutions.

These works have offered direct evidences that in concentrated solutions $ZnHal_2$ molecules form linearly polymerrized clusters with tetrahedral complexes $ZnHal_4^{2-}$, in which each zinc ion is surrounded by $4Hal^-$ ions and Hal^- -ion interacts with two zinc ions, being their elementary links.

Distribution of different organic substances between octane and solutions of the above salts in water, lower alcohols, acetone, ethylacetate, etc. has been studied as well as some physico-chemical properties of these solutions (density, viscosity, electrical conductivity, etc.).

The viscosity and electrical conductivity data so obtained confirm the data of [3,4].

The experimental interphase distribution constants (P) of electron-donating substances are additive quantities allowing one to consider the salt effect as that of hydrocarbon radical and of functional groups.

Extraction is stronger as salt concentration grows (Table 1). For fixed salt concentration, salination is especially strong for higher homologs in the diethyl ether > propanol > acetone ~ ethylacetate > methanol series which is bound up with decreasing CH_2 -group increment.

In the case of organic nonelectrolytes of different classes, the distribution constant is determined by the functional group nature. The distribution constants were the lowest for alcohols and sulfoxides due to low functional group increments.

Table 1. Decyl alcohol distribution constants and group increments in extraction octane - zinc bromide solution systems for different solvents

C_{ZnBr_2} , mol/l	Acetone			Propanol			Methanol		
	I_{CH_2}	I_{OH}	P	I_{CH_2}	I_{OH}	P	I_{CH_2}	I_{OH}	P
6.4	0.16	-3.37	0.019	0.12	-3.51	0.005	0.26	-4.25	0.025
5.0	0.16	-3.26	0.023	0.11	-3.12	0.010	0.22	-3.61	0.043
4.0	0.15	-3.02	0.035	0.10	-2.79	0.017	0.21	-3.31	0.072
2.0	0.11	-2.08	0.121	0.08	-2.25	0.039	0.17	-2.36	0.236

Table 1 (end)

C_{ZnBr_2} , mol/l	Diethyl ether			Ethyl acetate		
	I_{CH_2}	I_{OH}	P	I_{CH_2}	I_{OH}	P
6.4	-	-	-	0.16	-3.36	0.018
5.0	0.08	-2.29	0.036	0.15	-3.10	0.030
4.0	0.08	-2.09	0.048	0.13	-2.57	0.055
2.0	0.04	-1.24	0.140	0.08	-1.39	0.250

The increments of methyl, methylene and polar groups of Table 2 can be used to predict distribution constants and separation factors of organic substances differing in the nature of functional groups.

As for the ability to extract electron-donating organic nonelectrolytes, the salt phase of the above extraction systems greatly exceeds any polar phase used for separation. In concentrated nonaqueous salt solutions the value of I_{OH} achieves -4,0 and under while in the systems octane - water and ethanol, water and propanol mixtures, dimethylformamide, dimethylsulfoxide or water, the values of I_{OH} are, correspondingly, -1,38, -1,52, -1,76, -2,31 and -3,30. It can easily be seen that high extraction power of salty solutions owes to very low values of polar group increments at moderate- CH_2 -group increments (0,10-0,30).

The results were used to develop the separation and decontamination technique for organic nonelectrolytes of different classes.

Table 2. Functional group increments in distribution constant logarithm of extraction octane - aqueous and methanol zinc bromide solution systems

Methanol zinc bromide solutions								Aqueous zinc bromide solutions			
C_{ZnBr_2} mol/l	I_{CH_2}	I_{OH}	$I_{O<}$	$I_{C=O}$	$I_{C\leq O}$	$I_{S<}$	$I_{S=O}$	C_{ZnBr_2} mol/l	I_{CH_2}	I_{OH}	$I_{C=O}$
6.0	0.26	-4.26	-2.42	-3.10	-2.88	-2.91	-7.25	9.1	0.89	-6.46	-5.77
5.0	0.21	-3.61	-1.59	-2.47	-2.05	-1.81	-6.64	7.6	0.72	-4.89	-4.24
4.0	0.21	-3.31	-1.27	-2.22	-1.81	-1.25	-6.30	5.8	0.61	-3.79	-3.05
3.0	0.18	-2.78	-0.97	-1.86	-1.43	-0.87	-5.23	3.9	0.60	-3.45	-2.82
2.0	0.16	-2.37	-0.76	-1.57	-1.27	-0.46	-4.34	1.9	0.59	-3.33	-2.41
0	0.11	-1.79	-0.73	-1.13	-1.04	-0.34	-2.32	0	0.60	-3.52	-2.45

Production of higher alcohols by paraffine oxidation gives the mixture of those products. This mixture can be separated by the extraction system consisting of petroleum ether and zinc halide solution in lower alcohol or aluminium bromide in acetonitril. The purity of end products constitutes 98,8 to 99,9 per cent.

In production of halide alkyls from alcohols and PI_3 , the reaction mixture contains up to 3-5 per cent unreacted alcohol and 8-12 per cent phosphide acid ethers along with the end products. Water-alcohol salt solution treatment of halide alkyls gives the end product containing less than 0,1 per cent of admixtures.

In α -tokoferol production, the reaction mixture contains together with the main product, 12 per cent of isophytol which is removed from the mixture by treating it with propanole zinc chloride solution. As a result, α -tokoferol containing 98% of the main product is obtained.

Two functional groups available in a diole molecule offered the procedure to separate two polar nonelectrolytes such as monobasic and dibasic alcohols using aqueous-alcohol zinc bromide solution.

Low increments of functional sulfur groups offer the procedure to desulfurize oil products by their extraction with salt solutions. Single extraction results in 10 to 30-fold reduction of the amount of higher sulfur-organic compounds and traces of lower compounds.

Salt phase is diluted with water to obtain extracted substance. In this case, distribution constants of polar substances sharply increase. The latter are extracted by a phase of low-boiling solvent

(methylene chloride, chloroform, etc.). Upon its distillation, a pure polar substance is produced.

Thus, new extraction systems characterized by a unique ability of extracting higher homologs of electron-donating substances can be developed by using concentrated zinc and aluminium halides. It is also pointed out that extraction and clustering of salt solution are symbiotic processes. The above data demonstrate the effectiveness of the proposed extraction systems for fine separation and thorough refinement of different organic compounds.

References

1. Bleshinsky S.V. On salting out of organic substances. Frunze: ILLM, 1967.
2. Korenman Ya.I. Extraction of phenols. Gorky, izd. Volgo-Vyatsk, 1973.
3. Sadoc A., Fontaine A., Lagarde P., Raoux D. Local order study of $ZnBr_2$ solutions in ethyl acetate by EXAFS // J. Amer. Chem. Soc. 1981. Vol. 103. P. 6287-6290.
4. Nicolas M., Reich R. // Nouv. J. Chim. 1982. Vol. 6. P. 467-476.

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Our studies have been carried out into the extractions of aliphatic, aromatic, and alkylaromatic mono-, di-, and polycarbonic acids, phenols, and their oxy-, carboxy-, methoxy-, phenoxy-, sulfo-, nitro-, haloid-, and alkyl derivatives, amines, as well as some natural and semisynthetic penicillines, macrolide and polyene antibiotics, tetracyclines, steroids, phytohormones, vitamins, antitumour antibiotics, and other mono- and polyfunctional organic compounds (MFOC, PFOC) from aqueous solutions.

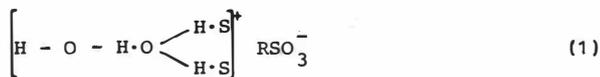
Extraction properties and mechanisms have been investigated with MFOC and PFOC distributed into ethers, esters, ketones, alcohols, chloroorganic solvents, tributylphosphate, various sulfoxides, alkylphenols, and mixed solvating media.

The compositions of solvates extracted have been estimated by the bilogarithmic method and, in some cases, by those of saturation and isomolar series. The model extracted complexes have been preparatively synthesized for certain systems. The results obtained have laid the basis to postulate the regularities of solvation of MFOCs and PFOCs extracted from aqueous solutions.

MFOC solvation. Nonhydrated monosolvates $[A \cdot S]$ and those hydrated out-of-sphere have been found to form mainly in extractions of MFOCs—mono-carbonic acids [1] and monoatomic phenols [2] with strong basic electron-donor solvents (SBES) such as sulfoxides and tributylphosphate taken in excessive amounts as related to the compound distributed. The similar extraction mechanism works with distributions of haloid-, nitro-, alkyl, methoxy-, phenoxy-, and other derivatives of phenol and carbonic acids each containing a single proton-donor group.

Under the conditions of SBES "deficiency", the distribution of mono-carbonic acid monosolvates occurs with the concomitant extraction of self-associated species [3], while with phenol, there have been observed the formation of a half-solvated $[Ph_2 \cdot S]$, a third-solvated $[Ph_3 \cdot S]$, and higher associated species solvated by one SBES molecule $[Ph_n \cdot S]$.

When one proceeds to extraction of strongly acidic MFOC such as sulfoacids [4], he can observe the extraction mechanism with SBES to suffer radical changes consisting in the formation of highly solvated hydrated complexes,

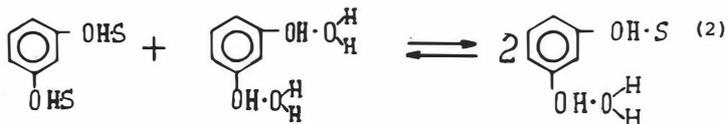


The solvation in this case has been shown to realize via the interactions of an extragent and the hydrated hydroxonium ion. The sum of solvation and hydration numbers comprises four thus being in good agreement with the solvation number for H_3O^+ .

As one could expect, the changed type of solvating agent should lead to changes in the extraction mechanism and in the compositions of extracted complexes. However, in a series of SBES similar by their properties, e.g. sulfoxides and tributylphosphate, the mechanism of MFOC extractions remains really unchanged, though certain differences exhibit themselves in the effect of an "inert" diluent, in the dependence of K_{01} value of extracted complexes on that of pK_a of distributed proton-donors and, surely, in the values of extraction constants.

With weak basic electron-donor solvents (WBES) such as ethers, esters, ketones, etc., the MFOC solvations undergo qualitative changes. Thus, monosolvates and self-associated species of distributed compounds can appear alongside with some amount of hydrated disolvates in extraction of monoatomic phenols and monocarbonic acids. The nature of deviations of the bilogarithmic dependences of distribution coefficients from the linear one affords the assumption of the formation of even trisolvates. Still, there has been furnished no evidence to the existence of a hydrated solvate $[A_3S \cdot H_2O]$.

PFOC solvation. It should be expedient to start the discussion of solvation regularities of PFOCs extracted from aqueous solutions with such compounds, which contain several similar functional groups RX_n . As a first approximation, the solvation regularities for such compounds may be represented by an additive scheme of MFOC solvation with respect to the number of solvated groups. Thus, in extraction of multiatomic phenols containing "separated" OH-groups and of polycarbonic acids with sulfoxides and tributylphosphate, there are mainly formed the extracted complexes possessing the solvation number equal to that of the proton-donor groups of the compounds distributed. As compared to MFOCs, no solvated self-associates of the $[A_n \cdot S]$ type have been found for PFOCs. At the same time, the reactions of re-solvation (2) have been observed

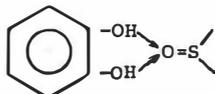


to result in the solvates coordinatively unsaturated by the extragent and in the hydration of a vacant OH-group. Thus, quite possible is the formation of mono- and disolvates [5] for the system sulfoxide- CCl_4 - H_2O -, that being dependent on the ratio of sulfoxide and resorcinol concentration.

With WBES as butyl acetate, the re-solvation (2) has not been considered typical due to the low ratio of extragent and PFOC concentrations in the organic phase, where the maximum solvation number may reach the doubled number of the PFOC proton-donor groups $q=2n$ to be in good agreement with the data obtained by Tcharykov [6].

Some important peculiarities of PFOC solvations of the RX_n type have

been found in extractions of o-isomers of aromatic polycarbonic acids and multiatomic phenols as well as of cis-isomers of unsaturated dicarbonic acids containing α -positioned $-\text{COOH}$ groups. The extraction of catechol with sulfoxides [7] has been thus ascertained to yield monosolvates only. The results obtained have been explained owing to the idea of bidentate coupling of the sulfoxide oxygen to both hydroxyl groups of catechol (3) to be supported by the abnormally high values of $K_{01}=2180$



(3)

and by the strongly marked shifts of the SO-group absorption bands $\nu_{\text{SO}}=40\text{cm}^{-1}$ in IR-spectra of isolated complexes and extraction phases. The effect of bidentate coupling has been also observed in extractions of catechol with methylcyclohexanone, ethers, esters, and some other WBESs.

Of special interest have been regarded the phenomena revealed in extractions of PFOCs possessing functional groups of different types RX_nY_m . It should be noted that such structures are inherent to the most part of biologically active compounds. The formation of complexes coordinatively unsaturated by the extragent with the solvation number equal to that of the most acidic functional groups has been established to occur in extractions of RX_nY_m containing proton-donor groups differing in their acidities pK_a for more than five units, while with strongly basic electron-donor solvents (SBES) - this being precisely the case of extractions of oxyacids, amidoacids, penicillines, antitumour antibiotics as variamicine and mitramicine, etc. [8,9]. The appearance of coordinatively unsaturated solvates may be explained by the strong dependence of K_0 on pK_a of proton-donor groups thus leading to the fact that at the background of intensive intermolecular interactions of SBES and the most acidic functional groups of distributed compounds, the specific solvation of less acidic functional groups turns out unrevealed by the distribution means and exerts no influence on the dependences of distribution coefficients on the SBES. Such a phenomenon may be called the effect of intramolecular competitive desolvation. A certain desolvation effect can be also exhibited by the so-called "inert" diluents. With the growing energy of interactions of diluent and extragent, the solvation numbers can decrease, while the coordinative unsaturation of the extracted complexes increases. The maximum solvation numbers have been observed with the employment of solvating extragents of parafinic and naphthenic hydrocarbons as diluents.

The use of WBESs as extragents results in a decreased coordinative unsaturation of the solvates formed because the dependence curve of $\lg K_0$ on pK_a is of more flat character.

The investigations of extraction of PFOCs with $pK_{a_i}/pK_{a_j} < 5$ have shown the distribution to be usually followed by the formation of solvates coordinatively unsaturated by extragent as it occurs in extractions of oxyaromatic carbonic acids. Therefore, the solvation number should be equal to that of proton-donor functional groups in extraction of such compounds with SBES. Still, in extraction of salicylic acid with sulfoxides, there have been only observed monosolvates formed due to the effect of bidentate coupling, i.e. the solvation number may decrease by a unit in extraction of o-isomers both in the case of PFOC $RX_n Y_m$ and of RX_n .

Peculiar regularities may be revealed in extractions of PFOCs containing both nucleophile and electrophile functional groups. Methoxyphenols, methoxy- and phenoxy carbonic acids, and steroids have been considered as appropriate models of such compounds. For the PFOCs mentioned above, the regularities of specific solvation with ES and PE become quite different. Thus, the extractions with chloroform result in the complexes coordinatively saturated by the extragent [10], while those with ES give the coordinatively unsaturated solvates formed in terms of the regularities postulated for extractions of MFOC and PFOC containing proton-donor groups only.

A mixture of electron- and proton-donor solvents used is often accompanied by mixed solvates $[RX_m Y_n \cdot q_1 S_1 \cdot q_2 S_2]$ formed to lead to the appearance of synergetic effects [11].

References

1. Egutkin N.L. Kandidatskaya dissertatsiya. Ufa: Bashkirian State University, 1975.
2. Egutkin N.L., Malaya I.P., Nikitin Yu.E.//Zh.fiz.khim. 1984. N 12. P. 2988-2990.
3. Egutkin N.L., Nikitin Yu.E.//Zh.fiz.khim.1984. N 10.
4. Nikitin Yu.E., Egutkin N.L.//Neftekhimiya. 1976. N 5. P. 794-797.
5. Egutkin N.L., Malaya I.P., Nikitin Yu.E.//Zh.prikl.khim. 1986. N 6. P. 1268-1291.
6. Tcharykov A.K. Doktorskaya dissertatsiya. Leningrad: Leningrad State University, 1985.
7. Egutkin N.L., Malaya I.P., Nikitin Yu.E.//Izv.AN SSSR. Ser.Khim. 1984. N 7. P. 1651-1653.
8. Egutkin N.L., Maidanov V.V., Nikitin Yu.E. et al.//Antibiotiki. 1983. N 4. P. 246-250.
9. Egutkin N.L., Denisenko Yu.I., Nikitin Yu.E., Budimirova V.S.//Khim.farm.zh. 1985. N 12 P. 214-217.
10. Egutkin N.L., Denisenko Yu.I., Maidanov V.V. et al.//Tezisy dokl. VII Vsesoyuznoi konferentsii po khimii ekstraktsii. Moscow, 1984. P. 99.
11. Egutkin N.L., Maidanov V.V., Nikitin Yu.E.//Khim.farm.zh. 1984. N 3.

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Research workers are not unanimous in their considerations of similarity and discrepancy factors in chemical equilibria realized in non-aqueous systems and in extractions of organics from aqueous solutions. Therefore, quite obvious turns out the necessity in the comparative analysis of such systems to provide for a range of application of distribution methods in estimating the compositions and stabilities of the H-complexes formed from one hand and, from the other, to justify the calculations and prediction of extraction equilibria according to the existing literature data on the constants of formation of molecular complexes in non-aqueous solutions obtained by the physico-chemical methods as IR, UV, NMR spectroscopies, etc.

Phenol (Ph) and p-fluorophenol (PFP) have been selected as the subjects of scientific research; the molecular complexes of these compounds with electron-donor solvents (ES) have been reported by many authors.

The bilogarithmic method has been applied to the estimation of compositions of H-complexes formed in extractions. The constants for monosolvate formation K_{01} have been calculated according to equation (1).

$$K_{01} = \frac{Y - Y_0 - nY_{ass}}{PXS_{fr}}, \quad S_{fr} = S_0 - (Y - Y_0 - nY_{ass}). \quad (1)$$

With the simultaneous formation of mono- and disolvates, the dependences (2) have been plotted to find the stepped formation constants K_{01} , K_{02}

$$\frac{D - P_0 - D_{ass}}{P_0 S_{fr}} = K_{01} + K_{01} K_{02} S_{fr}. \quad (2)$$

Figure 1 gives some bilogarithmic dependences of distribution coefficients D on the equilibrium concentration of ES in CCl_4 in extractions of Ph and PFP.

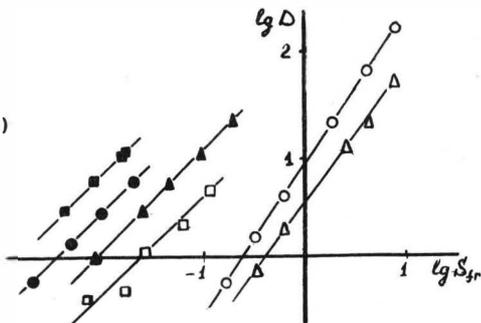
As it follows from Fig., with the strong basic electron-donor solvents (SBES) as TPPO, DHSO or DPSO, the angle tangent of bilogarithmic dependences is equal to 1 to evidence to the formation of the 1:1 extracted complexes only. The same conclusions are drawn [1-7] on the basis of physico-chemical studies of non-aqueous solutions. With the

System ES-Ph

- ▲ dihexylsulfoxide (DHSO)
- diphenylsulfoxide (DPSO)
- triphenylphosphine oxide (TPPO)
- methylcyclohexanone (MCH)
- △ butylacetate (BA)

System ES-PFP

- triphenylphosphine oxide (TPPO)



weak basic electron-donor solvents (WBES) as esters, ketones, etc., the inclination angle tangent of bilogarithmic dependences exceeds 1, i.e. alongside with the formation of monosolvates, there may appear higher solvated H-complexes in such extraction systems. According to the existing literature data [1-7], the solvation number $q=1$ for the analogous systems in non-aqueous media. Thus, with WBES there have been observed essential differences in chemical equilibria realized in extractions and in non-aqueous media. The symbatic changes in H_2O and Ph concentrations in the equilibrated organic phase in extractions with WBES afford a conclusion that the formation of highly solvated phenol H-complexes is conditioned by the presence of hydrated solvates.

The discrepancy between the extraction systems and non-aqueous solutions of phenol may probably lie either in the compositions of H-complexes or in the constant values of their formation. It is demonstrated [9] in what way the hydration factor influences the dimerization constants of proton-donor compounds. We have failed to find out the similar data for the heteroassociation processes resulting in the Ph·S solvates. To solve the problem, the distribution method has been employed to estimate K_{01} values of phenol and p-fluorophenol with ES for further comparison thereof to the literature data obtained for non-aqueous systems.

