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Synergetic Effects in the Extraction of Rare-Earth Ions by Mixed Organic Solvents
I. The Systems of Benzyldibutylamine with Bis(2-ethylhexyl) Hydrogen Phosphate or Tributyl Phosphate

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The objective of this paper was to determine the behaviour of the rare-earth ions during their extraction from the aqueous solutions by the organic extractants diluted in benzene. The organic extractant was either one-component (TBP, DEHPA, BDBuN) phase or a mixed (TBP—BDBuN or DEHPA—BDBuN) organic phase, always diluted with benzene.

Experiments showed that distribution ratios of La, Pr, Nd, and Sm obtained when extracting with DEHPA—BDBuN mixed organic phase were much higher than the corresponding distribution ratios in case of single-component extractant (either DEHPA or BDBuN) and aqueous solution only in such a case when the salting-out agent (8.5 mol dm^{-3} NH$_4$NO$_3$) was added to it prior to extraction. The synergetic coefficients of each element tested were very high. Extraction by TBP—BDBuN mixed organic phase was somewhat less satisfactory although the synergetic effect was also observed. The magnitudes of the synergetic coefficients of each rare-earth ion were lower than in the previous case.

The occurrence of the synergetic phenomena in extraction has been known for some time. It involves an enhancement of the extraction of a metal ion from the aqueous phase to the organic phase by the addition of another extractant to the organic phase. The solvent extraction of rare-earth metal ions by an extractant, *e.g.* tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO) was the subject of investigation of several researchers [1—5]. Benzyldibutylamine (BDBuN) was used for extraction by authors of papers [1, 6, 7]. On the other hand, the systematic study of the synergetic effects in the systems that consisted of the mixed organic solvents has been rather scarce [8].

The objective of this paper therefore is to contribute to the investigation of the synergetic effects in the systems BDBuN with DEHPA (bis(2-ethylhexyl) hydrogen phosphate) resp. TBP during the extraction of the following lanthanoids La, Pr, Nd, and Sm.

EXPERIMENTAL

The following organic solvents were used: TBP, DEHPA, and BDBuN (The Research Institute of Chemical Technology, Bratislava), benzene (Lachema, Brno). Rare-earth element (REE) salts of anal. grade were in the form of nitrates (Ventron, FRG).

The aqueous solutions of the REE nitrates were prepared by dissolving nitrate in the distilled water so that its concentration was 5×10^{-2} mol dm^{-3} Nitric acid was added to each solution so that its final concentration in all of them would be 0.5 mol dm^{-3} Two sets of solutions were prepared: one without the salting-out agent and another with 8.5 mol dm^{-3} of NH$_4$NO$_3$. The organic phase consisted either of one-component organic extracting agent, *i.e.* TBP, BDBuN, and DEHPA diluted with benzene or their mixture. Equal volumes of the organic and aqueous phases were taken and intimately mixed by mechanically shaking the test

tubes for 15 min. After emulsification the mixture was left for 20 min in order to allow the phases to disengage. Sample taken from the aqueous phase was then analyzed for lanthanoid content by the atomic absorption spectrophotometer 373 (Perkin—Elmer).

RESULTS AND DISCUSSION

The distribution ratios of each element between the organic and aqueous phases were calculated from the formula

$$D = \frac{c_{org}}{c_{aq}}$$

The distribution ratios of individual lanthanoids determined by their extraction by one-component (DEHPA, TBP, BDBuN) or mixed organic solvents from the aqueous phase without and with the salting-out agent are summarized in Tables 1 and 2. The results suggest that the salting-out agent favourably affected the distribution ratios of lan-

Table 1. Distribution Ratios of La, Pr, Nd, and Sm in Extraction by Mixed BDBuN—DEHPA Extractant