Table 1. Formation constants of 1:1 H-complexes of phenol and p-fluorophenol with different ES in CCl_4 at 25°C

N	H-complex	$K_{01}, l/mol$	Cited values	N	H-complex	$K_{01}, l/mol$	Cited values
I	$(C_6H_5)_2SO \cdot PFP$	120 ± 1	105 ± 1 [4] 107 [3]	VI	$(iso-C_3H_7)_2O \cdot PFP$	11.0 ± 0.5	11.2 [3]
II	$(C_6H_5)_3PO \cdot PFP$	1350 ± 12	1456 ± 80 [4] 1445 ± 60 [3]	VII	$(iso-C_3H_7)_2O \cdot Ph$	7.9 ± 0.3	8.14 [1]
III	$(C_6H_5)_3PO \cdot PFP$	657 ± 10	870 [2]	VIII	$CH_3OC_6H_5 \cdot PFP$	1.60 ± 0.05	1.05 [3] 2.3 [4]
IV	$(C_3H_7)_2O \cdot PFP$	7.7 ± 0.1	8.9 [7]	IX	$CH_3OC_6H_5 \cdot Ph$	1.6 ± 0.1	1.2 [5]
V	$(C_3H_7)_2O \cdot Ph$	6.0 ± 0.1	6.22 [1]	X	$CH_3COC_6H_5 \cdot PFP$	16.0 ± 0.6	13.5 [3]

For comparing the results obtained by different methods, one should account for the K_{01} values with respect to those of experimental errors, which unfortunately are not often cited. Thus, for example, the relative error in IR-spectroscopy reaches 10-40% [8].

The accuracy of K_{01} values is high enough (Table 2), which is determined by the correct use of interphase distribution data (ES diluted solutions, $Y \ll S_0$).

Table 2. Calculations of the formation constants for H complex $(C_6H_5)_3PO-Ph$ by the extraction data; $P_0=0.45$; $t=25^\circ C$; diluent - CCl_4

TPPO concentration, S_0 , mol/l	Phenol equilibrium concentration		$K_{01} = \frac{Y - P_0 X - nY_{assoc}}{P_0 X [S_0 - (Y - P_0 X - nY_{assoc})]}$
	aqueous phase $X \cdot 10^4$, mol/l	organic phase $Y \cdot 10^4$, mol/l	
$2 \cdot 10^{-3}$	1.97	2.01	670
$5 \cdot 10^{-3}$	3.57	6.36	654
$5 \cdot 10^{-3}$	1.41	2.56	632
$1 \cdot 10^{-2}$	2.44	7.49	622
$1 \cdot 10^{-2}$	3.64	12.1	709
$2 \cdot 10^{-2}$	2.30	13.4	633
$2 \cdot 10^{-2}$	6.00	33.2	667
$2 \cdot 10^{-2}$	13.7	64.6	670
			$K_{01} = 657 \pm 10$

Accounting for the above said, the examination of Table 1 shows the constants K_{01} of heteroassociation formation to possess rather similar values. As for some divergency with II, III, IV, there arises no ground for reliable conclusions, with respect to the error values, on the essential differences of the 1:1 H-complex formations in non-aqueous solutions and under extraction conditions.

With SBES as sulfoxides, the coincidence of K_{01} values results from the existence of non-hydrated monosolvates in the extraction phases [10]. With WBES, such a coincidence has been considered probable either in the case of preferable formation of non-hydrated monosolvates since monosolvate-monohydrate can transform into a hydrated disolvate, or in that of similarity of the stability constant values for the hydrated and non-hydrated monosolvates.

Since the extraction process is determined by the sum total of chemical equilibria, the available literature data on the constants of mono-

solvate formation, with WBES, those obtained by the physico-chemical methods for non-aqueous solutions, cannot be applied to the quantitative description of distributions and to the precise evaluation of WBES extractivities if one fails to take into account the hydration and the possible formation of highly solvated H-complexes.

At the same time, the reliable constant values for the formation of 1:1 H-complexes can be estimated on the basis of Ph and PFP distributions. The supposed observations of constants' interconnection for the formation of non-hydrated monosolvates and hydrated mono- and disolvates is believed to result in much extensive application of the constants obtained by physico-chemical methods in non-aqueous solutions to the extraction chemistry. As far as SBESs (sulfoxides, phosphine oxides, etc.) are concerned, the K_{01} values estimated by different methods afford the quantitative descriptions of extraction equilibria in rather a wide range of component concentrations.

References

1. Gramstad T.//Spectrochim.Acta. 1963. V.19. P.497.
2. Gramstad T.//Acta Chem.Scand. 1961. V.15. P.1337.
3. Taft R.W., Gurka D., Joris L.//J.Amer.Chem.Soc. 1969. V.91. P.4801.
4. Arnett E.M., Joris L., Mitchell E., et al.//J.Amer.Chem.Soc. 1970. V.92. P.2365.
5. Wayland B., Drago R.S.//J.Amer.Chem.Soc. 1964. v.86. p.5240.
6. Arnett E.M., Mitchell E.J., Murty T.S.S.R.//J.Amer.Chem.Soc. 1974. V.96. P.3875.
7. Pantchenko B.V., Oleinik N.M., Sadovsky Yu.S. et al.// Reaktsionnaya sposobnost' organicheskikh soedinenii. Tartu. 1980. V.17, vyp.1 61. P. 69.
8. Bilobrov V.M., Shurpatch V.I., Katchurin O.I.//Ukrain.chim.zh. 1985. V.51. P. 478.
9. Sergievsky V.V.// Itogi nauki i tekhniki. V.5. Moscow. 1976.
10. Egutkin N.L. Kandidatskaya dissertatsiya, Bashkirian State University, Ufa, 1975.

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The problem of mixture separation and isolation of pure individual chemical substances is one of a great practical importance. Liquid extraction as mixture separation technique has received recently much attention. This arose from the fact that this process has some advantages over rectification [1].

Ethyl and n-butyl alcohols, toluene and chlorobenzene have been found wide application in different fields of chemical industry. Aqueous mixtures of above - mentioned solvents are formed in several processes for production of organosilicon resins, varnishes and other products. The purpose of this article is to study extraction of considered aromatic hydrocarbons from alcohols with which they form in the presence of water complex triple azeotropes hardly separated by rectification.

To evaluate the possibilities of this method and calculate subsequently the statics of process and equipment liquid - liquid equilibrium in tripple systems with limited solubility of components, formed by ethyl and n-butyl alcohols, water, toluene and chlorobenzene has been studied. We studied also the influence of butyl alcohol on equilibrium in ethyl alcohol - water - butyl alcohol system and the influence of chlorobenzene in ethyl alcohol - water - butyl alcohol, water - toluene - butyl alcohol, ethyl alcohol - water - toluene systems.

In the course of equilibrium investigation we determined separately the position of binodal and equilibrium composition lines at 293.15 K. Equilibrium compositions were analyzed by chromatograph with relative error no more than 7%. Some diagrams of phase equilibrium of studied systems are shown in Fig. 1. As mutual solubility of water and toluene as well as of water and chlorobenzene is small and practically equal, equilibrium data for 4-component systems formed by above-mentioned alcohols, hydrocarbons and water are presented as pseudotriple diagrams. Diagrams of systems formed by ethyl alcohol, water, toluene and chlorobenzene have closed-type lamination region which adjoined the binary sides of Gibbs triangle - hydrocarbon - water. Diagrams of systems which contain n-buthyl alcohol, water and above - mentioned aromatic hydrocarbons have opened type lamination region which adjoined the following sides of triangle: alcohol - water and water - hydrocarbon.

In ethyl alcohol - water - toluene and ethyl alcohol - water - chlorobenzene systems coefficient of alcohol distribution takes on values

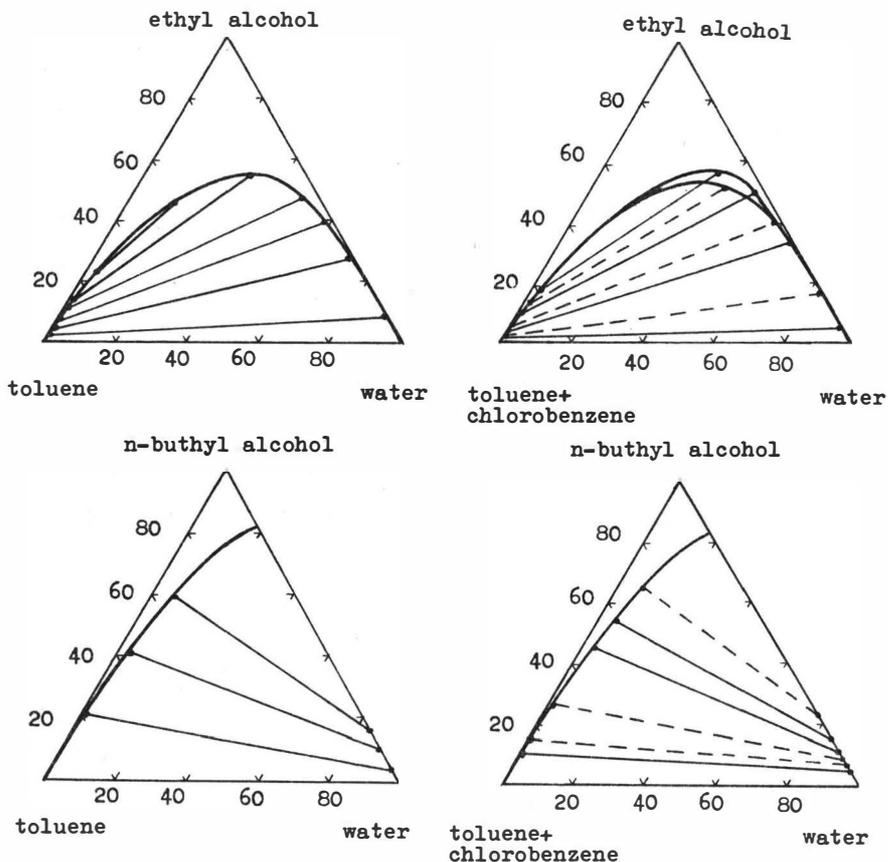


Fig. 1. Liquid-liquid phase equilibrium diagrams of systems formed by ethyl and n-butyl alcohols, water, toluene and chlorobenzene at 283.15 K; weight %

from 4 to 30 and 48.5, respectively. It should be noted that chlorobenzene addition to ethyl alcohol-water-toluene mixtures increases alcohol distribution coefficient up to 54 in the field of it's diluted solutions. In this way, separation of ethyl alcohol from above-mentioned aromatic hydrocarbons by extraction using water as extractant does not seem to be complex.

As illustrated in Fig. 2 the coefficient of butyl alcohol distribution decreases as it's concentration in aqueous phase increases. The coefficient dependence of butyl alcohol distribution on ethyl alcohol content in aqueous phase in the systems formed by above-mentioned alcohols, water, toluene and chlorobenzene is shown in Fig. 2. The analysis of results presented in Fig. 3 shows that the coeffi-

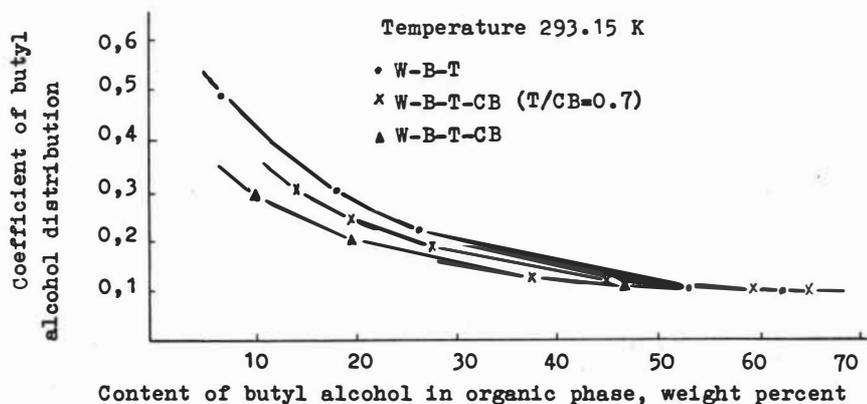


Fig. 2. The results of examination of liquid-liquid equilibrium in systems formed by butyl alcohol (B), water (W), toluene (T) and chlorobenzene (CB)

ent of butyl alcohol distribution decreases in the presence of aromatic hydrocarbons and remains constant up to 12% by weight ethyl alcohol concentration in aqueous phase. As ethyl alcohol content in aqueous phase increases the coefficient of butyl alcohol distribution increases too. By this means, addition of ethyl alcohol during extrac-

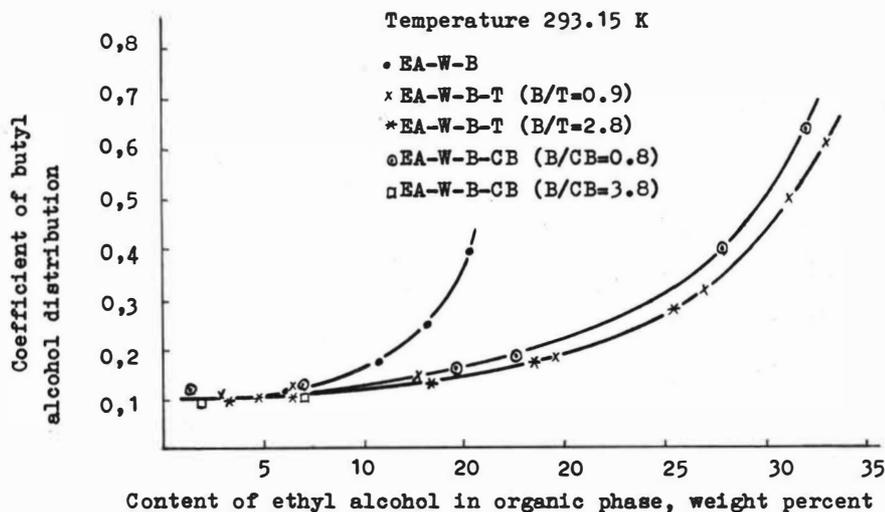


Fig. 3. The results of examination of liquid-liquid equilibrium in systems formed by ethyl alcohol (EA), water (W), butyl alcohol (B), toluene (T) and chlorobenzene (CB)

tion of butyl alcohol will promote it's separation from hydrocarbons by water.

Separation of ethyl and butyl alcohols from toluene and chlorobenzene by extraction has been studied in the laboratory on standard mixtures. Four-staged countercurrent process was simulated in separating funnels in accordance with technique proposed in [2]. In the course of experiments, proportions between extractant and starting mixture and concentration of ethyl alcohol in it has been varied. Toluene - chlorobenzene ratio in model starting mixtures was kept constant and equal to 20. Raphinade and extractant were analyzed chromatographically. The experiments showed that maximum concentration of ethyl alcohol in raphinade of toluene and chlorobenzene mixture was not more than 0.005% by weight. It consistent well with conclusions made on the basis of data relative to liquid-liquid phase equilibrium of corresponding systems. The results obtained during studing of extraction process are shown in Fig. 4 as dependence of butyl alcohol concentration in raphinade on the ratio of alcohols in starting mixture. As illustrated in Fig. 4, extent of butyl alcohol extraction from the mixtures of toluene and chlorobenzene increases with increasing of ethyl alcohol concentration relative to butyl alcohol in starting mixtures.

The results obtained show that there is possibility of practically complete separation of alcohols from hydrocarbons by extraction using water as extractant and adding, if necessary, ethyl alcohol.

We used above-mentioned method in which water and ethyl alcohol are used as extractants as the basis for designing extraction unit of technological process for solvent regeneration during production of silicone lacquers and resins.

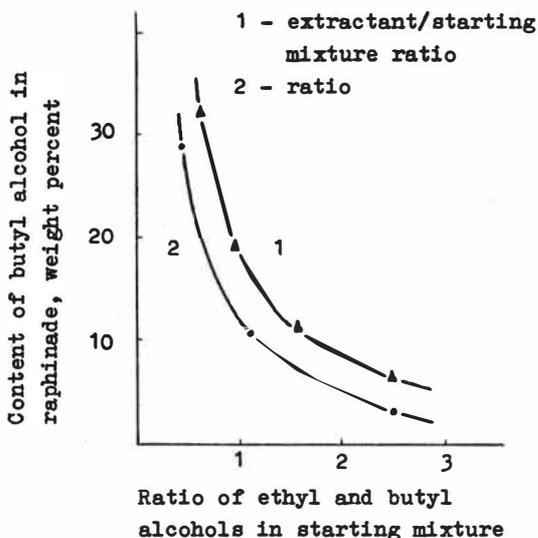


Fig. 4. The results of butyl alcohol separation from hydrocarbons by extraction

References

1. Treybal R. Liquid extraction. M.: Khimia, 1966. P. 15.
2. Ibid. P. 404.

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Coal-tar oils like a middle oil, naphthalene oil, light oil or a wash oil contain numerous different components (aromatic and heteroaromatic hydrocarbons). Therefore, isolation of a highly concentrated group of individual components (phenols, bases, etc.) is not a simple task.

At present, extraction with an alkali solution is the method most frequently used for removal of phenols from tar oils. This method gives a vast amount of toxic waste materials.

The purpose of the present work is to present a new no-waste process for the removal of phenols from tar oils involving a two-step extraction with a diluted aqueous solution of monoethanolamine (MEA) in the first step and with methyl tert-amyl ether (TAME) in the second step.

The literature [1,2] contains some data concerning MEA as the extractant for phenols. However, the selectivity of the separation of phenols from aromatic hydrocarbons has been found with this solvent to be unsatisfactory. The data were presented for a concentrated MEA-water solution.

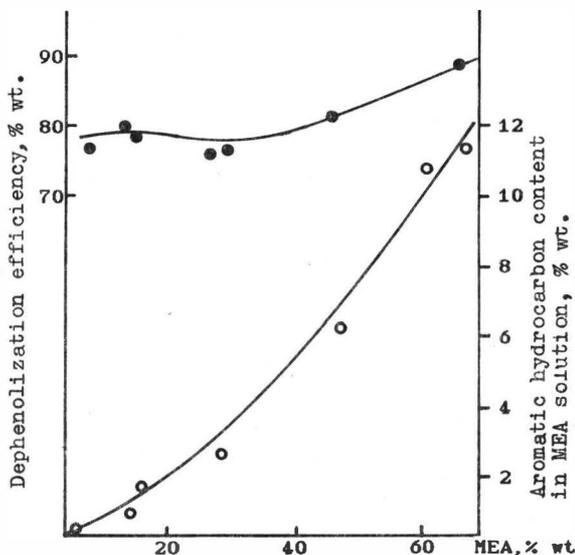


Fig. 1. Dephenolization efficiency and aromatic hydrocarbon content in MEA as a function of MEA concentration

Figure 1 shows the influence of the MEA concentration and of the content of aromatic hydrocarbons in it on the efficiency of dephenolization. The selectivity of aqueous MEA solutions increases as the concentration of the amine is decreased. At low MEA concentrations (below 10 wt.%) this effect is rather small. Addition of water to the amine causes in general a decrease in the

distribution coefficient K for phenols (expressed as the ratio of the weight fraction of phenols in aqueous MEA solution to that in the tar oil). However, at 15 wt.% of MEA, the extraction efficiency was found to rise. Between 10 and 40 wt.%, the value of K was found to remain practically constant. For process design purposes a 15 wt.% MEA concentration was chosen for the first extraction step.

In Figure 2, the extraction equilibrium curves for middle oil- phenols- 15 wt.% aq. MEA systems at 333 and 293 K are presented. As may be seen from Figure 2, the effect of dephenolization is greater at 333 K. The boiling points of phenols and MEA are rather close, therefore the amine cannot be separated by a simple

distillation. Thus, a reextraction step with a low-boiling organic solvent in the second step was proposed. This solvent should meet the following requirements: the boiling point must be much lower than that of phenols; it must be chemically and thermally stable, possibly least soluble in the primary solvent (MEA solution) and have a high distribution coefficient K for phenols. The K -factors expressed as the ratio of the weight fraction of phenols in the organic and the MEA phases for several commonly used organic solvents are presented in Table 1. A very low value of K obtained for benzene eliminates this compound as a solvent. Butyl acetate hydrolyses in alkaline solutions. From the group of ketones and ethers the best results were obtained with methyl tert-amyl ether (TAME) (see Table 1). Some physical and chemical data for the chosen reextraction solvent(TAME) are presented in Table 2.

Figure 3 shows a simplified flow sheet of the MEA-TAME dephenolization process of a middle oil. In the block diagram all the intermediate operations necessary for the production of high-purity phenols as well as the approximate material balance are shown.

A phenols-containing coal-tar oil is fed to a countercurrent extraction column, where phenols are extracted with an aqueous 15 wt.% MEA. To obtain hydrocarbons-free high-purity phenols, the MEA-phenols extract is washed with a naphtha fraction prior to the TAME reextraction step. Next the phenols are reextracted with TAME and the

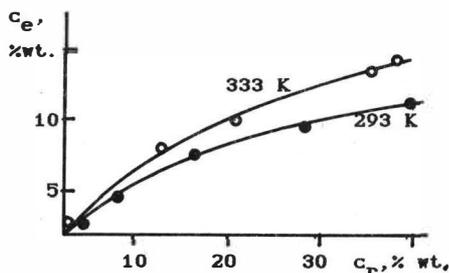


Fig. 2. Phase-equilibrium curves for system phenols-carbolic oil MEA 15% wt.aq. solution

MEA-water solution is recycled to the first step of the process. From the phenols-ether solution, the residual amine and pyridine bases are removed by the use of carbon dioxide and diluted sulphuric acid, respectively. Then TAME is distilled off and recycled, yielding pure phenols as the bottoms product which leaves the rectifying column. The process is closed with no waste and no effluents.

Table 1. Distribution factor for phenols K in different organic solvents

Solvent	Phenols content in aqueous MEA, % wt.	$K=c_e/c_r$	Extraction efficiency, % wt.
Benzene	10.4	0.5	25.3
	18.6	1.2	39.2
Butyl acetate	10.4	8.7	88.2
	18.6	9.2	91.2
Methyl iso- butyl ketone	10.4	6.2	87.6
	18.6	7.5	90.7
Diisopropyl ether	10.4	2.5	77.5
	18.6	3.5	83.3
TAME	10.4	10.5	93.5
	18.6	12.3	96.2

Organic solvent: monoethanolamine (MEA) 15% wt. aqueous solution
ratio- 1:1

Temperature: 295 K

c_e, c_r - concentration of phenols in the organic solution and in
water, % wt, respectively.

Table 2. Selected properties of TAME

Formula	Value
molecular weight, kg/kmol	102
boiling point, K	359.2
density at 293 K, kg/m ³	776
vapour pressure at 293 K, kPa	9.4
solubility in water at 293 K, % by wt.	1.2

References

1. Chang Y. C., Johannsen R. C. // J. Inst. Fuel. 1959. Vol. 216. P.174.
2. British Pat., 1931, No.344614.

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The process of aromatics extraction from reformed naphthas or hydrogenated pyrolysis gasoline by selective solvents takes an important place among the other processes in the petrochemical industry. Various organic solvents found an efficient commercial application up to now/1-6/. Different processes in the recovery of aromatics are developed.

In the present study, therefore, characterization of phase equilibrium in liquid-liquid systems paraffins-aromatics-sulpholane has been carried out. The equilibrium data of the investigated systems have not been found in the literature because of the peculiarity of the applied paraffinic part of the systems i.e. paraffinic mixture based on n-hexane. The obtained results have been compared with those respective to the case when pure n-hexane was used as a paraffinic part. This work is a part of our extensive investigation on the equilibrium in the process of aromatics extraction with different solvents/7/.

Following systems were investigated:

- I.1) n-hexane - benzene - sulpholane;
- I.2) n-hexane - toluene - sulpholane;
- II.1) paraffins - benzene - sulpholane;
- II.2) paraffins - toluene - sulpholane.
- II.3) paraffins - (benzene+toluene) - sulpholane.

The paraffins in the second group of the systems were hexane fraction (Oil Refinery Skopje), consisting of 54,8% of n-hexane and 45,2% of other lower paraffins (all in weight percent).

Since the systems belong to the second group are polycomponent, the components were classified according to their chemical similarities as: paraffin (the first component), aromatic (the second) and solvent (the third component) So, with this simplification, in the further investigation the respective systems were treated as pseudo-threecomponent ones, which enabled their analysis by the methods valid for classic threecomponent systems /8/.

The process of aromatics extraction from paraffin/paraffins mixture was carried out at 303 K and atmospheric pressure.

Aromatics concentration in the starting mixture was from 0-100% (by volume) and keeping the solvent-to-feed ratio 1:1 constant.

The equilibrium data for all investigated systems are presented in the equilateral triangle phase equilibrium diagrams.

Comparing diagrams for the systems I.1 and II.1 (figure 1) an increase of the heterogeneous region limited by the binodal curve in the case of the system II.1 is noticeable, which certainly points at the paraffin type influence on the equilibrium.

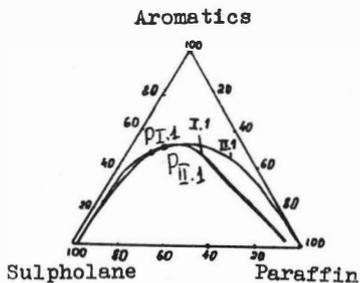


Fig. 1. Phase equilibrium diagrams for systems I.1 and II.1

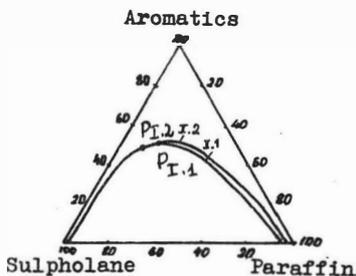


Fig. 2. Phase equilibrium diagrams for systems I.1 and I.2

Regarding to the systems with the same paraffinic part and different aromatic (n-hexane-benzene/toluene-sulpholane) it can be noticed larger heterogeneous region when heavier aromatic (toluene) is present (Figure 2), which could be explained as an influence of aromatic type on the equilibrium.

The tie lines when plotted in their respective phase equilibrium diagrams show a convergence to the solvent corner which means that, at the investigated temperature, the solubility of aromatics in the paraffin-rich phase (raffinate) is better than in the sulpholane-rich phase (extract). As an illustration, only the phase equilibrium diagram for the system II.3 with tie lines in it is presented in Figure 3.

For all investigated systems the values of the distribution coefficient (K_D) were determined. There is a tendency of a decrease with the increase of the aromatic concentration in the starting mixture (x_{AP}). Higher K_D -values of lighter aromatic are obtained.

In Figure 4, a plot of the distribution and selectivity curves is presented for all investigated systems. The disposition of the distribution curves below the diagonal line ($K_D=1$) is evident. The distribution curve for the system

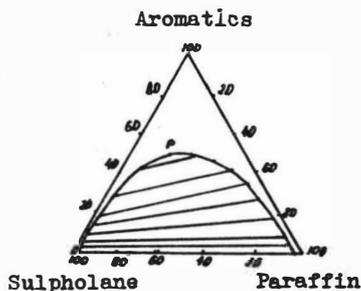


Fig. 3. Phase equilibrium diagram for system II.3

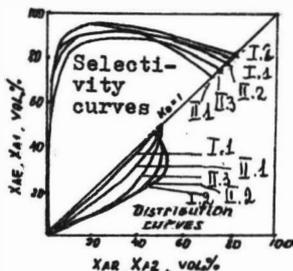


Fig. 4. Distribution and selectivity curves for paraffins-aromatics-sulpholane systems

II.2 is the lowest one, while the distribution curve for the system I.1 is situated very near by the diagonal.

According to the distribution curves as well as the distribution coefficient values it could be considered greater sulpholane capacity to lighter aromatic (benzene).

The selectivity curves showing the dependence of the aromatic concentration in the solvent-free extract phase (x_{A1}) on the aromatic concentration in the solvent-free raffinate phase (x_{A2}) indicate better sulpholane selectivity toward lighter aromatic - Figure 4.

The values of sulpholane selectivity extent (β) were determined (as ratio between the aromatic and paraffin distribution coefficients). The dependence of the selectivity extent on the aromatic concentration in the starting mixture is shown in Figure 5. Generally, for all investigated systems a decrease of the selectivity extent with an increase in aromatic concentration in the starting mixture is evident. Analysing the systems from the point of view of the same aromatic concentration in the starting mixture the lowest values of sulpholane selectivity extent to aromatics appear in the case of system II.3.

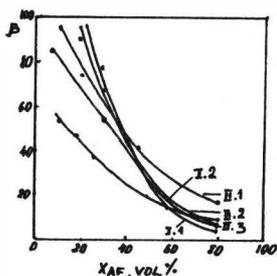


Fig. 5. Comparison of solvent selectivity in the systems paraffins-aromatics-sulpholane

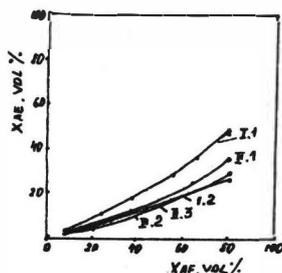


Fig. 6. Summary diagram of the dependence $x_{AE} = f(x_{AF})$

From the summary diagram - Figure 6. - which shows functional dependence of aromatic concentration in the extract phase (x_{AE}) on the aromatic concentration in the starting mixture (x_{AF}) is evident an increase in the aromatic concentration in the extract phase with an increase of aromatic concentration in the starting mixture. It is noticeable that at the same aromatic concentration in the starting mixture aromatic concentration in the extract phase is the highest in the case of system I.1. This is in an agreement with the previously deduced conclusion about the higher sulpholane capacity for lighter aromatic.

For each of the investigated systems, the plaitpoints (P) are determined by Treybal's method [11], shown in Table 1.

Table 1. Plait-points for the systems paraffins-aromatics-sulpholane

System	Paraffin, vol%	Aromatic, vol%	Sulpholane, vol%
I.1	16,0	50,0	34,0
I.2	11,0	47,0	42,0
II.1	19,5	49,0	31,5
II.2	13,0	46,0	41,0
II.3	16,0	49,0	35,0

It is evident that the points in which the composition of the extract and raffinate phase equalize are very close i.e. comparing all investigated systems the aromatic concentration at the plait-point is between 46,0vol% and 50,0vol%.

In order to complete equilibrium data necessary for construction of binodal curve the empirical correlation of Hand/9/ and Othmer-Tobias/10/ were tried. As a criteria for agreement of the calculated with the experimental data the value of the root mean square deviation (σ) was used. The results of the comparison of the calculated with experimental equilibrium data for all investigated systems are given in Table 2.

Table 2. Root mean square deviation (σ) of the calculated with the experimental equilibrium data of the systems: paraffins-aromatics-sulpholane

System	σ	
	Hand	Othmer-Tobias
I.1	0,0420	0,0395
I.2	0,0097	0,0139
II.1	0,0096	0,0208
II.2	0,0025	0,0096
II.3	0,0063	0,0035

Good agreement was achieved using both of the correlation in the case of all investigated systems, which enables their further use in order to reduce the experiments number in the determination of equilibrium data as well as to predict them.

References

1. Somekh G.S. // Hydrocarbon, Process. Pet. Refin. 42(7), 161(1963).
2. Broughton D.B., Asselin G.F. // 7th World, Pet. Congr. 4, 65(1967).
3. Bikulov A. et al. // Khim. Technol. Topl. Masel. 16(10), 15(1971).
4. Renon H., Raimbault C., Jeanjean P., Rosado C.J. // 8th World Pet. Congr. 1971, 4, 197.
5. Cenelli E., Noe S., Paret G. // Hydrocarbon Processes, 1972. 51(4), 141.
6. Nagapal J.M., Rawat B.S. // J. Chem. Techn. Biotechnol. 31, 146(1981).
7. Poposka F., Bliznakovska B., Meško V., Grizo A. // Int. Solv. Extr. Conf. Munich, 1986, Prepr. Vol. 3, p. 481.
8. Nelson W.L. Petroleum Refinery Engineering, 1985: Mc Graw-Hill.
9. Hand D.B. // Phys. J. Chem. 34, 1961(1930).
10. Othmer F., Tobias E.P. // Ind. Eng. Chem. 34, 693(1942).
11. Treybal R. Židkostnaja ekstrakcija. Moskva: Himija, 1966.

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A new hydrocarbons extragent - 1,3-dimethylimidazolidine-2-one (DMI) with high extractational and operating properties, superior to all known industrial extragents (triethylene glycol (TEG), sulfolane, N-methylpyrrolidone (NMP), phenol) is developed and studied.

DMI - a colourless liquid with faint amine odour, miscible with water and aromatic hydrocarbons in any proportions. The physical-chemical constants of DMI and main industrial extragents are given in Table 1.

Table 1. Physical-chemical characteristics of extragents

Index	Extragents				
	DMI	sulfolane	TEG	NMP	phenol
Melting point, °C	6	27,5	-7,2	-24	42
Boiling point, °C	224	288	287	206	181
Density at 20 °C, kg/m ³	1052	1260	1125	1033	1071
Viscosity (at temperature, °C), mN·s/m ²	1,918 (25)	10,34 (30)	38 (20)	1,022 (20)	3,49 (50)
Heat capacity at 25 °C kJ/(kg.deg)	1,75	1,47	2,56	1,68	2,35
Evaporation heat at b. p., kJ/kg	429	514	477	486	447
Flash-point c.c., °C	104	165	155	95	75

DMI is more thermo- and hydrolytically stable than sulfolane and NMP (Table 2).

Table 2. Hydrolytical and Thermo stability of extragents

Experiment conditions	Extragent decomposition rate, %/h			
	DMI	sulfolane	TEG	phenol
Sealed ampules, at 200 °C, anhydrous samples	0,0003	0,001	0,001	0,0005
The same samples with 5% water (mass.)	0,0007	-	-	-
Metal bombs, at 350 °C, anhydrous samples	0,01	-	-	-
Free air access at 150 °C	0,22	0,37	0,135	0,30
Limited air access at 150 °C	0,005	0,007	0,003	0,008

DMI and its decomposition products are corrosion non-active as for ordinary and alloy steels and do not destroy most of the packing materials (Table 3).

Table 3. Materials stability in DMI medium with 10% of water

Material	Temperature, °C	Corrosion rate, mm/year	Stability
Steel 3	150	0,02-0,04	stable
Steel 3	350	0,07-0,09	"
Steel 12X18H10T	150	absence	absolutely stable
Steel 15X5M	150	"	"
Fluoroplast-4	150	-	stable
Paronite	150	-	unstable
Rubber	100	-	relatively stable
Rubber Buna	100	-	stable
Rubber Viton	100	-	unstable

DMI is slightly toxic in comparison with phenol and TEG: LD₅₀ 1150 mg/kg (rats) and 2130 mg/kg (mice). The product is referred to the 3rd class by acute toxicity parameters.

The use of DMI was studied during aromatic hydrocarbons extraction from different reforming catalysate fractions [1], where DMI is considerably superior to TEG and is just as good as sulfolane (Table 4).

Table 4. Conditions and Results of the Reforming catalysate extraction process (fr. 62-105°C)

Indexes	Extragent		
	DMI	sulfolane	TEG
Solvent/raw materials ratio, mass	3	3,2	7
Water contents in extragent, % mass	10	0,6	7
Extraction temperature, °C	40	76-99	150
Recycle/raw materials ratio, mass.	0,3	0,3	0,5
Extraction stages number	7/11	11	7
Recovery ratio, % mass.			
benzene	100/100	100	99,9
toluene	99,5/99,8	99,6	99,0
Specific consumption:			
solvent, t/t	0,00025	0,001	0,0024
vapour, Hcal/t	0,514	0,520	0,640
water, m ³ /t	47,3	41,4	54,5

Table 5. Conditions and Results of the oil fraction selective treatment (from West Siberian oils) process

Indexes	II fraction		III fraction			IV fraction			Asphalt - free oil		
	DMI	phenol	DMI	phenol	NMP	DMI	phenol	NMP	DMI	phenol	NMP
Solvent/raw material, vol.	1,0	1,0	1,7	2,0	2,0	2,0	1,8	2,4	2,7	3,0	3,4
Water contents in the solvent, % mass.	0,6	2,0	0,35	1,0	1,3	1,8	2,0	2,7	0,35	2,0	0,3
Water to the bottom of the extractor, % mass. (to the solvent)	1,5	1,0	1,0	3,0	4,0	1,4	4,0	5,3	1,0	1,5	5,3
Temperature, °C	35	40	50	50-62	50-62	58	65-72	65-72	86	75-85	75-85
Separation stages number	3	3	3	3	3	4	3	3	4	3	3
Raffinate yield, % mass.	71,3	62,0	69,5	60,6	61,8	65,0	55,0	62,5	76,3	59,5	61,4
Raffinate n_D^{50}	1,4600	1,4600	1,4665	1,4672	1,4670	1,4760	1,4760	1,4765	1,4845	1,4845	1,4835
Sulfur contents in the raffinate, % mass.	-	-	0,68	0,73	0,86	0,95	0,98	0,99	0,98	1,03	1,07
Paraffin-free oil coke	-	-	-	-	-	0,05	0,15	0,18	0,28	0,43	0,46
Paraffin - free oil viscosity index	-	-	115	91	90	102	89	85	112	95	91

During selective oils cleaning DMI is much more effective than phenol and more effective than NMP (Table 5).

High effective DMI utilization was studied during kerosene-ga-soil fractions extractational dearomatization [2], extractive rectification hydrocarbons C₄, C₅ and highly aromatized hydrocarbon fractions, absorptive refining of industrial and waste gases from acid impurities [3].

DMI allows intensification of aromatic hydrocarbons removal from middle oil by 2-5% as compared with NMP and furfural and production of a more concentrated extract. During isoprene extraction from isopentane dehydration products DMI increases degree of extraction by 2-3% as compared with acetonitrile and dimethylformamide. DMI has a higher capacity in terms of SO₂ as compared with sulfolane, NMP and dimethylsulfoxide and, in contrast to the latter, is not decomposed during recovery.

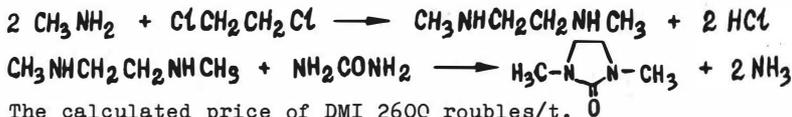
The processes of DMI preparation from available raw materials is developed and carried out on a pilot unit, in accordance with the following schemes:

Method 1



The calculation price of DMI 2600 roubles/t

Method 2



The calculated price of DMI 2600 roubles/t.

References

1. Authors certificate 583994 (USSR), Int.cl.² C07C 7/10. The process of aromatic hydrocarbons extraction from hydrocarbon mixtures/ V.K.Kaporsky, G.F.Yukhno, A.Z.Bikkulov et al. Filed 14.09.76 Publ. 15.12.77.
2. Authors certificate 941341 (USSR), Int.cl.³ C 07 C 7/10. The process of aromatic hydrocarbons extraction from hydrocarbon mixtures/ V.V.Pismennaya, V.K.Kaporsky, G.F.Yukhno et al. Filed 13.02.80. Publ. 07.07.82.
3. Authors certificate 1101280 (USSR), Int.cl. B 01 D 53/13; C 01 B 17/60. The process for gases cleaning from sulfurous anhydride/ A.V.Kurochkin, O.A.Kolyadina, Yu.I.Murinov et al. Filed 29.07.82. Publ. 07.07.84.

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Deepening of oil refining and involving medium and heavy petroleum cuts into petrochemical synthesis processes require a new approach to separation process on the chemical composition rather than the molecular weight.

The most progressive trends in this case is the extraction process making it possible to separate aromatic hydrocarbons concentrates with simultaneous obtaining of refined product - raffinate according to wasteless technology. Though easy to implement extraction is a complex physico-chemical process which is impossible to use without understanding the essence of the process it is based upon.

In order to establish the mechanism of aromatic hydrocarbons recovery from light and heavy petroleum cuts of various composition the extractive separation was carried on by sulfolane, watery sulfolane, N,N-dimethylimidazoline at the temperatures 303 K to 343 K.

Experimental studies were carried on using $^1\text{H-NMR}$, EPR - and mass spectroscopy.

As was shown earlier [1] the increment of the number of paramagnetic particles because of excitation and (or) homolytic dissociation of diamagnetic molecules is observed upon heating of petroleum products (see Fig. 1).

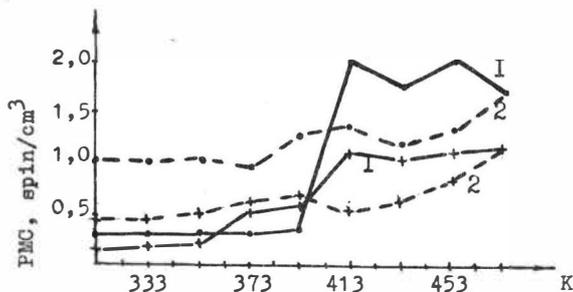


Fig. 1. Modification of the number PMC in gasoil depending on temperature
1 - the growth of temperature;
2 - reverse motion;
• - heavy gasoil;
+ - light gasoil

The same effect is expected to be observed in the extractive separation process at the elevated temperatures.

In fact investigations according to EPR have shown that the excitation process or homolytic dissociation is taken place alongside with the process of hydrocarbon cuts extraction at the temperatures above 323 K as testified by the growth of paramagnetic particles. However experiments on extraction made at temperature 303 K have shown that under the influence of extra-agent energy dynamics of change of extract and raffinate paramagnetic properties is observed.

Table shows the results of experiment of light gasoil extraction of catalytic cracking and mixing of obtained extract and raffinate. The data presented in the Table I shows that the number of paramagnetic centers in the discharged pattern is smaller than in the initial product.

Extraction of light catalytic gasoil

Product	Concentration PMC, $\cdot 10^{16}$ spin/cm ³
LIGHT gasoil extract	$3.5 \cdot 10^{-1}$
raffinate	6.24
mix of extract and raffinate	$1 \cdot 10^{-15}$
	At the same time paramagnetic properties are not observed. In 35 days it returns to the value $3.5 \cdot 10^{-1} \times 10^{16}$ spin/cm ³

The results obtained show that extraction mechanism of medium and heavy petroleum cuts is more complicated than it was supposed earlier [2] due to complex formation in extra-agent aromatic hydrocarbon system.