$c(NH_4NO_3)$ in aq. phase mol dm⁻³	φ(Extractant)/% BDBuN	DEHPA	D_{La}	D_{Pr}	D_{Nd}	D_{Sm}
0	50	0	1.56	0.05	0.02	0.03
0	40	10	1.60	4.25	–	–
0	25	25	1.36	–	3.13	–
0	10	40	0.58	0.11	0.21	0.5
0	0	50	0.13	5.45	0.03	11.1
8.5	50	0	0.56	0.63	1.6	0.54
8.5	40	10	59	303	251	38.7
8.5	25	25	120	241.8	251	38.7
8.5	10	40	2.97	55.3	2.15	30.8
8.5	0	50	0.14	4.58	0.04	7.34

Table 2. Distribution Ratios of La, Pr, Nd, and Sm in Extraction by Mixed TBP—BDBuN Extractant

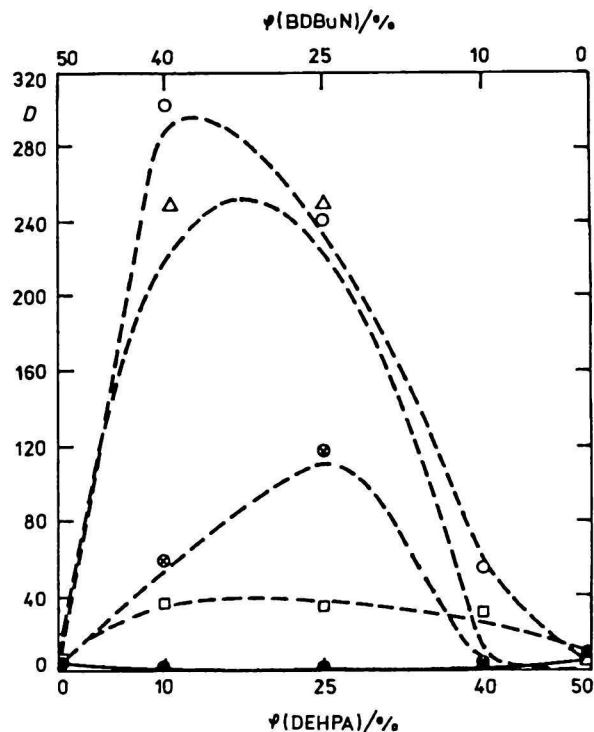| $c(NH_4NO_3)$ in aq. phase mol dm⁻³	φ(Extractant)/% TBP	BDBuN	D_{La}	D_{Pr}	D_{Nd}	D_{Sm}
0	50	0	0.28	0.04	0.005	0.01
0	40	10	0.11	0.03	0.005	0.03
0	25	25	1.44	0.03	0.007	0.02
0	10	40	0.20	0.11	0.02	0.03
0	0	50	0.28	0.04	0.05	0.01
8.5	50	0	0.79	3.59	3.6	9.74
8.5	40	10	10.20	16.0	24.2	16.40
8.5	25	25	5.90	9.10	7.7	7.40
8.5	10	40	2.56	2.20	3.2	1.52
8.5	0	50	0.56	0.63	1.6	0.54

Fig. 1. Distribution ratios of La, Sm, Pr, and Nd vs. composition of the mixed BDBuN—DEHPA extractant.
○ Pr, △ Nd, □ Sm, ⊗ La.
Initial composition of the aqueous phase: $c(REE)_0 = 5 \times 10^{-2}$ mol dm⁻³, $c(HNO_3)_0 = 0.5$ mol dm⁻³, ——— without NH_4NO_3, – – – with $c(NH_4NO_3) = 8.5$ mol dm⁻³.

thanoids if TBP was used as an extracting agent. With other one-component extracting agents the favourable effect has not been detected. For this reason we decided to carry out further extractions from both the aqueous solution that contained the salting-out agent as well as from the ones without the salting-out agent. The distribution ratios of lanthanoids determined from the experiments in which mixed organic solvents were used are plotted vs. composition of the organic phase in diagrams presented in Figs. 1 and 2. Synergetic coefficients of each element were calculated from the formula

$$S = \frac{D_{AB}}{D_A + D_B}$$

where D_{AB} is the distribution ratio of a lanthanoid in case that the organic phase consisted of two organic solvents A and B, D_A, D_B are the distribution ratios of a lanthanoid between the aqueous phase and single extracting agent. The synergetic coefficients are given in Table 3.