On the basis of the carried out investigations it has been established that the highly molecular aromatic hydrocarbons extraction from hydrocarbons of petroleum by selective solvents the competitive processes of excitation and (or) homolytic dissociation of diamagnetic molecules, recombination of radicals and complex formation - associative combination formed by the solvents are being carried out in the system.

The advantage of the process depends on temperature, raw material, ratio and the structure of extra-agent delivered.

The calculation of paramagnetic balance in extraction process was carried out according to formula:

$$F = \frac{PMC_e \cdot V_e + PMC_r \cdot V_r}{PMC_{raw} \cdot V_{raw}} 100\%, \quad \text{where}$$

PMC_e, PMC_r, PMC_{raw} - PMC in extract, raffinate, raw, accordingly.

V_e, V_r, V_{raw} - volume of extract, raffinate and raw, accordingly.

Fig. 2 shows the results of calculations.

Discovered regularities of change of paramagnetic particles number in extract raffinate and distributions of aromatic hydrocarbons with substituents in α -, β - and γ - positions make it possible to

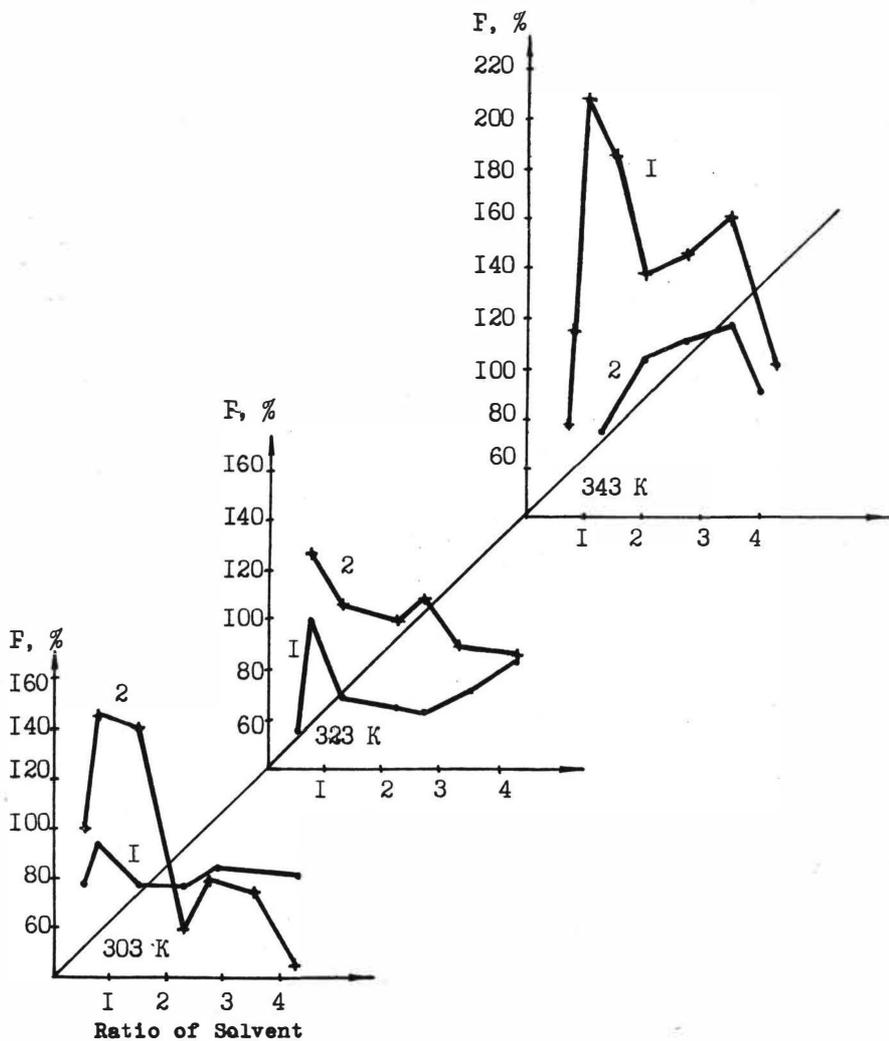


Fig. 2. Value F of Ratio of solvent under light gasoil extraction.

1 - sulfolane;

2 - sulfolane + 7% H₂O

obtain (using various extra-agents) products with the same content of aromatic hydrocarbons but different in its structure that is to obtain products with required physical properties (see Table 2)

Table 2. Extraction of light gasoil with sulfolane and N,N-dimethylimidazoline

	Sulfolane		N,N-dimethylimidazoline	
	Extract	Raffinate	Extract	Raffinate
Benzene hydrocarbons content	98.0-99.0		98.0-99.0	
Density, d^{20}	1.0299		1.0340	
Molecular composition, %				
aliphatic-benzene ratio	1.6	7.0	1.3	5.5
proton alpha substitution	40.2	23.6	41.7	23.3
proton beta substitution	14.6	43.3	9.0	38.4
proton gamma substitution	6.0	19.7	5.5	21.5
PMC, spin/cm ³	$1.47 \cdot 10^{17}$	$2.76 \cdot 10^{15}$	$1.0 \cdot 10^{17}$	$3.67 \cdot 10^{15}$

References

1. Unger F.G. Issledovanie sostava i struktury tyazholyh nephteproduktov. TsNIITEnephtehim. 1982. P. 151.
2. Nesterchuk G.T., Yakushin M.I., Grishenko N.F., Sidorov V.N., Rogozkin V.A. O podborye novykh ekstragentov aromaticsikh uglyevodorodov. TsNIITEnephtehim. 1976. P. 30.

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Refining of organic chemicals is probably the most popular process in industrial chemical synthesis. Distillation still seems to be the most effective method of purification of many products and nearly all solvents used in chemical processes. Besides of purified products distillation processes produce more or less residues which generally consist of organic products of thermal destruction and inorganic compounds (catalysts, complexing agents etc.). Distillation residues are often semi-liquid, easily solidifying and crystallizing products so their treatment and neutralization in industrial scale may cause many difficulties. These problems may not be even seen in a laboratory scale but they appear when processes are applied in industrial scale in chemical plant.

The One Stage Double Extraction (OSDE) method (1,2) eliminates many of the difficulties met in everyday industrial practice. The OSDE method depends on a selective extraction and liquidization of distillation residues by the means of both water and lyphophylic combustible liquid. Water dissolves organic hydrophylic matter and inorganic substances whereas organic liquid liquidizes organic matter, especially polymers and other organic high boilers which are mainly responsible for solidification of the residues and clogging of bottom outlets of distillation vessels. When liquidization/extraction processes are over water layer can be separated from organic phase and poured out from distillation vesses into sewage system of the factory. Organic layer can be easily combusted in any type of incineration installation.

Another possibility of treatment of distillation residues can be application of aqueous solution of surface active agents (SAA method). The SAA method let transform viscous, adhesive liquids into easy in treatment materials. The paper describes application of the OSDE and the SAA methods in treatment of difficult residues appearing during regeneration of acetic acid in one of Polish chemical plants.

Experimental. Discussion

In an original industrial process acetic acid was regenerated by distillation. Liquid before distillation consisted of: acetic acid (70% appr.), chloroacetic acid (5% appr.), zinc chloride (10% appr.) and other compounds. The above mixture in a quantity of about 600 l. was loaded into a distillation vessel. When the regeneration process was finished

Table 1. The application of the One Stage Double Extraction method in treatment of distillation residues from regeneration of acetic acid in industrial scale

Batch No	Residues /g/	Toluene /ml/	Water /g/	Others /g/	Results
1	140	40	350		Liquidization. Good separation of phases
1	140	30	350		As above
1	140	30	342	28 /NaOH/	Emulsions in both phases.
2	140	40	350		Liquidization. Good separation of phases
2	140	30	350		As above
2	140	30	346	24 /NaOH/	Emulsions in both phases
3	150	30	350		Liquidization. Good separation of phases
3	150	30	346	14 /NaOH/	Emulsions in organic phase
4	160	30	350		Liquidization. Good separation of phases
4	160	30	342	28 /NaOH/	Emulsions in organic phase
4	160	30	346	24 /Na ₂ CO ₃ /	As above
5	190	30	350		Liquidization. Good separation of phases
5	190	30	346	24 /Na ₂ CO ₃ /	Emulsions in organic phase.

(the residues were still liquid in a temperature of distillation but its continuation could cause crystallization, solidifying and clogging the bottom outlet of the vessel making evacuation extremely difficult). the residues were poured out into containers. Samples were taken in this moment and the OSDE or SAA method was applied and investigated.

Application of the OSDE method (Table 1) depended on adding both water (aqueous basic solution) and lyphophylic non miscible with water

Table 2. The application of surface active agent aqueous solutions in treatment of distillation residues from regeneration of acetic acid

Residues /g/	Water /g/	S.a. agent /g/	NaOH /g/	Final pH	Results
70	200	-	30	6,1	Light brown precipitate of a high adhesion to glass
70	200	span 35 /5/	30	6,1	Light brown precipitate. Easy evacuation and separation
70	200	tween 80 /5/	30	5,9	As above
70	200	tween 80 /1/	30	6,3	Light brown precipitate of a high adhesion to glass
70	200	kokosal ¹ /5/	30	6,4	Light brown precipitate. Easy evacuation and separation
70	200	kokosal /2/	30	6,3	Light brown precipitate of a high adhesion to glass
70	400	kokosal /5/	30	6,3	As above
70	200	tween 80 /5/	20	4,1	Tar still present
			30	6,1	Light brown precipitate. Easy evacuation and separation
1 - trade name of a mixture of synthetic detergents.					

liquid. Liquidization took place in every experiment but separation of phases was impossible in cases of further neutralization of the obtained mixture.

Application of the SAA method resulted in (Table 2) transformation of distillation residues of tar consistence into a mixture consisting of a precipitate dispersed in aqueous solution. The precipitate was a mixture of zinc hydroxide and organic compounds in a relation depending on pH. Generally in a presence of a surface active agent treatment of the obtained mixture (evacuation, filtration) did not cause any trou-

bles while absence of detergent making the obtained precipitate highly adhesive to glass caused many troubles with evacuation and further separation of the mixture.

Conclusions

Distillation residues from acetic acid regeneration process can be effectively treated by the means of the OSDE or the SAA method.

The OSDE method does not require any additional equipment when applied in industrial scale. However, a mixing device is necessary in a vessel where the OSDE treatment is to be carried out.

Sewages free of zinc can be obtained as a result of application of the SAA method. The SAA method requires a separation device to separate the obtained precipitate.

References

1. M. Žak, The application of extraction methods in elimination of post distillation residues. Proceedings from the International Solvent Extraction Conference. Munchen, 1986.
2. M. Žak, The application of the One Stage Double Extraction method in safe elimination of distillation residues from benzyl cyanide industrial process. Proceedings from the 6th international conference Chemistry for Protection of the Environment. Torino. 1987.

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According to the guide-lines of the chemical industry active environmental protection requires a reduction of the amounts of waste water and its load of pollutants. The object is not only to remove pollutants from industrial waste waters but also, if possible, to recover them as valuable material. To this end solvent extraction has been applied successfully for several decades. As will be illustrated below, the development of new, highly efficient multicomponent extractants exhibiting low solubility in water has greatly increased the area of application of solvent extraction.

A well known example of simultaneous elimination and recovery is the extraction of phenol from aqueous waste streams. The long known Phenosolvan process, originally using butyl acetate (distribution coefficient $D = 49$) and later diisopropyl ether ($D = 20$) as extractant, suffered from the high solubility in water of these extractants. Amines, especially tertiary amines, which may associate as basic components with the acidic phenol, promised to be more efficient. Using [®]Hostarex A 327 from Hoechst containing trioctyl- and tridecyl amine in equal parts, distribution coefficients from 11 to 13 were obtained for phenol contents ranging from 0.1 to 2 wt.% in the aqueous phase. Hostarex A 327 has a boiling point of over 350°C and a solubility in water of less than 10 ppm. D may be increased considerably if the tertiary amine is converted to an amine salt, e.g. to amine sulfate $(R_3NH)_2SO_4$ /1/. To limit viscosity only 70 % of the Hostarex A 327 are converted, the remaining 30 % acting as diluent for the amine salt. With this extractant system D -values of over 800 are obtained, enabling the phenol content of a waste water to be decreased from 5 wt.% to less than 1 ppm in a 3-stage counter-current extraction plant having a phase volume ratio (extractant/aqueous feed) of $X/W = 1/2$. Due to the high boiling point of the extractant system phenol may be recovered by distillation. A re-extraction of phenol using a sodium hydroxide solution is not necessary.

In the production of aromatic chemical intermediates large quantities of waste water containing halogenated and nitrated phenols are involved. These substances which are mostly toxic and biologically only partially degradable are generally removed without recovery by oxidation or by adsorption on activated carbon followed by combustion. Besides losing valuable substances, the forming of dioxines during the combustion of chlorophenols must be pretended. Solvent extraction using Hostarex A 327 avoids this and permits nitrophenols to be removed completely from waste waters, which could not be achieved by extraction so far. Moreover, the high solubility in water of commonly used extractants such as methylene chloride and methyl ethyl ketone always requires supplementary processing.

For the extraction of 4-nitrophenol from water effluents long-chained amines have been tested (s. Table 1). Their extraction power is considerably enhanced by forming

amine salts /2/. Using amine hydrochlorides, 4-nitrophenol distribution coefficients of over 10 000 are obtained, even higher values (12 000) are found if the sulfate form is employed. Thus a feed ratio of X/W = 1/10 in a single stage contacting device will suffice to decrease the content of 4-nitrophenol from 7000 ppm to some few ppm or to less than 0.1 ppm if more than one extraction stage is used.

Table 1. Extraction of 4-nitrophenol from waste water using amines (25 °C, phase volume ratio X/W = 1/10, *) X/W = 1/4)

Extractant	HCl in Feed (wt. %)	4-Nitrophenol in		D
		Raffin. (ppm)	Extract (wt. %)	
Hostarex A 327	0	576	5.21	91
Hostarex A 327 (40 % in n-dodecane* dto. in Solvesso 150*	1.3	8.5	2.89	3400
Hostarex A 327	1.4	6.6	7.20	10900
Hostarex A 327 (70 % in sulfate form)	0	4.5	5.46	12130

This remarkable extraction power of amine salts is the higher the more acidic the phenol derivatives are (s. Table 2). The distribution coefficient may reach values of over 150 000, giving a residual content of the phenolic compound of less than 0.2 ppm after a single contact with X/W = 1/10. The regeneration of the loaded amine phase can also be performed in a single stage with NaOH.

Table 2. Extraction of Nitrophenols from aqueous solutions using Hostarex A 327 hydrochloride (25 °C, X/W = 1/10, *) X/W = 1/20)

Solute	Concentration		D
	Raffin. (ppm)	Extract (wt. %)	
2-Nitrophenol	6.4	2.02	3150
4-Chloro-2-nitrophenol	0.2	0.20	9800
2,4-Dinitrophenol*	0.5	0.65	13000
2,4,6 Trinitrophenol	0.3	1.53	50970
3-Trifluoromethyl-4-nitrophenol	0.2	3.07	153400

Chlorophenols are particularly troublesome to the biological waste water processing. 2-Chlorophenol may be extracted with toluene (D = 9), n-hexanol (D = 130), diethyl ether (D = 179) and methyl ethyl ketone (D = 200), respectively. But all these extractants are too soluble in water. In a single small plant trichloroethylene /3/ is known to be used and the ecologically unfavourable methylene chloride is mentioned as extractant for chlorinated phenols /4/. However, in both cases an additional distillation and an adsorption step is needed. This is not necessary if Hostarex A 327 hydrochloride or -sulfate is used as extractant, which have distribution coefficients of over 80 000 (s. Table 3) /5/. A residual pollutant content of 0.1 ppm may be reached by a single step extraction.

Table 3. Extraction of halogenated phenols from aqueous solutions using Hostarex A 327 hydrochloride (25 °C, X/W = 1/10, 1) using pure amine, 2) X/W = 1/15)

Solute	Concentration		D
	Raffin. (ppm)	Extract (wt. %)	
2-Chlorophenol 1)	527	5.20	99
2-Chlorophenol	25	5.91	2360
2-Fluorophenol	97	5.54	570
2,4-Dichlorophenol	49	5.17	1050
2,4,5-Trichlorophenol	0.1	0.99	99000
Pentachlorophenol 2)	<0.02	0.017	>8500

For other acidic organic substances like carboxylic and sulfonic acids extraction processes for the recovery of valuable substances have been developed too for a long time, e.g. for removing acetic acid (HAC). For its extraction from diluted aqueous wastes (< 5 wt.%) trioctylphosphine oxide (TOPO) and long-chained amines, especially trialkyl amines, were found to be suitable. Although TOPO is applied in technical plants /6/, the low distribution coefficient of 3 at the most and the low loading capacity render this process quite expensive. It may be improved by using a liquid phosphine oxide like Cyanex 932 /7/.

The extraction of HAC with amines /8/, which give D-values of up to 4.7 seems more attractive. The extraction power of amines still may be enhanced by the addition of polar diluents /8-10/. Studies about the synergistic influence of alcohols /11/ showed the strongest effect with n-butanol (D = 32, HAC-content in raffinate: 0.06 wt.%), followed by n-pentanol (D = 29), n-octanol (D = 18), 2-ethyl-hexanol (D = 16.5), isodecanol (D = 12.8). However, if HAC is distilled off the alcohols may form esters with HAC. This does not happen if nonyl phenol is used as additive to amines /11/. With an extractant system comprised of 30 wt.% Hostarex A 327 and 70 wt.% nonyl phenol according to a ratio of 4 moles nonyl phenol per mol Hostarex a distribution coefficient of over 250 is obtained. Using this extractant 99 % of HAC may be recovered from waste waters by contacting both phases only once. As all the extractant components have boiling points above 300°C and are chemically stable with HAC the latter may be simply distilled off.

The synergistic influence of nonyl phenol on the tertiary amine also favours the removal of other carboxylic acids from waste waters like butanoic, malonic, glycolic and lactic acid for which the distribution coefficients are enhanced by a factor of 10 to 100 compared to the pure amine /11/.

Aromatic sulfonic acids as well may be removed totally like phenol sulfonic acids from mineral acidic waste waters using Hostarex A 327.

Many of the technologies of coal processing and the production of organic chemical intermediates involve vast aqueous streams containing well water soluble heterocyclic compounds having N as heteroatom like pyridines, piperidines and pyrrolidines. These compounds may be distilled off but the azeotropes formed often have water contents of up to 50 wt.%.

To extract pyridin from waste waters aromatic hydrocarbons like benzene (D = 2.7) and alcohols like n-hexanol (D = 6.1) and n-octanol (D = 2.9) have been tested. Better extractants proved to be carboxylic acids being immiscible with water and

Table 4. Extraction of N-containing heterocycles using carboxylic acids (25 °C, X/W = 1/1)

Solute	Extractant	Concentr. (g/kg)		D
		Extract	Raffin.	
Pyridine	Isononanic acid	153.9	16.1	9.6
α -Picoline	Isononanic acid	183.0	15.7	11.7
α -Picoline	n-Caprylic acid	97.5	4.1	23.8
α -Picoline	Laurinic acid	101.9	3.4	30.0
2,6-Lutidine	Isononanic acid	95.5	6.6	14.5

having distribution coefficients of 10 to 30 for pyridine and α -picoline (s. Table 4) /12/. Since these long-chained carboxylic acids have boiling points of 230°C and more the solutes may be directly distilled off and obtained free of water.

The extraction of chlorinated hydrocarbons (CHC) from aqueous streams is not yet a common process. Long-chained CHC or alcohols like decanol may be used as extractants. Paraffinic hydrocarbons (C_{10} - C_{12}) possess a lower solubility in water (<1 ppm) enabling the CHC to be distilled off /13/.

On an optimal combination of waste water processing and recovery of valuable material is reported by Michelsen /14/. From the effluent stream of a nitration plant nitroglycerol and nitroglycol have been extracted using dinitrotoluene, which is another common component of explosives. Therefore, the laden extractant may be directly recirculated to the production process.

Caprolactam may be removed from industrial waste waters using dodecyl phenol isomers /15/. From the aqueous stream containing 2 % caprolactam 99 % thereof may be recovered applying a phase volume ratio of $X/W = 1/4$.

Summarizing, it can be stated that during the last years the importance of solvent extraction for waste water processing has increased considerably. This is mainly caused by the development of synergistically acting extractant systems.

References

1. Braun G. et al. // Preprints of ISEC 1986. Vol. 3. p. 885.
2. DE-PS 3 627 653 (1986) Hoechst AG.
3. Klapproth H., Krause G. // *Moderne Abwasserreinigungsmethoden*. p. 173-181. München-Wien: Oldenbourg, 1978.
4. US-PS 3 931 001 (1976) Dow Chem. Co.
5. DE-PS applied (1987) Hoechst AG.
6. Kohn P.M. // *Chem. Eng.* 83 (1978), N 6. p. 58.
7. Watson E.K. et al. // Preprints of ISEC 1986. Vol. 3. p. 775.
8. King C.J. // Preprints of ISEC 1980, paper 80-66.
9. Siebenhofer M., Marr R. // Preprints of ISEC 1983. p. 219.
10. Wardell J.M., King C.J. // *J. Chem. Data*, 23 (1978), N 2. p. 144.
11. Wojtech B., Mayer M. // *Chem.-Ing.-Techn.* 57 (1985), N 2. p. 134.
12. DE-PS applied (1987) Hoechst AG.
13. Rückl W. et. al. // *Chem. Ind.* 37 (1985), N 12, p. 861.
14. Michelsen O.B., Oestern S. // *Environ. Sci. Technol.* 13 (1979), N 6. p. 735.
15. US-PS 4 013 640 (1977) Union Carbide Co.

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The waste waters from the Chloramine B production contain, besides HCl, a considerable amount of benzenesulphonic acid (BSAC) and its amide (BSAM), the acids being present in the form of their ammonium salts. There are both economic and environmental reasons for recovering BSAC and BSAM from these effluents. If sufficiently pure, they can be reused as intermediates in the process, either as a mixture, or preferentially separated from each other. In the present paper an extraction process is devised allowing this separation.

It has been found that BSAC can be easily separated from acidified waste waters by means of extraction by the solution of tertiary aliphatic amines (TAA) in some organic diluents. Soviet commercial trialkylamine C₇-C₉ was used in the form of 0.4 M solution both in xylene and in MIBK.

Amine extraction of acids can be described by reaction

$$H^+ + A^- + \overline{R_3N} \rightleftharpoons \overline{R_3NHA}$$

The following values of concentration extraction constants of this reaction have been found:

	xylene	MIBK
K(HCl)	2.71 · 10 ³	6.18 · 10 ³
K(BSAC)	1.51 · 10 ⁵	3.92 · 10 ⁵

As can be seen from these values, efficient separation of acids is possible.

In case of xylene solutions it has been found that the complexes between amine and acids are able to extract BSAM according to "physical" extraction, the mean value of distribution coefficient being D = 11.0. Therefore BSAC and BSAM can be extracted simultaneously. Reextraction is carried out by the aqueous solution of NaOH. BSAM behaves like a weak acid under these conditions.

In case of MIBK it was found that BSAM is extracted "physically" by the pure diluent, the value of the distribution coefficient being D = 12.7. This allows a two-step separation process. In the first step the waste water is contacted with pure MIBK to extract BSAM. In the second step the separation of BSAC from acidified raffinate is carried out by contacting it with the solution of amine in MIBK. In both steps the reextraction is carried out by the aqueous solution of NaOH.

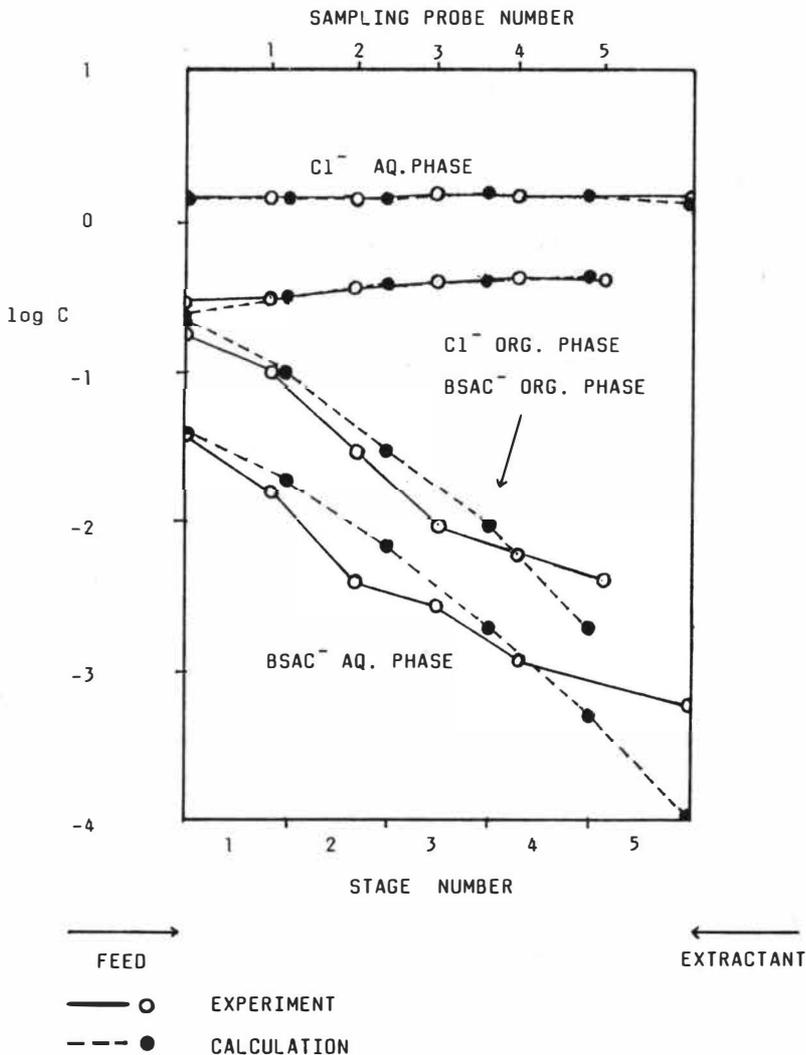


FIG. 2. CONCENTRATION PROFILE OF THE SECOND STEP
(COMPETITIVE EXTRACTION OF HCl AND BSAC BY TAA IN MIBK)

yield of extraction was 98.1 % for BSAC and 98.6 % for BSAM. The extract contained 6.92 g/l HCl (11.8 %), 33.02 g/l BSAC (56.3 %) and 18.68 g/l BSAM (31.9 %) (mass percent on the solute free basis). 4 theoretical stages were realized for both BSAC and BSAM.

In case of two-step process the waste water containing 0.128 M H^+ , 1.38 M Cl^- , 0.0384 M BSAC⁻ and 0.035 M BSAM was processed. In the first step it was contacted with pure MIBK, the ratio of the organic and aqueous phase volumetric velocities being 1:5.9. The yield of BSAM extraction was 97.1 %. The extractor was equipped with 5 sampling probes by which separate samples of each phase could be taken. In fig.1 the experimental concentration profiles are compared with the calculation for 4 theoretical stages (constant HETS, no backmixing).

In the second step the raffinate from the first step was contacted with 0.413 M TAA in MIBK. The ratio of the organic and aqueous phase volumetric velocities was 1:5. The yield of BSAC extraction was 98.4 %. The extract contained 25.9 g/l BSAC (74.2 %) and 9.0 g/l HCl (25.8 %) (mass percent on the solute free basis). In fig.2 the experimental concentration profiles are compared with the calculation for 5 theoretical stages (constant HETS, no backmixing).

Both processes make it possible to separate BSAC and BSAM with high efficiency and reasonable purity. A higher degree of separation of BSAC and BSAM from HCl can be reached by stripping the TAA extract with the aqueous solution of BSAC.

References

1. Procházka J.//Dechema Monographien.1970. Vol.65. P.325.
2. Bízek V., Procházka J.//Chem.Biochem.Eng.Q.1987. Vol.1. P.1.

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The decision of the problem of environmental water protection is connected with reliable and operative control of the toxicant content in natural waters and effluents. The composition of natural waters is essentially influenced by ejection of municipal and industrial wash, as well as waters from agricultural areas, because washes from fields along with fertilizers contain various toxic chemicals.

The most distributed industrial organic toxicants are oil products and phenolic compounds. Being the products of metabolism of some pesticides, phenols accumulate in soils and pollute underground waters. Toxicity of phenolic compounds is due to their cumulative properties, ability to form stable complex compounds with haemoglobin of blood to destroy the oxyde regime of reservoirs. That is why the extreme admissible concentrations (EAC) of many organic compounds are very low, for instance, in waters they are not more than 10^{-1} mg/l oil products, 10^{-3} mg/l phenol, 10^{-4} mg/l chlorphenol and so on [1], therefore it is necessary to work out new analytical technique and methods, characterized by low limits of detecting such toxicants. The latest investigations devoted to quantitative determination of organic compounds are mainly carried out by means of the methods [2], whose sensitivity is higher than EAC of many organic toxic substances in waters. In order to raise the resolving power of analytical methods different variants precondensation (freezing-out, sorbtion, liquid extraction) are widely used.

The rational method of extraction concentration consists in the beforeplanned (with the problem to decide in view) effects on the extraction systems to raise their efficiency. Extraction concentration differs greatly from other methods of concentration in its well-known versatility (it may be used to determine isomers and homologues, mono- and polysubstituted), in the possibility to carry out experiments both with macro- and microconcentrations of substances, expressness in comparative simplicity of operations in the absence of complex equipment. Unlike gas chromatography, it is possible to directly concentrate and separate not only volatile but non-volatile components as well. Besides, there is also an additional possibility to raise efficiency of this method of concentration (reextraction into the water phase). In the absence of reextraction practically complete transition of the substance into the extract takes place, as the calculations show, at distribution constants D of the order of 1400-1800

(one-time extraction, the volume ratio of water and organic phases being $r = 100$). But quite a few hardly extractible (i.e. easily soluble in water) organic toxicants are known for which even such extragents as higher alcohols, alkylacetates, tributylphosphate and others are in general low effective. Additional methods of increasing extraction characteristics are required, which, as a rule, cannot restrict themselves by the action of the well-known individual factors - salting-out, sinergetic and solvotropic effects, the transformation of hardly extractive compounds into the comparatively easily extractive ones and so on.

In this connection the advantages of means of different ways of influencing the extration system should be noted. For instance, the introduction of salting-out substances into the analyzed water increases the coefficients of phenols distribution 4-6 times on an average, the extraction in the presence in the extragent phase of extragent of solvotrope reagent (camphor, benzophenone, dialkylphthalate and others) is accompanied by the increase of effectiveness of the process by one order. Simultaneous introduction into the corresponding phases of the salting out substance and solvotropic reagent raises the phenolic coefficients of distribution 50 and more times. Such technique allows to effectively extract toxicants from the liquid analyzed provided that distribution constants constitute the minimum of 30-40. The range of organic solvents used in this case as extragents, is here rather wide and includes also such in general little efficient solvents as hydrocarbons. It is clear that at such concentration both volatile and non-volatile components turn into the extract. The selectivity of determination is achieved by means of sublimation and subsequent concentration of volatile and non-volatile toxicants separately.

Preliminary halogenation, alkylation or nitration of the substances being determined directly in the analyzed water samples raises the completeness of one-time extraction, for instance, phenols from 70% to 90-93%, $r = 100$. As an example Table 1 gives constants of distribution of phenol, 2-methylphenol, 2-nitrophenol, 2-nitro-6-methylphenol, 2-chlorphenol and 2-brominephenol in the systems of water solvents of different classes. By means of simple operations the initial compound (phenol) is transferred into the substituted one, characterized by much higher (sometimes by 3 orders) distribution coefficients. It is accompanied by the increase of completeness of one-time extraction and the decrease of limits of the further toxicant determination in the water sample being analyzed.

In general the extraction concentration and separation of organic substances is as follows. The salting-out agent is introduced into the analyzed water, the water is acidified (to suppress ionization of the distributed substances) and extracted by an organic solvent in

which the solvotropic reagent has preliminary been dissolved, almost 100-fold concentration is achieved with one extraction ($r = 100$). Re-extraction into alkalinized water solution of the photometric reagent raises the concentration coefficient 3-5 times more. The high general coefficient of concentration (300-500) results practically in the complete transition of a substance into reextract and its subsequent photometric determination of the concentrations of 10^{-8} - 10^{-9} mol/l.

The method of concentration proposed has the evident advantage over the routine distillation with water vapour, as losses during distillation are excluded, and the time of determination is considerably reduced. Another variant of a multifactor effect on the extraction system consists in the extraction of the toxicant by binary mixture of organic solvents consisting, e.g. of an active extractant and a comparatively less effective solvent. Additional increase of completeness of the toxicant extraction occurs during the introduction of solvotropic reagent into the combined extractant.

Table 1. Constants of distribution of phenol and some of its substituted between water and organic solvents

Extractants	Phenol	2-Methyl-Phenol	2-Nitro-Phenol	2-Methyl-6-Nitro-Phenol	2-Bromine-Phenol
$C_2H_4Cl_2$	4,0	23	395	1810	71
$CHCl_3$	1,9	17	140	2150	44
$C_6H_5CH_3$	1,6	12	180	1600	41
CCl_4	0,6	4,7	82	345	34

The further analysis of the concentrate is carried out by photometric or chromatographic methods. The advantage of extraction-gas-and-chromatographic method

is in the possibility of separate determination of compounds with identical physico-chemical properties, for instance, isomers and homologues. By the photometric method it is possible to determine only the total content of the substance. That is why the extraction gas chromatographic method of analysis of oil- and phenol-containing waters should be considered as rather perspective for the separate determination of related volatile components contained in waters in very small amounts when direct chromatography is impossible.

Without preliminary concentration gas chromatographic analysis of phenol-containing waters allows to determine phenols with the minimum $10^{-3}\%$ concentration, which is quite sufficient according to the sanitary hygienic norms of water purification. To low the limit of detection a method based on the combination of extraction concentration with the further gas chromatographic separate determination of phenols in extracts [3] is recommended. Phenol content in the analysed waters is of the order of $10^{-5}\%$ (0,1 mg/l); the chromatograph is "Tsvet-110" with the flame ionizing detector. The use of high efficient capillary columns

makes it possible to carry out experiments at rather low temperatures which is especially important when separating high boiling organic substances. With the aim of selective concentration volatile compounds are preliminary distilled with water vapour, extracted by a low boiling organic solvent, transferred into the non-volatile compounds, then the extragent is evaporated under vacuum. Thus the concentration of the determined substances increases 10^3 - $5 \cdot 10^3$ times, organic compounds hindering the analysis (e.i. oil products during the determination of phenols) evaporate with extragent vapours.

To combine extraction concentration with chromatographic separation it is necessary that the extragent should have different holding time as compared to the separable substances, dissolve them well and be slightly soluble in water; alkylacetates C_6-C_9 meet their requirements. For instance, extraction by n-butylacetate from water-salt solution and gas chromatographic analysis of the concentrate makes it possible to determine phenol and cresoles separately with quite a satisfactory exactness (Table 2).

The preliminary extraction concentration by hexane or tetrachloromethane with further gas-and-liquid chromatography or high efficient liquid chromatography detection is used for separation and determination of hydrocarbons in sea water [4] as well as for determination of oil products in natural waters [5].

Table 2. Gas chromatographic determination of phenols after concentration (n = 3, p = 0,95)

Separable components	Content, mg/l		S
	introduced	found	
Phenol	0,20	0,18	0,019
p-Cresol	0,18	0,17	0,016
Phenol	0,085	0,076	0,014
p-Cresol	0,090	0,079	0,011

The review of modern methods of determination of organic toxicants in waters allows to make a conclusion about wise possibilities of extraction concentration when determining traces of organic compounds both in stationary conditions and with automatic control of quality of natural and purified effluents.

References

1. Grushko Ya.M. Toxic organic compounds in industrial effluents. L.: Chemistry, 1982. 214 p.
2. Lurye Yu.Yu. Analytical chemistry of industrial effluents. M.: Chemistry, 1984. 447 p.
3. Korenman Ya.I., Bortnikova R.N., Prikhodko A.A., Fedyanin A.A. // J.Anal.Chem. 1977. V. 32. P. 2413.
4. Desideri P., Lepri L., Heimler D., Gianessi S. // J.chromatogr., 1984. V. 284, N 10. P. 167.
5. Dmitriyev F.V. Au.cert. N 879459, B.I. 1981, N 41.

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There is a lot of organic pollutants with high water solubility in sewage waters. They can be refer to hydrophilic substances. On some evaluations [1] they constitute for about 70-80% of COD in purified sewage water. Hydrophilic substances are characterized by presence of more than one polar functional group or their combination. There are substances of different classes in sewage waters depending on the type of the functional groups and their combination.

It is necessary to search the new extraction systems for extracting hydrophilic substances from water as their partition coefficients are very low - not more than 0,01-0,1 - into traditional hydrophobic extractants. Their typical representatives are chloroform, diethyl ether, ethyl acetate, isobutanol. We have chosen the way of directed changing of water qualities in solutions with organic substances under the influence of electrolytes. The organic solvents, such as low alcohols, cyclic ethers, amines, amides, carbonic acids, sulfoacids which are completely mixed with pure water can be converted under the influence of electrolyte into extractants. We have proposed to regard such extractants as hydrophilic [2-4].

Hydrophilic extractants lead to the increase of partition coefficient in comparison with hydrophobic ones. This fact gives a possibility for extracting hydrophilic substances from water solutions and their concentrating. Further increase of the degree of concentration may be achieved due to the usage of such hydrophilic extractant's properties as their high polarity. It is possible to undertake homogenic derivatization reactions in their media and by hydrophilic extractant to full-fill the derivatization of the active groups of hydrophilic organic [5] substances in the presense of boron trifluoride. By this action it is possible to run into the next step concentrating by converting hydrophilic substances derivatives into the medium of hydrophobic extractants. The choice was made among a large quantity of electrolytes which are capable to convert water soluble solvents into extractants taking into consideration the universe action. Phase separation was studied in the presense of electrolyte addition as the pure salt and as its saturated water solution. The last procedure was studied especially as to apply in the presense of surfactants as it required no intense mixing and excluded foaming of solution. The most universal action is attributed to potassium carbonate and fluoride, ammonium sulfates and fluoride.

These salts cause phase separation both in the presence of pure salt and its saturated water solution. The same action is characteristic for potassium and sodium hydroxides.

The composition of coexisting phases was explored. Minimal quantity of the electrolyte which causes the maximal equality of the developed organic phase layer to that of the organic solvent added to water was determined. The evolution of organic layer from homogeneous water-organic mixture takes place in the presence of 0,1 - 0,2 g of electrolyte per 1,0 g of water in 1:1 water - solvent relationship. In this case the volume of organic layer considerably exceeds the volume of added organic solvent. By the further increase of electrolyte quantity the volume of the organic phase sharply decreases and in the presence of 0,3 - 0,4 gram of electrolyte per 1,0 g of water the volume of organic phase differs from the volume of extractant not more than by 10 - 20 %.

The evolved organic phase includes some water. This amount of water in organic phase is one more criterium of hydrophilic electrolyte choice as the criterium for minimal quantity of salts on water mass unity. By gas chromatography the quantity of water in organic phase for different hydrophilic extractants was detected in the case of some electrolyte usage. The dependence of volume part of water in organic phase (% H₂O) from the relationship between the volumes of the

added saturated electrolyte solution and water sample (V_s/V_w) is given. Fig. 1 shows the example of the system of water-isopropanol-ammonium sulphate, potassium carbonate, potassium fluoride and ammonium fluoride. The optimum properties from the point of minimal water quantity possess fluorides. The water content in organic layer for potassium salt doesn't exceed 2 - 5 % in optimal range.

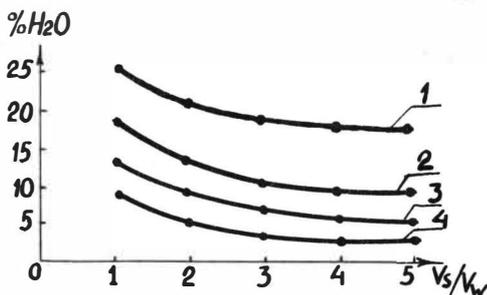


Fig. 1. Water content in organic layer : 1 - $(\text{NH}_4)_2\text{SO}_4$; 2 - K_2CO_3 ; 3 - NH_4F ; 4 - KF

The gas chromatographic determination of the partition coefficient into hydrophilic extractants in the presence of different electrolytes was performed for such hydrophilic compound as diethylene glycol. The aliquot parts of both layers were acylated before gas chromatographic treatment. The obtained results are illustrated in Table 1.

The partition coefficients into hydrophilic extractants have been increased and are in the range of 1 - 10 for the first members of polyoxyethyleneglycol serie. Maximal partition coefficient values for diethylene glycol into 4 from the most typical representatives of 20 studied

Table 1. Partition coefficients of diethylene glycol

Hydrophilic extractant	Partition coefficient			
	$(\text{NH}_4)_2\text{SO}_4$	K_2CO_3	KF	NH_4F
Acetone	2,3	1,8	0,55	0,40
Dioxane	2,6	1,8	0,50	0,38
Acetonitril	0,66	1,2	0,40	0,28
Isopropanol	2,2	4,4	2,0	1,1

hydrophilic extractants were in the presence of ammonium sulphate.

According to the character of changing of the partition coefficient in homological serie of extractants shown it is possible to suppose the existense of partition coefficient logarithm dependence on the number of carbon atoms in the molecules of homological serie of hydrophilic extractants. This dependence has the same character as shown in [6] for hydrophobic extractants. Such dependences for diethylene glycol and diethanol amine in the process of extraction by the members of homological serie of alcohols (from hydrophilic - methanol to hydrophobic - pentanol) in the presence of potassium carbonate are shown in Fig. 2.