Extraction of La by the mixed organic solvents DEHPA—BDBuN can be characterized by relatively extensive synergetic effect which is re-
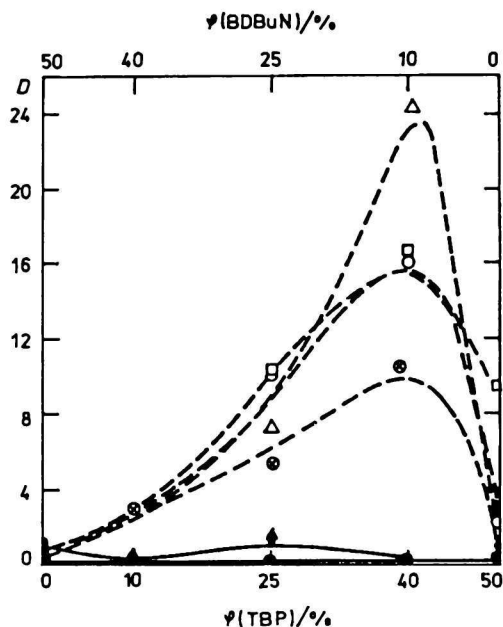
Fig. 2. Distribution ratios of La, Sm, Pr, and Nd *vs.* composition of the mixed BDBuN—TBP extractant.
○ Pr, △ Nd, □ Sm, ⊗ La.
$c(\text{REE})_o = 5 \times 10^{-2}$ mol dm^{-3}, $c(\text{HNO}_3)_o = 0.5$ mol dm^{-3},
——— without NH$_4$NO$_3$, – – – – with $c(\text{NH}_4\text{NO}_3)$ = 8.5 mol dm^{-3}.

flected in the synergetic coefficients. The synergetic coefficient becomes highest if lanthanum is extracted by the mixed organic phase consisting of 25 vol. % DEHPA and 25 vol. % BDBuN; the value is 342.9. As in this case the extracting organic phase consisted of equal volumes of BDBuN and DEHPA we can assume that La is extracted in an associate in which the molecules of BDBuN and DEHPA occur in the ratio 1:1. In case La ions were extracted from the aqueous solution that did not contain the salting-out agent there was no synergetic effect in the entire range of organic phase compositions tested.

Extraction of Pr from the aqueous solutions without the additions of the salting-out agent was also unsatisfactory regardless of the composition of the DEHPA—BDBuN organic phase. With the

Table 3. The Synergetic Coefficients of La, Pr, Nd, and Sm Extraction by Mixed Extractants

φ(Extractant)/%			S_{La}	S_{Pr}	S_{Nd}	S_{Sm}
DEHPA	BDBuN	TBP				
40	10	0	13.3	14.6	6.1	5.2
25	25	0	342.9	92.8	306.1	9.8
10	40	0	123.9	213.4	194.8	21.3
0	40	10	44.2	1.8	1.6	1.85
0	25	25	11.3	7.5	2.9	1.4
0	10	40	13.7	5.3	7.6	2.1

additions of the salting-out agent to the aqueous phase the situation improved considerably. The synergetic effect was observed and the maximum synergetic coefficient value, 213.4 corresponded to organic phase composition 40 vol. % BDBuN and 10 vol. % DEHPA as shown in Fig. 1. The organic complex consisted therefore of BDBuN and DEHPA in the ratio 4:1.