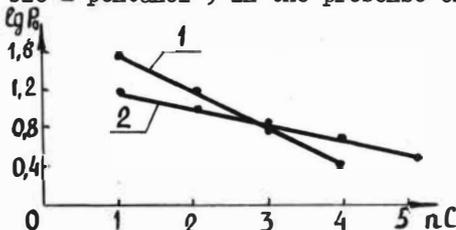


Fig. 2. Variation of partition coefficient in homological serie of extractants : 1 - diethanolamine, 2 - diethyleneglycol

The partition coefficient change of homological serie of polyoxyethylene glycols with general formula $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$, where n varies from 1 to 8 has been studied. The results show that for hydrophilic extractants the other, typical for hydrophobic extractants dependence of partition coefficient logarithm on increments in molecular structure of distributed substance conforms. The meanings of partition coefficient increments for one oxyethylene unit in hydrophobic extractants is in the range of 0,21 - 0,23 and 0,29 - 0,31 for hydrophilic ones. This difference is the witness of realised additional molecular interactions in hydrophilic extractants.

The usage of hydrophilic extractants is possible not only for polyoxyethylene glycols, but also for the other hydrophilic poly- and heterofunctional organic compounds with hydroxy- and aminogroups. The comparative data for glycerol, pentaerithritol, diethanolamine in the process of their extraction from water solution into hydrophilic extractants are shown in Table 2. Here also isobutanol is shown, which is cited as hydrophobic extractant with maximal extracting activity in reference-books [7].

The electrolyte affects extracting system changing its homogeneity and evolving organic layers. Further increase of the added electrolyte

Table 2. Partition coefficients P_0 of hydrophylic organic compounds

Substance	Hydrophylic extractant	Electrolyte	P_0	P_0 in isobutanol
Glycerol	Dimethylformamide	$(\text{NH}_4)_2\text{SO}_4$	1.2	0.1
Pentaerythritol	Dimethylacetamide	$(\text{NH}_4)_2\text{SO}_4$	2.9	0.14
Diethanolamine	Methanol	K_2CO_3	39	0.19

quantity causes only the change of coexisting phase volumes and water contents in organic phase without the influence on partition coefficient values. Due to this fact there is no need in the case of hydrophylic extractants usage to define electrolyte concentration in the layer. It is quite enough to add such a quantity of electrolyte that will evolve organic layer. The resulting meaning of partition coefficient will not further depend on the quantity of salt in the system.

So we have separated a new class of extractants - hydrophilic one for which the validity to use them in detection of hydrophilic substances in water was shown. The studied class of extractants has great perspectives in organic assay. These extractants can be proposed for separation and concentration of polyfunctional (glycols, polyols, polyamines) and also heterofunctional (aminoalcohols, hydroacids, aminoacids) organic compounds.

References

1. Kasiske D., Klinkmüller K.D., Sonneborn M. // J. Chromatogr. 1978. Vol. 149. P. 703.
2. Nevinnaya L.V., Kofanov V.I. // Metody analiza objectov okruzhayushey sredy: Tez. dokl. Vsesoyuz. conf. Moskva, 1983. P. 67.
3. Kofanov V.I., Nevinnaya L.V. // Proceed. 11 USSR - Japan Joint Symposium on Analytical Chemistry. Moscow; Kiev, 1984. P. 203.
4. Nevinnaya L.V., Kofanov V.I. // Khimiya i tekhnologiya vody. 1984. Vol. 6. N 4. P. 326.
5. Nevinnaya L.V., Klyachko Yu.A. // Zh. analyt. khimiy. 1986. Vol. 41. N 12P. P. 2257.
6. Korenman I.M. Ekstraktsiya v analize organicheskikh veschestv. Moskva: Khimiya, 1977. 200 s.
7. Korenman I.M. Constanty raspredeleniya organicheskikh veschestv mezhdu dvumya fazamy. Gorky: Gork. Un-t., vyp. 1 - 5. 1975 - 1979.

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Introduction: A major advantage of carbon dioxide used as a solvent is, that the process can be designed at a temperature level which is below the temperature to which e.g. a natural raw material is exposed in nature and where no residual solvent in extract or raffinate is allowed. In the present work a high pressure equipment is used where solid feedstocks are extracted in a batch autoclave, liquid solutions can be extracted in a counter current extraction column.

Experimental equipment. The high pressure equipment for extraction out of a solid matrix contains of an extraction autoclave (0,5 l) a separator (0,5 l), a solvent storage vessel and a diaphragm pump for liquid CO₂. The maximum CO₂ flow is 12 kg/h at a pressure of 325 bar. All apparatus are double coated and temperature controlled.

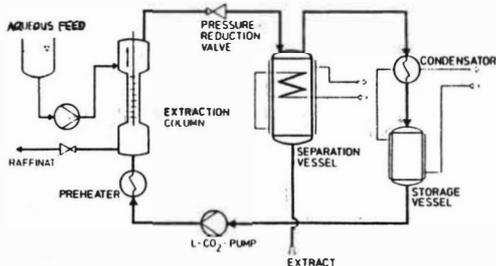


Fig.1. Flow-sheet

The CO₂ undergoes a continuous cycle: the CO₂ pump draws liquid CO₂ from the storage vessel and compresses it to extraction pressure. Preheated CO₂ passes the extractor and is charged with the solubles. Stripping is done by depressuring and evaporation in the separator.

The stripped gas is condensed and flows back to the storage vessel. The studies of liquid liquid systems are carried out in a continuous counter current Karr type column. The column (Fig.2) has an inner diameter of 35 mm and an active height of 1,5 m. The 28 sieve plates are raised up and down using a magnetic coupled drive at a frequency of 30 to 300 strokes per minute. The level of the liquid interface is observable at the top of the column by sight glasses. With the help of the sampling valves along the active column the concentration profile can be measured.

As shown in Fig.1 the liquid liquid extraction process is identical to the leaching process except the fact that instead of a batch autoclave the column is used.

Extraction of pyrethrines: Pyrethrum is a strong natural insecticide which is non toxic for warm blooded animals and humans. It is obtained by the extraction of dried and grinded chrysanthemum flowers and contains of 6 active esters the chrysanthemum mono-(I) and dicarboxylic acid (II). Pyrethrines are unstable if exposed to heat and ultra-violet light. In all known production processes the flowers are treated with a lipophil solvent (mainly hexane). This extraction results in a dark semi-liquid oleoresin (crude extract). For raffination of this crude extract to commercial requirements several consecutive process steps with high energy consumption are necessary.

As known from previous work CO_2 is a selective solvent for the pyrethrines /1,2/. So the numerous refining steps for the crude extract could be replaced by a carbondioxide extraction. The used crude extract (97,5 g) had a content of 23,1 % Pyr.I and 17,3 % Pyr.II. Extraction was carried out at 100 bar and 40° C, separation at 60 bar and 30° C. The



Fig.2. Extraction column

CO_2 throughput was 6 kg/h. During the testing time 7 fractions were taken out. For better distribution of the crude extract the extraction autoclave was filled with glasballs with a diameter of 3 mm as filling material. After a test time of 195 min a total yield of 91 % is calculated. The residue in the autoclave had a content of 0,6 % Pyr.I and 0,2 % Pyr.II.

Summerising an upgrading from 40% pyrethrine content to about 80% pyrethrine content takes place. The residue contains mostly colouring and polar organic impurities. With this process a cost reduction of more than 35% for the investment costs as well as operating expenses for a plant with annual capacity of 3000 tons/a pyrethrum was calculated.

Extraction of Pyrethrine-Crude-Extract

Fraction	Extr. Time (min)	Extr. Quant. (g)	C o n t e n t s	
			PyrI (%)	PyrII (%)
I	5	3,8	39,5	22,5
II	15	8,8	51,3	27,1
III	30	9,4	49,4	29,8
IV	60	13,0	46,5	36,1
V	90	5,7	34,6	36,3
VI	150	4,7	26,3	38,4
VII	195	5,9	8,6	20,8

Extraction of furfural. At ISEC '86 we presented a new process for furfural extraction out of aqueous solution/4/. In the presence of organic acids resinification and decomposition of furfural can occur which leads to fowling of heated surfaces. So the main idea of the process was to minimize the time furfural is exposed to heated surfaces. The best solvents for this were chlorinated hydrocarbons. Meanwhile we tested carbondioxide as solvent and succeeded in selective furfural extraction even in presence of organic acids. Another advantage is that there is no more need of c_{CO_2} [%] wt

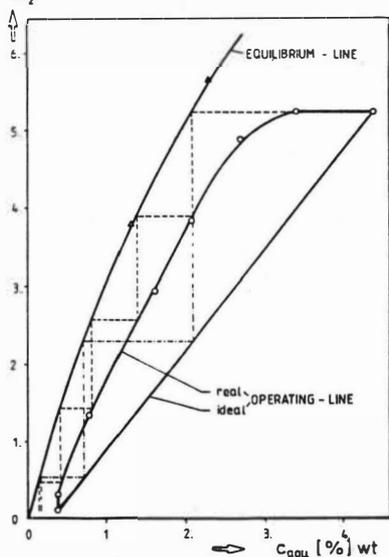


Fig.3. Furfural Extraction

reextraction of the solvent out of the raffinate as in the case of extraction with chlorinated hydrocarbons.

Fig.3 shows the McCabe Thiele construction for the extraction of furfural with carbon-dioxide at 80 bar and 40°C from a solution with 4,3 % wt.furfural.

The solvent/feed ratio was 0,8. As shown an extraction rate of more than 93 % can be achieved with less than 2 theoretical stages. The real operating line in Fig.3 is derived considering backmixing and mass transfer with the dispersion model.

Extraction of aroma components. As known from literature /3/ acetates and esters have a higher distribution coefficient between water and CO_2 than n-alcohols. Fig. 4 shows the distribution coefficients m (molar basis) of the n-alcohols and n-esters in liquid CO_2 at saturation pressure at $16,7^\circ \text{C}$. The distribution of the alcohols is about 10 times lower than the ester with the same molecular weight. The equation $m = e^{(C_1 \cdot n + C_2)}$ fits the two curves with $C_1 = 0,9$ (0,99) and $C_2 = -2,9$ (-0,2) for the n-alcohols (esters). This behaviour was used for the selective extraction of wine flavour. A CO_2 /wine ratio of 0,5 was used to extract the aroma components. Although the resulted extract has an ethanol content of about 65% what means an upgrading of concentration with factor 6 the aroma components above C_5 in common are upgraded 100 to 150-fold. These extracts may be used for back-addition to original wines or to the raffinate after distillation.

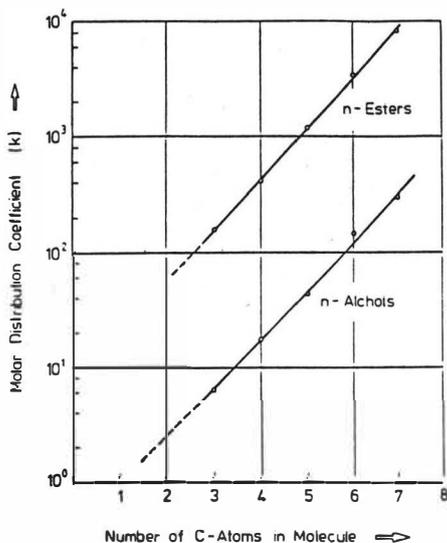


Fig.4. Distribution coefficients

References

1. Bunzenberger G., E.Lack and R.Marr // Ger.Chem.Eng. 7 (1984).25-31.
2. Stahl E., K.W.Quirin and D.Gerard // Verdichtete Gase zur Extraktion und Raffination. Berlin: Springer-Verlag, 1967.
3. Schultz W.G. and J.M.Randall, Liquid Carbondioxide for Selective Aroma Extraction // Food Technol.Vol.24 (11/1970), S.1282.
4. Bunzenberger G., M.Siebenhofer and R.Marr, Recovery of Furfural from Papermill-Effluents by Liquid-Liquid-Extraction Economical and Technical Considerations // ISEC '86, 11.-16.9.1986, München.

EFFECT OF MASS TRANSFER RATE ON THE EXTRACTION EFFICIENCY OF α -AMYLASEM. Dekker¹, K. Van 't Riet¹, B.H. Bijsterbosch², R.B.G. Wolbert³ and R. Hilhorst³

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¹Department of Food Science, Food- and Bioengineering group²Department of Physical- and Colloid Chemistry³Department of Biochemistry**INTRODUCTION**

In biotechnology there is a need for new protein recovery processes, which have a high selectivity for the desired product and can be scaled up easily. Liquid-liquid extraction of an aqueous solution with an organic solvent containing reversed micelles is a promising process for the selective recovery of proteins from a fermentation broth. A reversed micelle consists of a spherical aggregate of surfactant molecules in an apolar solvent surrounding an inner core of water (Fig. 1a). The polar environment inside such a micelle makes it possible for polar compounds, such as proteins, to be solubilized in a largely apolar solvent (Fig. 1b).

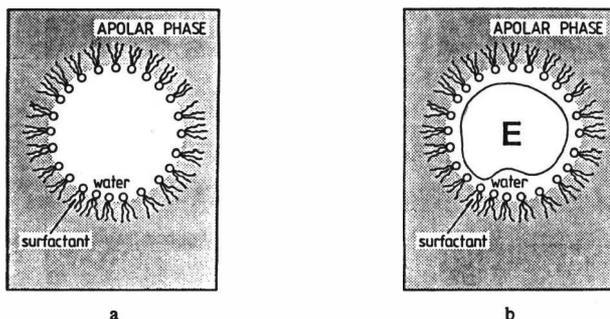


Fig. 1. a. Schematic representation of a reversed micelle.
b. Enzyme solubilized in the water core of the reversed micelle

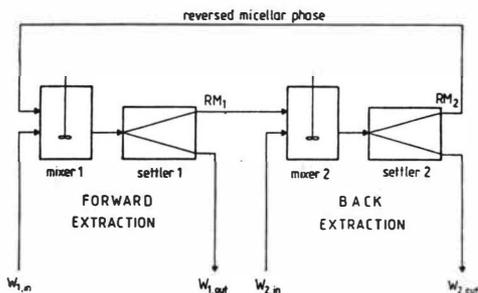
It has been demonstrated that under certain conditions proteins can be transferred from an aqueous phase towards a reversed micellar phase and back [1-4]. The partitioning of proteins between a reversed micellar phase and an aqueous phase will depend on several factors, among which interactions between the protein and the reversed micelle. These interactions can be of electrostatic nature involving charged groups of the protein and the surfactant head groups or of hydrophobic nature involving hydrophobic parts of the protein and the surfactant interface or the apolar solvent. The fact that electrostatic interactions play an important role is demonstrated by the effect of the aqueous phase pH and ionic strength on the partitioning of proteins between the reversed micellar phase and the aqueous phase [2-6]. Differences in distribution behaviour have been used to separate a mixture of three proteins to show that selective extraction is possible [6].

To apply the reversed micellar extraction for recovery of proteins, a continuous forward and back extraction process can be used. Previously we have investigated the performance of this process in two mixer/settler units as shown in Fig. 2 [3]. A reversed micellar phase of the surfactant trioctylmethylammonium chloride (TOMAC) in isooctane is used to concentrate the enzyme α -amylase by performing the forward extraction at a pH value with maximal distribution coefficient (9.9) and the back

extraction at a much lower pH value. In this way the α -amylase concentration could be increased eight times. During the extraction a loss of 30% of the enzyme activity was observed; 45% of the initial amount of the α -amylase was present in the second aqueous phase, while 25% remained in the first aqueous phase after the extraction.

In this paper the modelling of the extraction is described. As predicted by this model, activity recovery could be improved by increasing the mass transfer rate during the forward extraction.

Fig. 2. Flowsheet of the combined forward and back extraction for two mixer/settler units, with the reversed micellar phase circulating between the two extraction units (see ref. 3 for construction details).



MODELLING OF EXTRACTION

To be able to describe and optimize the extraction process, a mathematical model was formulated, which describes the concentration of active enzyme in all the phases during the extraction. In this model both the mass transfer as well as the inactivation of enzyme during the extractions are taken into account [equation 1-4].

$$W1 : \frac{dC_{W1}}{dt} = \frac{C_{W1,i} - C_{W1}}{r_1} - \frac{K_{O1} \cdot A_1}{1 - \epsilon_1} \cdot (C_{W1} - C_{W1}^*) - k_{i w1} \cdot C_{W1} \quad (1)$$

$$RM1 : \frac{dC_{RM1}}{dt} = \frac{C_{RM2} - C_{RM1}}{r_1} + \frac{K_{O1} \cdot A_1}{\epsilon_1} \cdot (C_{W1} - C_{W1}^*) - k_{i r m} \cdot C_{RM1} \quad (2)$$

$$W2 : \frac{dC_{W2}}{dt} = \frac{0 - C_{W2}}{r_2} + \frac{K_{O2} \cdot A_2}{\epsilon_2} \cdot (C_{RM2} - C_{RM2}^*) - k_{i w2} \cdot C_{W2} \quad (3)$$

$$RM2 : \frac{dC_{RM2}}{dt} = \frac{C_{RM1} - C_{RM2}}{r_2} - \frac{K_{O2} \cdot A_2}{1 - \epsilon_2} \cdot (C_{RM2} - C_{RM2}^*) - k_{i r m} \cdot C_{RM2} \quad (4)$$

C_j : concentration of active enzyme in phase j (kg/m^3);

C_j^* : equilibrium concentration of active enzyme in phase j (kg/m^3);

t : time (s);

r_j : residence time in mixer j (s);

K_{Oj} : overall mass transfer rate constant in mixer j (m/s);

A_j : specific surface area in mixer j (m^2/m^3);

ϵ_j : hold-up of dispersed phase in mixer j (-);

k_{ij} : inactivation rate constant in phase j (1/s).

Enzyme inactivation during the extractions is due to the formation of an insoluble complex between surfactant molecules and the enzyme in the aqueous phase [7,8]. This complexation is faster at higher pH; inactivation by this mechanism therefore only takes place during the forward extraction. Although the equilibrium concentration of free surfactant in the aqueous phase is very low, it can be continuously supplied during extraction out of the reversed micellar phase, when complexation occurs. This mechanism is also the main reason of surfactant loss during the extraction [3].

Because of the fact that inactivation predominantly takes place in the first aqueous phase, the extraction efficiency should increase by lowering the steady state enzyme concentration in the first aqueous phase. This can be achieved by a high mass transfer rate and/or a high distribution coefficient of the enzyme during the forward extraction.

The distribution coefficient of α -amylase was found to be increased by the addition of a nonionic surfactant (Rewopal HV5) to the reversed micellar phase [9]. A 12 fold increase in enzyme concentration in the second aqueous phase as compared to the initial concentration of the first aqueous phase was obtained.

EXPERIMENTAL RESULTS

Mass transfer rates as a function of the stirrer speed (N_1) during the forward extraction are measured by performing this extraction in continuous mode in one mixer/settler unit, with $C_{RM2} = 0$ and $C_{W1,in} = 1$ g/l. The concentrations C_{RM1} and $C_{W1,out}$ are measured as a function of time until a steady state is reached. By using equation 1 and 2 both the mass transfer rate coefficient ($K_{O1 \cdot A1}$) as well as the inactivation rate constant in the first aqueous phase (k_{iw1}) can be calculated for this extraction ($k_{irm} < 10^{-5} \text{ s}^{-1}$). In Figure 3 the results of the mass transfer rate measurements are given.

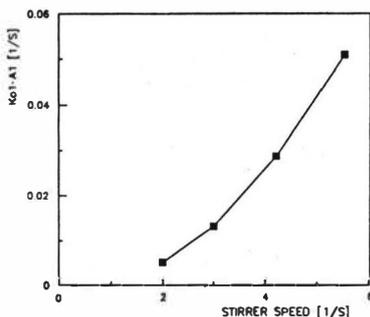


Fig. 3. Mass transfer rate coefficient during forward extraction of α -amylase to a reversed micellar phase as function of stirrer speed. Composition of the two phases is the same as described in [9].

The value of $K_{O1 \cdot A1}$ is proportional to $N_1^{2.3}$. This power of N_1 is in good agreement with the theoretical value of 2.1 found for continuous-phase-diffusion controlled mass transfer [10,11].

The inactivation rate constant in the aqueous phase was found to be $4 \cdot 10^{-3} \text{ s}^{-1}$ and independent of the stirrer speed for $N_1 \geq 3 \text{ s}^{-1}$. At $N_1 = 2 \text{ s}^{-1}$ this constant was lower ($2 \cdot 10^{-3} \text{ s}^{-1}$), which could be due to slower surfactant transfer from the reversed micellar phase to the aqueous phase.

As predicted by the model, the total enzyme recovery increases with increasing stirrer speed, since the steady-state aqueous phase enzyme concentration, which is susceptible to surfactant inactivation, is lower.

For the back extraction a similar measurement was performed at a stirrer speed (N_2) of 4.0 s^{-1} . This resulted in a calculated value for $K_{O2 \cdot A2}$ of $1.6 \cdot 10^{-2} \text{ s}^{-1}$.

To show that the total extraction efficiency of the reversed micellar extraction will be improved by a higher mass transfer rate, the combined forward and back extraction was performed at $N_1 = 5.5 \text{ s}^{-1}$ and $N_2 = 4.0 \text{ s}^{-1}$. The results are shown in Fig. 4. The total yield of active α -amylase in the second aqueous phase was about 84%, at a concentration of 17 g/l (17 times the initial concentration of the

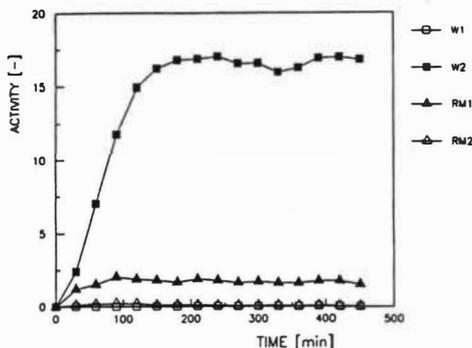


Fig. 4. Concentration of active α -amylase in the four phases during the extraction

first aqueous phase). This concentration factor is within 10% of the model prediction. Only 3% of active enzyme remained in the first aqueous phase after the extraction. Surfactant losses were 2.5% per circulation of the reversed micellar phase (67 min).

CONCLUSIONS

The recovery of enzymes by a combined forward and back extraction can be described and optimized by a theoretical model containing the mass transfer rate and inactivation rate of the enzyme during the extractions.

Both an increase in the distribution coefficient as well as in the mass transfer rate coefficient during the forward extraction have been demonstrated to improve the extraction efficiency by reducing enzyme inactivation and surfactant losses.

ACKNOWLEDGEMENT

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REFERENCES

1. P.L. Luisi, F.J. Bonner, A. Pellegrini, P. Wiget and R. Wolf. // *Helv. Chem. Acta*, **62** (1979), 740.
2. K. Van 't Riet and M. Dekker. // *Proc. 3rd Eur. Congr. Biotechnol. Munich*. Vol. III (1984), 541.
3. M. Dekker, K. Van 't Riet, S.R. Weijers, J.W.A. Baltussen, C. Laane and B.H. Bijsterbosch. // *Chem. Eng. J.* **33** (1986), B27.
4. K.E. Göklén and T.A. Hatton. // *Biotechnol. Progr.* **1** (1985), 69.
5. M. Dekker, K. Van 't Riet, J.W.A. Baltussen, B.H. Bijsterbosch, R. Hilhorst and C. Laane. // *Proc. 4th Eur. Congr. Biotechnol. Amsterdam*, Vol II (1987), 507.
6. K.E. Göklén and T.A. Hatton. // *Proc. ISEC86. München*. Vol. III (1986), 587.
7. C. Laane and M. Dekker. // *Surfactants in Solution Proc. VIIIth Int. Symp. on Surfactants in Solution*, New Delhi, Aug. 22-28, 1986, in press.
8. M. Dekker *et al.*, in preparation.
9. M. Dekker, J.W.A. Baltussen, K. Van 't Riet, B.H. Bijsterbosch, C. Laane and R. Hilhorst. // *Biocatalysis in Organic Media*. Eds. C. Laane, J. Tramper and M.D. Lilly, Elsevier (1987), 285.
10. S. Middleman. // *A.I.Ch.E. J.* **11** (1965), 750.
11. J.W. Van Heuven and W.J. Beek. // *Proc. ISEC71, Amsterdam*, Vol. I (1971), 70.

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INTRODUCTION

In the production of carboxylic acids, processes such as fermentation yield low concentrations of carboxylic acids in an aqueous multicomponent solution. The subsequent separation, purification, and concentration of the carboxylic acids is often difficult due to the nature of the solute. Carboxylic acids interact strongly with water, resulting in low solute activity coefficients in aqueous solution. Moreover, the affinity of the acids for water is often manifested as low volatility of the solute relative to water, which makes conventional distillation difficult. The low aqueous solute activities result in low equilibrium distribution ratios of the acid into most organic solvents, making conventional solvent extraction difficult or impractical.

The recovery of organic acids from dilute aqueous solutions has been an important industrial problem for many years. An extensive amount of papers have been published dealing with this problem and only the last trends are reviewed here. There are mainly three classes of solvents which are proposed; namely carbon-bonded oxygen-donor solvents, long-chain amines and phosphorus-bonded oxygen-donor solvents. The first one suffer from the disadvantage that it gives equilibrium distribution coefficients ($K_D = \text{wt. fraction acid in solvent phase} / \text{wt. fraction acid in aqueous phase, at equilibrium}$) of order unity or less.

The other two classes of solvents take advantage of their basic nature to provide higher values of K_D .

The extractant used in this work is a liquid mixture of trialkylphosphine oxides containing C6 and C8 alkyl groups (cyanex[®] 923) [1]. It was designed to overcome limitations encountered in the use of trioctylphosphine oxide (TOPO) which has a melting point of 47-52°C and must be dissolved in a diluent.

The main objective of the present work was to study the recovery of lactic acid or lactate anion from fermentation broth with cyanex 923 so as to identify and interpret conditions leading to the most favorable values of K_D and α (separation factor defined as K_D / K_{H_2O}).

EXPERIMENTAL

Extraction studies were performed by placing known volumes of aqueous solution and solvent in a thermostated cell equipped with a mechanical stirring device. The mixture was shaken for 15 min. After the two layers has separated for 1/2 h, aliquot of both phases were withdrawn and analyzed by titration (lactic acid solution) or absorption at 360 nm after addition of $\text{FeCl}_3 - \text{HCl}$. The water solubility in extract was measured by the Karl Fischer method.

RESULTS AND DISCUSSION

The results obtained are tabulated in table 1.

Table 1. Extraction of lactic acid or acidified lactate at 50 °C.

Run N°	Solute	wt/% (as lactic acid)	H ₂ SO ₄ M/M Lact.	pH	K _D	α
1	Lactic acid *	2.12	-		3.06	48.3
2	Lactic acid *	4.5	-		1.79	30.15
3	Lactic acid *	21.2	-		0.72	16
4	Lactic acid	2.12	-		2.8	53
5	Lactic acid	4.5	-		1.8	48.9
6	Lactic acid	21.2	-		0.71	19.5
7	Calcium lactate	4.29	.3	3.62	0.39	16.6
8	" "	3.96	.5	3.62	0.39	16.6
9	" "	3.96	.8	2.15	2.98	233
10	" "	3.96	1	1.36	2.93	190
11	Ammonium Lactate	1	.5		1.59	22.4
12	" "	1	.56		1.71	28
13	" "	3	.5		1.24	23.2
14	" "	4.51	.67	1.29	1.47	27.7
15	Fermentation broth **	3.37	.2	3.64	1.03	
16	" "	3.24	.38	2.31	1.14	
17	" "	3.12	.57	1.28	1.89	
18	" "	0.35	.67	1.7	1.72	

(*) : 25 °C
 (**): Neutralization with NH₄OH during fermentation - final pH = 5,32 at 15,3 °C

When considering first lactic acid extraction, it appears that an increase of temperature from 25 to 50 °C has only a small effect on distribution ratio and separation factor (runs 1-3 and 4-6); a temperature of 50 °C was then choosed for next runs since the solvent viscosity drops from 40 mPa.s at 25 °C to 13,7 mPa.s at 50°C. Furthermore, it has been observed that an increase of temperature has a favorable effect on decantation time. In both cases, the distribution ratio increases with a decrease in acid concentration. For comparison, these distributions ratios and separation factors are higher than those compiled by Sorensen and Alt [2] with solvents such as ketones or alcohols where K_D-values lower than 2 and α-values lower than 5 were reported. Lactic acid K_D-values observed in this work are also higher than tho-

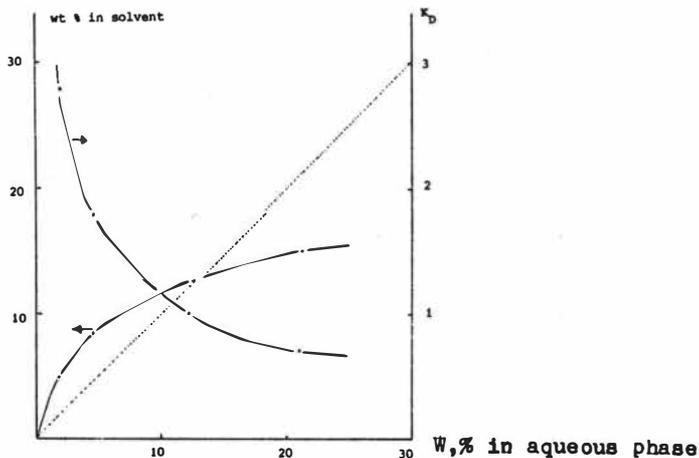


Fig.1. Distribution curve of lactic acid at 50°C

se obtained with TOPO dissolved in kerosene [3] or with a mixture of immiscible organic acid and amine dissolved in a solvent [4]. They are comparable with K_D -values found by Ratchford et al [5] who tested triamyl- and trioctylamine in chloroform or alcohols.

Fig.1 shows the equilibrium curve for lactic acid between water and Cyanex 923. From there it can be seen that the distribution coefficient is heavily influenced by the aqueous feed concentration.

Runs 7 to 18 were planned to study the extraction of lactic acid from acidified lactate solutions since it is known that the acid formed during fermentation has to be neutralized in order to prevent inhibition.

Two synthetic mixtures were studied: solution of calcium and ammonium lactate were prepared by neutralization of the acid with the corresponding base. Then aliquots of these solutions were acidified with increasing amounts of sulfuric acid.

Runs 7 and 8 show that increasing the amount of sulfuric acid to the equivalence ($0.5 \text{ M H}_2\text{SO}_4/1 \text{ M lactate}$) increases the distribution ratio to 1.02 but additional amounts of acid has a more profound effect since K_D reaches 2.98.

Lactic acid doesn't ionize appreciably in aqueous solution when the pH goes under the value of pK_a (pK_a of lactic acid = 3.86). Since the greatest jump of K_D is observed when the pH decreases from 3.37 to 2.15, this means that the distribution ratio is not directly related with the unionized lactic acid. (Fig. 2).

This is confirmed by results obtained with acidified ammonium lactate since at a pH of 1.29, a K_D value of only 1.47 is obtained (run 14). The differences in K_D values and separation factors observed between calcium and ammonium lactate solutions could be linked to the great difference in solubility of the salts formed ($\text{CaSO}_4 \sim 0.2$ and $(\text{NH}_4)_2\text{SO}_4 \sim 84 \text{ g}/100 \text{ gr H}_2\text{O}$ et 50 °C).

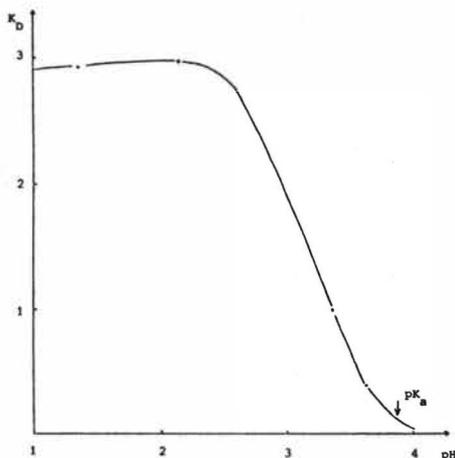


Fig.2. Influence of pH on distribution ratio of lactate at 50°C

Results obtained with filtered fermentation broth (runs 15 to 18) are similar to those issued from ammonium lactate solutions: this is not surprising since the neutralization of lactic acid during fermentation was made with ammonia.

Sulfuric acid is distributed between both phases and a distribution ratio of 0.23 has been calculated at 25 and 50 °C for solution containing 0.2 M/L H_2SO_4 . This observation explains that sulfuric acid is used in greater quantities than the stoichiometric ones to displace lactate from its salt.

The solubility difference between $CaSO_4$ and $(NH_4)_2SO_4$ and the partition of sulfuric acid between both phases explain the higher K_D and α values found in the case of acidified calcium lactate.

Preliminary calculation have shown that a feed/solvent ratio of 6 and six mixer-settlers could be sufficient to recover 95 % of lactic acid (8 mixer-settlers for 99 % recovery).

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REFERENCES

1. WATSON E.K., RICKELTON W.A., ROBERTSON A.J., BROWN T.J.// International Solvent extraction Conference (ISEC). Vol. III. P.775. München,1986.
2. SØRENSEN J.M., ARLT W.//Liquid-Liquid Equilibrium Data Collection in Chemistry Data Series. Vol.V, Part 2. Dechema,1980.
3. GRINSTEAD R.R. Dow Chemical U.S. Pat 3.980, 702, 3.980,703, 3.816,254.
4. BANIEL A.M. Miles Lab. Inc, Eur. Pat 0049 429 (1981).
5. RATCHFORD W.P., HARRIS E.H., FISHER C.H., WILLITS C.O.// Ind. Eng. Chem. 43,778 (1951).

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Introduction. - Recovery of benzylpenicillin from fermentation broth involves solvent extraction, purification and concentration steps [1].

Several extraction and reextraction stages are carried out in order to obtain a purified penicillin solution. Butylacetate is generally used as solvent and pH effect on the penicillin solubility in water and in organic solvents is exploited [2]. In the last stage of the process, the potassium salt of benzylpenicillin (KBP) is obtained by extraction with a KOH solution.

Concentration and purification of KBP are carried out by a crystallization process where n-butyl alcohol is added to the aqueous solution containing KBP in order to lower the evaporation temperature.

Design and operation of the process require to know the thermodynamic behavior of water-butanol-KBP and water-butylacetate-KBP systems.

Since very few data are reported in the literature, we are carrying out a systematic study on phase equilibria involving KBP and pure organic solvents or their aqueous solutions. Some results on the solubilities of solid KBP on ethanol, n-propanol and n-butanol at different temperatures have been published in a previous work [3].

In this communication we report:

- experimental data on the solubilities of KBP in butanol-water mixtures;
- ternary liquid-liquid equilibrium (LLE) data of KBP - water- butanol mixtures; the distribution of KBP between aqueous and organic phases is also reported;
- dissociation constants of KBP in alcohols and water-butanol solutions obtained from conductivity measurements.

Experimental. - Benzylpenicillin potassium salt was supplied by Fluka with a purity claimed greater than 99%. Ethanol, n-propanol and n-butanol were supplied by Carlo Erba with a purity claimed greater than 99.8%. Finally redistilled water was used.

KBP concentration in alcoholic and aqueous solutions was determined by an ultraviolet spectrophotometer (Perkin Elmer Lambda5). Details on the analytical procedure are reported elsewhere [3].

Solubilities were measured by contacting an amount of solid KBP exceeding the saturation value with the aqueous solutions. The experiments were carried out in a magnetically stirred flask at temperature of 20 ± 0.1 °C. After the equilibrium was achieved, a liquid sample was analyzed spectrophotometrically in order to evaluate the KBP concentration.

Miscibility gap of benzylpenicillin - water - butanol system was determined by a titration procedure. Weighed amounts of KBP and butyl alcohol were introduced in a thermostated glass flask at 20 ± 0.1 °C and the amount of water required to obtain two liquid phases was determined. Then the titration was carried on until a homogeneous liquid phase is obtained.

Tie-lines were determined by equilibrating the ternary mixtures in glass flasks magnetically stirred for at least two hours. After a settling period, samples of each phase were withdrawn by means of a syringe. The samples were analyzed spectrophotometrically in order to evaluate the KBP concentration in each phase.

Specific conductance of solutions containing a known concentration of KBP was determined by a Beckmann conductivity bridge (RC-18A) with a measuring frequency of 3kHz. Experiments on very diluted penicillin solutions in ethanol, propanol and butanol and water-butanol mixtures were carried out. From conductance data, the dissociation constants K_d of KBP were obtained, according to the Ostwald dilution law [4].

Results and discussion

Table 1 reports the solubilities of solid KBP in aqueous solutions of butanol at 20°C. LE data at the same temperature are reported in Fig. Finally, Table 2 reports the values of the dissociation constant of KBP in organic and aqueous solutions.

Liquid-liquid equilibrium data show a raising distribution ratio of KBP between organic and aqueous phases at raising KBP concentration. Furthermore mutual solubility of water and butanol increases at higher KBP concentration and complete miscibility is achieved at penicillin concentration greater than about 8% by weight.

A thermodynamic model of these systems should take into account the presence of K^+ and BP^- ions in the liquid solution.

These ions undergo the following equilibrium reaction both in aqueous and organic phase:



with an equilibrium constant K_d .

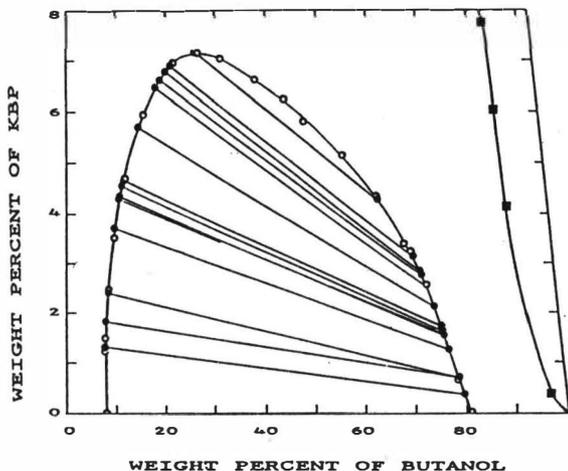
Furthermore, in aqueous solutions hydrolysis phenomena should be considered, owing to the presence of BP^- ion corresponding to the weak acid HBP:



Hydrolysis allows to explain pH influence on the penicillin distribution between aqueous and alcoholic phases in the extraction process.

Table 1. Solubility of solid KBP in aqueous solutions of n-butanol at 20°C

Solvent composition (weight % of butanol)	KBP solubility (mole/cm ³)x10 ⁴
0.967	0.08
0.920	0.95
0.911	1.42
0.909	1.36
0.900	1.86
0.879	2.80
0.871	3.09
0.847	5.14
0.817	5.39
0.762	7.82
0.676	10.80
0.615	12.46
0.549	14.18
0.409	17.09
0.321	18.68
0.233	20.36
0.174	20.18
0.126	20.50
0.079	21.01
0.042	21.36
0.017	21.26



Liquid-liquid equilibrium data for the system KBP-water-butanol

According to these observations we propose a model which should be able to describe the experimental data of solid liquid equilibria and ternary LLE.

The equilibrium between solid KBP and its liquid saturated solution:

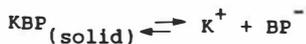


Table 2. Dissociation constant of KBP

Solvent	K_d (mol/cm ³)x10 ⁷
Ethanol	29.2
Propanol	5.5
Butanol	2.65
Water-butanol mixtures (weight % of butanol)	
0.906	5.43
0.879	9.04
0.815	10.90
0.050	109.00

is described in terms of the solubility products K_s :

$$K_s = [K^+] [BP^-] \gamma_{\pm}^2$$

Therefore the model allows us to evaluate the solubility product from solubility data if the dissociation constant K_d of KBP in pure solvents and water-alcohol mixtures is known. Furthermore hydrolysis constant K_H of HBP in aqueous mixtures must be known at various compositions.

The proposed model can be applied also to the solid-liquid equilibrium of KBP in organic solvents neglecting the hydrolysis effects.

Also liquid-liquid equilibrium data can be described by the proposed model. In this case physical equilibrium conditions of the true chemical species in the two phases must be taken into account together with the chemical equilibrium conditions above described.

References

1. Hatton T. A. // Comprehensive Biotechnology Ed. Moo-Young M. Vol.2. Oxford: Pergamon Press, 1985
2. Robinson R. G., Cha D. Y. // Biotech. Prog. 1985. Vol.1. P.18.
3. Annesini M.C., Capparucci C., Gironi F., Marrelli L. // Paper at V Yugoslavian - Austrian - Italian Chemical Engineering Conference. Portoroz, 1986. P.91.
4. Weissberger A. Physical methods of organic chemistry. New York: Interscience Publishers, 1949.

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Application of chemical scientific achievements in industry and agriculture is accompanied by the extension of human contacts with chemicals. Most of chemical exercise harmful influence on human skin causing occupational allergic dermatosis. Among various preventive and medical measures there are different protective ointment which are very important for skin protection against harmful exposure to chemicals.

Membrane extraction principles can serve as medical ointment preparation. In many cases such ointment are more effective than the traditional ones. The advantage of the new ointments lies in the possibility to extract harmful substances-sensibilizers from skin surface into ointment and to fix harmful substances in the bulk of ointment.

Traces of sensibilizer on the skin can be absorbed by ointment. It prevents their penetration into a wound or unprotected areas of the skin. Afterwards the ointment with the absorbate-sensibilizer can be washed away by water and soap. The ointment consistency resembles the usual one but the protective properties of the new ointment are much better.

Like it is in liquid membrane extraction the extractable system is emulsion w/o. It consists of liquid membrane with carrier and internal phase with reagent fixing transferred solute to undissociated complex.

This system forms three phases membrane extraction system with droplets substance-sensibilizer solution at the skin or with biological liquid in skin pores. So the latter are external feed with main solute-sensibilizer. This can be illustrated by Fig.1.