When extracting Nd ions from the aqueous solutions that contained salting-out agent the synergetic effect occurred at two compositions of the mixed organic phase, namely 10 vol. % DEHPA and 40 vol. % BDBuN, 25 vol. % DEHPA and 25 vol. % BDBuN. The variation of the distribution ratio with the composition of the mixed organic phase is depicted in Fig. 1. The maximum magnitude of the synergetic coefficient was 306.1 as determined in experiments in which the extractant consisted of equal volumes of DEHPA and BDBuN, which implies that the ratio of the molecules of two extracting solvents in the extracted organic complex was probably 1:1.

Extraction of Sm ions exhibited the synergetic effect only in case when the salting-out agent was added into the aqueous solution as shown in Fig. 1. The maximum magnitude of the synergetic coefficient, 21.3, given in Table 3 was found when extracting Sm ions by mixed organic extractant consisting of 10 vol. % DEHPA and 40 vol. % BDBuN, which suggests that the molecules of DEHPA and BDBuN were present in the associate in the ratio 1:4.

Further experimental investigation was carried out with the objective to study the extraction of lanthanoids by BDBuN—TBP mixed extractants. Results of experiments are plotted in Fig. 2. In the case that the aqueous phase was without NH$_4$NO$_3$, the distribution ratios of all four studied lanthanoids were negligibly small within the entire range of the composition of the extractants which were tested here. On the other hand, however, extraction of La, Pr, Nd, and Sm ions from the aqueous phase which contained the salting-out agent was very satisfactory. The synergetic coefficients given in Table 3 reached maxima for each lanthanoid when extracting with the organic phase consisting of TBP and BDBuN in the ratio 4:1.

CONCLUSION

It is very convenient to use mixed organic solvents when extracting Pr, Nd, Sm, and La ions from the acidified nitrate aqueous phase instead of one-component extractants. Enhancement of the extraction has been observed only in the case when the salting-out agent was added to the aqueous phase prior to solvent extraction.

Mixed organic solvent consisting of DEHPA and BDBuN yielded best synergetic coefficients if La and Nd ions were extracted and the extractants were present in the mixture in the ratio 1 1. Extraction of Pr ions proceeded with the maximum synergetic coefficient when the organic phase consisted of DEHPA and BDBuN in the ratio 1 : 4.

The mixed organic phase that contained TBP and BDBuN in the ratio 4 : 1 was found to be best suited for extraction of all four lanthanoids that were tested in this study.

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The Stability Constants of Complexes of L-Proline with Nickel(II), Cobalt(II), and Copper(II) Determined by the Potentiometric Method

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Protonation constants of L-proline, as well as stability constants of its complexes with Ni(II), Co(II), and Cu(II) were determined with the use of the potentiometric method.

L-Proline (2-pyrrolidinecarboxylic acid) is an amino acid interesting from the theoretical and biological point of view [1], its complexing properties are due to the ring nitrogen atom and COOH group in the molecule.

In the studies of *Albert* [2—4] dealing with L-proline complexes with some bivalent metal ions, the stability constants were determined by the potentiometric method. The complex formation between L-proline and Cu(II) was investigated in aqueous solution at the varying ionic strength values at the temperature of 20 °C; the found stability constant was equal to 6.31×10^{16} *Jacymirski* [5] determined using the above method the stability constants of L-proline complexes with Co(II), Ni(II) resp. Cu(II) listed in Table 1. *Karczyński* and *Kupryszewski* [6] also determined the stability constant of the L-proline complex with Cu(II) at

constant ionic strength equal to 0.1 at the temperature of 20 °C using the spectrophotometric method. These authors obtained the 3.1×10^{15} value, different from that of *Albert* [2—4].

In the present work we determined the protonation constants of L-proline and stability constants of its complexes with Ni(II), Co(II), and Cu(II) using the potentiometric method described in literature [7]. The method applied by us is simple and convenient, we used it also in our previous investigation concerning determination of stability constants of some metal complexes; the obtained results were very good [8—12].

EXPERIMENTAL

The following reagents were used: L-proline (Reanal, Budapest), $[\alpha](D, 20\ ^\circ C, \rho = 6\ g\ dm^{-3}$,