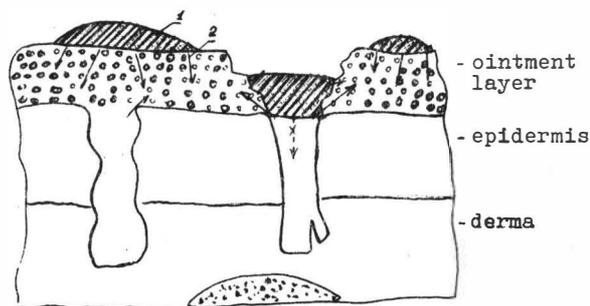


Fig.1.

Schemē of skin
protection
1-sensibilizer
solution droplets,
2-sensibilizer
transfer

Such ointment can be applied on the skin not only before but also after contact with sensibilizator. Ointment can extract substances-sensibilizators from skin pores.

Many ordinary extractants can be chosen as carriers. They do not injure skin because their concentration is small.

The preparation of chromium protection skin ointment can be considered as a model. The general scheme of chemical processes which occur in this system are presented in Fig.2.

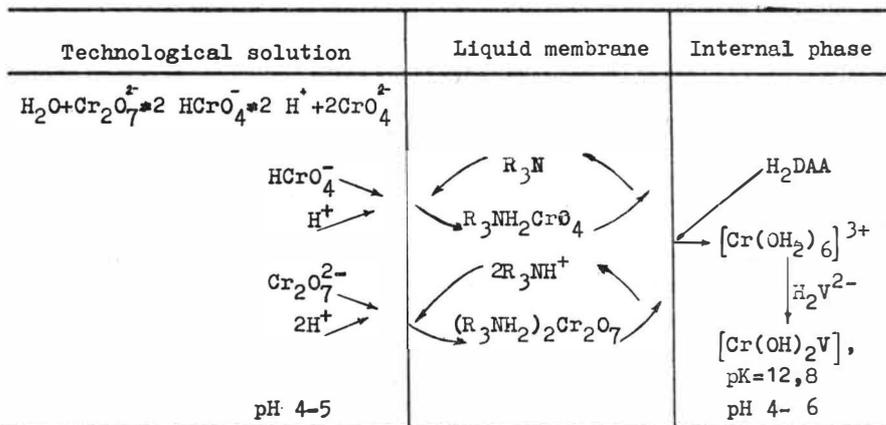


Fig.2. Scheme of chemical processes
(H_2DAA - ascorbic acid solution, H_2V^{2-} - ethylenediaminetetraacetic acid)

Chromium is extracted from chromium solution by carrier - tri-n-octylamine and then it transfers through liquid membrane into internal phase where chromium (VI) is reduced to chromium (III) by ascorbic acid. Catalyst-manganese compound is also used for faster reduction. Then chromium (III) yields low-dissociated complex with ethylenediaminetetraacetic acid in internal phase.

The small chromium concentration in liquid membrane is necessary because liquid membrane contacts with the skin. Such low concentration of chromium can be achieved by weak concentration of carrier in liquid membrane and binding of chromium in undissociated complex in internal phase.

The important property of ointment is stability to breaking. Obtained compositions are stable half a year and can be used after this period.

If period of storage is protected the ointment capacity decreases. This can be seen in Table 1.

Table 1. Relationship of emulsion capacity from time of storage

Time of storage, months	Chromium concentration in ointment, mg/g
0	0.957
0.03	0.955
0.23	0.953
0.36	0.950
0.50	0.945
2.50	0.890
3.50	0.875
5.00	0.762

Sensibilizer absorption rate depends on factors but liquid membrane viscosity is the most important. Fig.3 shows that membrane viscosity influences chromium extraction rate.

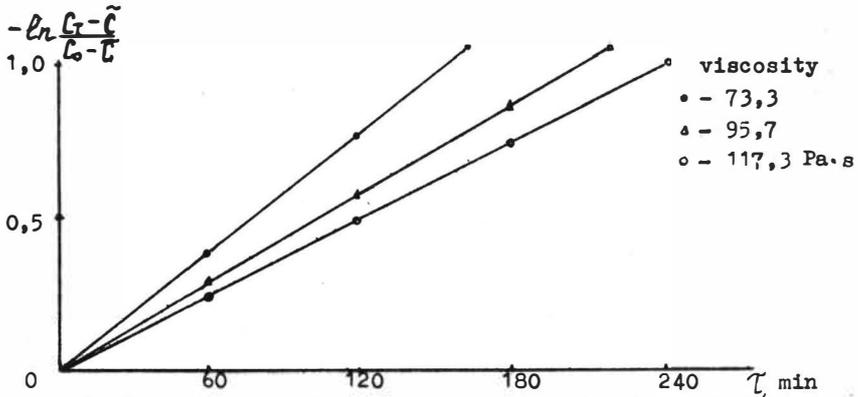


Fig.3. Chromium extraction rate versus extraction time for various liquid membrane viscosity

As shown in Fig.4, the type and concentration of surfactants influence ointment stability.

Many other kinds of ointments against various sensibilizers can be prepared due to such liquid membrane principle. Extensive extraction equilibrium information can be used for the choice of the internal phase composition and carrier (Fig.5).

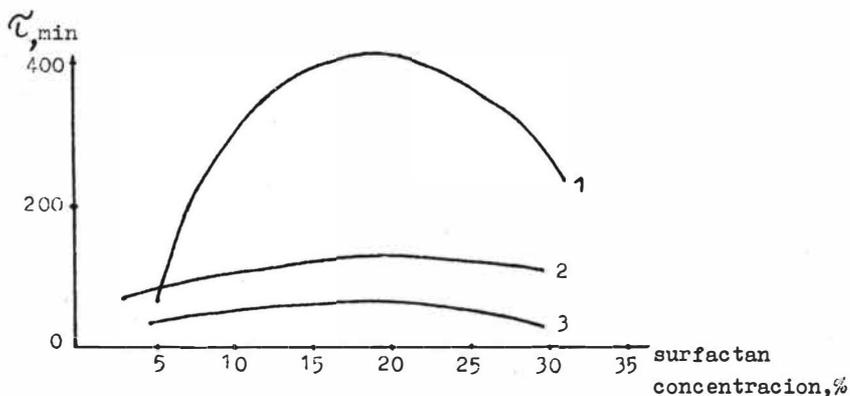


Fig 4. $\tau_{1/4}$ - ointment breaking vs. surfactan concentration

- 1 - chostacerin;
- 2 - sorbitanooleat,
- 3 - pentol

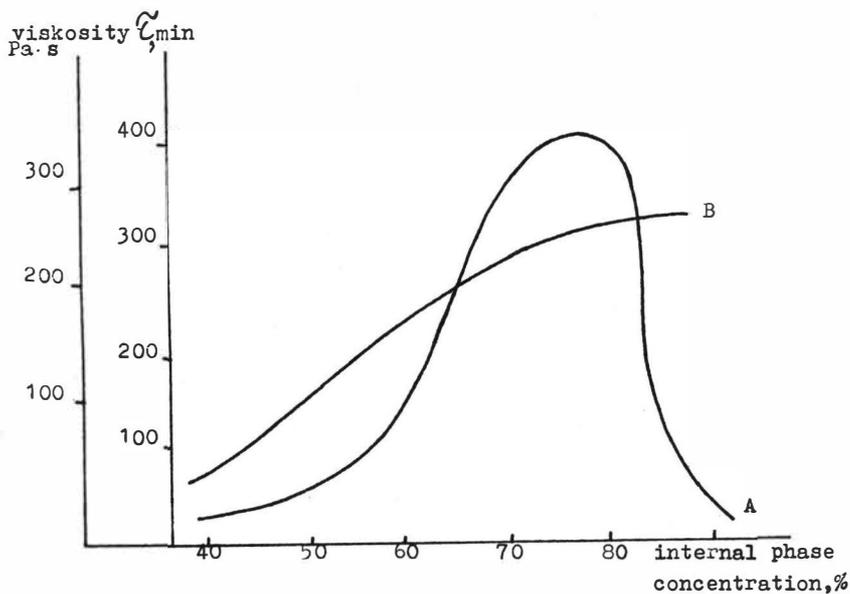


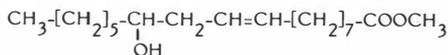
Fig.5. $\tau_{1/4}$ - ointment breaking and viscosity vs. internal phase concentration. A- ointment breaking, B- viscosity

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Methyl ricinoleate is an important starting material used to prepare 11-aminoundecanoic acid which is the monomer of Rilsan B, a nylon type of fiber. Its production is based on the transesterification of castor oil by methanol. Castor oil is a mixture of triglycerides, mainly of ricinoleic acid (about 85%), but also of various other fatty acids : oleic, linoleic, stearic, dihydroxystearic, etc. The chemical formulae of the main compounds found in the product of esterification are given below :

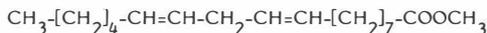
(i) *methyl ricinoleate*



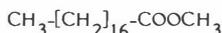
(ii) *methyl oleate*



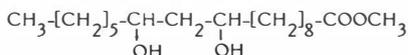
(iii) *methyl linoleate*



(iv) *methyl stearate*



(v) *methyl dihydroxystearate*



} denoted "metiloils"

All these compounds contain 19 carbon atoms, but are different one another either by the number of double bonds C=C or the number of OH groups. Methyl dihydroxystearate easily cristallizes and is conveniently removed by a mere filtration. The "metiloils" can lead to various by-products during the synthesis of 11-aminoundecanoic acid and should preferably be eliminated prior to this synthesis.

The purpose of this paper is to show that such a separation can be efficiently achieved by solvent extraction by using two immiscible (or poorly miscible) organic phases, one of which is polar and the other one non polar.

I. PARTITION OF METHYL RICINOLEATE AND "METILOILS" BETWEEN TWO IMMISCIBLE (OR POORLY MISCIBLE) ORGANIC PHASES

The partition coefficient of any organic compound between water and octanol can be estimated by the REKKER's method [1]. For instance, the calculated partition coefficients are $10^{6.7}$, $10^{8.4}$, $10^{8.2}$ and $10^{8.7}$ for methyl ricinoleate, methyl oleate, methyl linoleate and methyl stearate, respectively. Such values show that methyl ricinoleate is significantly more hydrophilic than the "metiloils", in reason of the presence of an OH group in its

molecule. However, in spite of such a difference, methyl ricinoleate cannot be separated from the "metiloids" by a partition process between water and octanol because all these compounds have an extremely low solubility in water. The situation might be different by using a two-phase system consisting in two immiscible organic phases [2 - 4].

In this work, we have investigated the partition of methyl ricinoleate [RM] and of the "metiloids" [MO] between various couples of poorly miscible organic phases. The results are given in Table.

Partition coefficients of methyl ricinoleate (K_{RM}) and of the "metiloids" (K_{MO}) between various couples of immiscible organic phases

$$K_X = [X]_{\text{alkane phase}} / [X]_{\text{polar phase}} \quad \text{with } X = \text{RM or MO}$$

Extraction systems	K_{RM}	$K_{MO}^{(*)}$	K_{MO} / K_{RM}
Furfural / hexane	0.24	2.6	10.8
Furfural + 15% methanol / hexane	0.19	-	-
Acetonitrile / hexane	0.40	4.1	10.2
Acetonitrile + 15% methanol / hexane	0.27	-	-
Acetonitrile + 15% eau / hexane	0.82	11.4	13.9
Acetonitrile / octane	0.35	3.6	10.3
Acetonitrile + 15% eau / octane	0.80	11.1	13.8

Experimental conditions : $V(\text{alkane}) / V(\text{polar phase}) = 1$; $V(\text{RM or MO}) / V(\text{polar phase}) = 0.1$ with $V = \text{volume}$. $(*) K_{MO}$ has been determined by using a mixture of methyl oleate, methyl linoleate and methyl stearate and should be considered only as a rough estimate of the partition coefficient of each of the three esters present in the mixture.

Examination of these results shows that the partition coefficient K_{MO} of the "metiloids" is between 10 and 14 times greater than the one, K_{RM} , of methyl ricinoleate. Such a difference between K_{RM} and K_{MO} is in rather good agreement with the estimates according to REKKER. Moreover, it allows this time the separation of methyl ricinoleate from the "metiloids" since methyl ricinoleate prefers the polar phase ($K_{RM} < 1$) and the "metiloids" prefer the non polar phase ($K_{MO} > 1$). It should also be pointed out that the addition of modifiers such as water or methanol to the polar phase has a great influence on the values of K_{RM} and K_{MO} , but also a noticeable influence on their ratio K_{RM} / K_{MO} . The influence of the percentage of water in the polar phase on the partition behaviours is reported in more detail in figure 1 for the couple acetonitrile / hexane. The presence of water has a double role : firstly, it reduces the solubility of all long chain organic compounds in the polar phase, so that both K_{RM} and K_{MO} increase when the percentage of water is increased; secondly, the presence of water is favourable to the solubilization of polar compounds, so that the above-mentioned repulsion of methyl ricinoleate is partly inhibited and K_{RM} increases less than K_{MO} (i.e. the ratio K_{MO} / K_{RM} increases) when the concentration of water is increased.

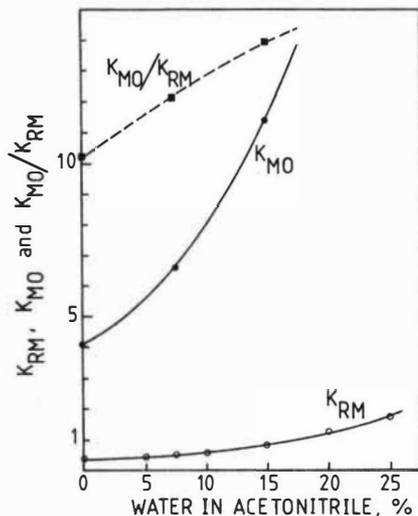


Fig. 1. Variation of K_{RM} , K_{MO} and K_{MO} / K_{RM} as a function of the percentage of water in acetonitrile, at 20°C. [non polar phase : hexane; $V(\text{hexane}) / V(\text{acetonitrile} + 15\% \text{ water}) = 1$; $V(\text{RM or MO}) / V(\text{acetonitrile} + 15\% \text{ water}) = 0.1$; $V = \text{volume}$]

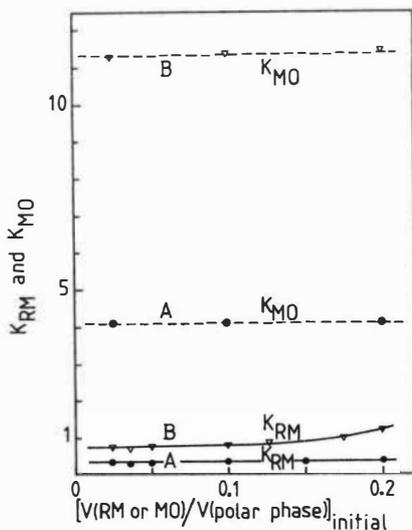


Fig. 2 . Variation of K_{RM} and K_{MO} as a function of the concentration of RM and MO in the system, respectively, at 20°C. Extraction systems : (A) acetonitrile / hexane; (B) acetonitrile + 15% water / hexane. For (A) and (B) : $V(\text{hexane}) / V(\text{polar phase}) = 1$; $V = \text{volume}$

Examination of the results given in figure 2 show that K_{MO} is independent on the concentration of the "metiloils" in the system, as expected from an "ideal" law partition. On the other hand, K_{RM} cannot be regarded as a true constant in the presence of water since it significantly increases when the concentration of methyl ricinoleate is increased.

II. APPLICATION TO THE SEPARATION OF METHYL RICINOLEATE FROM THE PRODUCT OF ESTERIFICATION OF CASTOR OIL

An example of separation is given in figure 3. It can be noticed that at the issue of the first extraction stage good quality methyl ricinoleate is obtained in the acetoneitrile

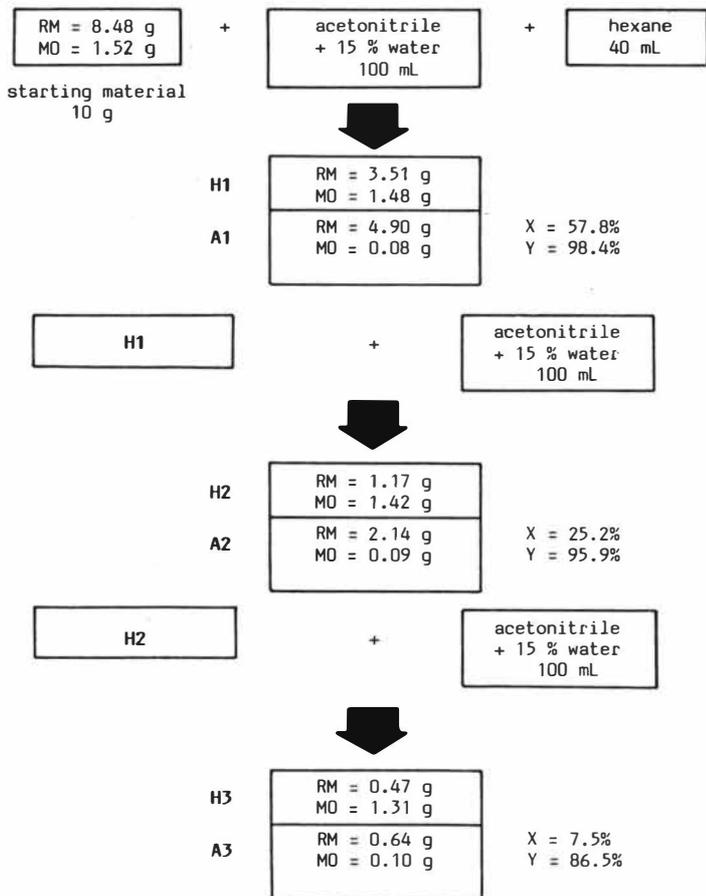


Fig. 3 . Example of separation of methyl ricinoleate from the product of esterification of castor oil by solvent extraction. Y and X denote the purity and the yield of recovery of methyl ricinoleate in the acetoneitrile phases, respectively

phase A1, but with a yield of recovery lower than 60%, which obliges to treat the hexane phase H1. By increasing the number of extraction stages, the degree of purity of the product found in the acetonitrile phases decreases in favour of the global yield of recovery. Nevertheless a satisfying compromise can be reached. For instance, by mixing the three acetonitrile phases A1 + A2 + A3, one reaches a yield of recovery greater than 90% with a degree of purity equal to 96%.

It should also be pointed out that all phase transfers are rapid (equilibrium attained within less than five minutes) and that there is no problem of settling and coalescence. Finally, the elimination of the solvents to get the products from their solutions can be achieved without any difficulty by distillation; that is why it is advantageous to use low boiling point solvents.

REFERENCES

1. R.F. Rekker. The hydrophobic fragmental constant - Its derivation and application - A means of characterizing membrane systems . Amsterdam; Oxford; New-York; Elsevier Scientific Publishing Company, 1977.
2. C.M. Lakshmanan and G.S. Laddha//J. Madras Univ. 31B, 303 (1961).
3. K. Kasturirangan and G.S. Laddha//J. Madras Univ., 25B, 213 (1955).
4. R.O. Butterfield, H.J. Dutton and C.R. Scholfield//Anal. Chem., 38, 86 (1966).

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Two-phase ternary systems (TPTS), formed by salting-out polar organic solvents from their aqueous solutions (Timmermans systems) can be used for the purification and fractionation of various classes of substances: amino acids, peptides, proteins, lipids [1-3].

In the systems studied the distribution coefficients may vary from 10^{-3} to 10^4 , depending of the properties of distributed substance and the nature of TPTS.

The present study shows that in TPTS formed by salting-out some aliphatic alcohols (n-PrOH, i-PrOH and t-ButOH) by neutral electrolytes (NaCl, Na_2SO_4), the distribution of different substances (amino acids, 3-aminophthalimide [4], certain dyes and pharmacologically active compounds) can be described by the following equation:

$$D = a \varphi^\alpha$$

where D - distribution coefficient; φ - ratio of alcohol concentration in co-existing phases; a, α - constants.

Coefficient α has been found to be closely related to hydrophobic properties of the distributed substance. Thus in nor- α -amino acid series (Gly - Leu) a linear dependence is observed between the number of CH_2 -groups in the aliphatic chain and α coefficient. A good correlation is also observed between α coefficient values with salting-out constants of amino acids reported in [5].

A further investigation of the distribution mechanism can reveal new applications of TPTS in the purification and fractionation processes and also can be useful for the theory of substance solvating in mixed water-organic solution with a high salt content.

References

1. L.G.Domshkaln, V.K.Kulakova, E.S.Vainerman and S.V.Rogozhin. Avt. svid. N 873498 /1979/.
2. V.Y.Ryashentsev, M.A.Voscoboinikov, E.S.Vainerman and S.V.Rogozhin //J.Chromatogr. 216 /1981/ 346-349.
3. V.Y.Ryashentsev, E.S.Vainerman and S.V.Rogozhin //Mater. VII Vsesoyuznoi conf. po khimii ekstraktsii. Moscow: Nauka, 1984. 50.
4. V.Y.Ryashentsev, E.S.Vainerman and S.V.Rogozhin //J.Chromatogr. 288 /1984/. 43-49.
5. P.K.Nandi and D.R.Robinson //JACS. 94 /1972/. 1299-1308.

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