

Synergetic Effects in the Extraction of Rare-Earth Ions by Mixed Organic Solvents

II. The System of Tributyl Phosphate with Bis(2-ethylhexyl) Hydrogen Phosphate

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The extraction of trivalent ions of La, Pr, Nd, and Sm from aqueous nitrate solutions was experimentally tested with the organic extractants diluted with benzene. The organic extractants were either one-component (TBP or DEHPA) or a mixed organic phase (TBP—DEHPA). The aqueous phase composition was $5 \times 10^{-2} \text{ mol dm}^{-3}$ of rare-earth ions and 0.5 mol dm^{-3} of HNO_3 . The objective of experiments was to find out if the presence of a salting-out agent (NH_4NO_3) enhanced extraction. This assumption was confirmed when extracting Sm, Pr, and La ions with TBP whereas the extraction of Pr and Sm ions with DEHPA was inhibited.

The synergetic effect was discovered only in the case when the aqueous phase contained NH_4NO_3 . By partial substitution of TBP by DEHPA in the extraction the distribution ratio of Pr and Sm decreased if the aqueous phase was free of the salting-out agent.

The separation factors of each rare-earth ion tested were both calculated and verified experimentally.

Liquid extraction of rare-earth elements from acidic aqueous solution has been the subject of investigation of many researchers. Among the organic liquids used for this purpose belong tributyl phosphate (TBP), bis(2-ethylhexyl) hydrogen phosphate (DEHPA), benzyldibutylamine, etc. These may either be used as pure liquids diluted with an organic carrier or as a mixture. Among those who studied the extraction of La from the aqueous solutions belong *Yagodin et al.* [1] who used TBP. *Tornes and Choppin* [2] used DEHPA diluted in toluene to extract Eu and Am. *Mikhailichenko and Pimenova* [3] suggested that TBP extracts rare-earth ions from the nitrate solutions in the form of $\text{M}(\text{NO}_3)_3 \cdot 3\text{TBP}$. In their later paper [4] they described extraction of rare-earth elements by DEHPA and found that the distribution coefficient of all elements decreased with the increasing concentration of HNO_3 in the aqueous phase. The distribution ratios of all elements pass through the minima at HNO_3 concentration between 2 and 4 mol dm^{-3} but they rise again at higher acidity of the aqueous phase. The authors conclude that mechanism of extraction at high HNO_3 concentration is different from the mechanism at HNO_3 concentration below 2 mol dm^{-3} in the aqueous phase. Extraction and separation of Y from lanthanoids (La to Gd) was experimentally studied by *Scargill, Alcock et al.* [5] with TBP as an organic liquid and acidic aqueous solutions containing NaNO_3 . Extraction was efficient when

HNO_3 concentration exceeded 5 mol dm^{-3} . The separation factors increased with the growing acidity of the aqueous phase.

The synergetic effect in liquid extraction is a well-known phenomenon. It involves an enhancement of the extraction of an element by using two types of extractants in the same extraction process [6]. *Huang and Bautista* [7] used a mixture of TBP and Aliquat 336 for extraction of Sm and Gd from aqueous phase with concentration of NH_4NO_3 4 mol dm^{-3} .

In the present paper the extraction of several rare-earth elements was studied. The extractant employed was DEHPA with additions of TBP diluted with benzene. By comparing extractions with individual extractants we searched for the synergetic effect.

EXPERIMENTAL

The following materials were used: reagent grade TBP (Soyuzkhimreaktiv), benzene and NH_4NO_3 (Lachema, Brno); nitrates of rare-earth elements of anal. grade (Ventron, FRG), DEHPA (The Research Institute of Chemical Technology, Bratislava).

All extraction experiments were carried out at room temperature ($22 \pm 2 \text{ }^\circ\text{C}$). The organic and aqueous phases of equal volumes were intimately mixed by shaking in a test tube for 5 min. After

this, 20 min were allowed for the phase disengagement. The aqueous phase was then analyzed by emission atomic spectrophotometry with the inductive plasma excitation in the case when the aqueous phase contained two or more rare-earth elements or by the atomic absorption spectrometry if ions of a single metal were extracted. The equilibrium content of lanthanoid in the organic phase was calculated as the difference between initial content and the aqueous phase content.

The synergetic effect was tested by extracting La, Pr, Nd, and Sm from the nitrate solutions. In each case the concentration of the rare-earth ions in the aqueous solution was $5 \times 10^{-2} \text{ mol dm}^{-3}$ and that of HNO_3 0.5 mol dm^{-3} . The objective of adding HNO_3 was to avoid hydrolysis. Two series of aqueous solutions were prepared, namely one containing 8.5 mol dm^{-3} of NH_4NO_3 and the other without any salting-out agent. The concentration of all other components of the solution and the experimental conditions were identical. Each organic phase comprised 50 vol. % of the organic extractant with 50 vol. % of benzene. The latter were either one-component organic extractants like DEHPA and TBP or their mixture.

RESULTS AND DISCUSSION

In this study the salting-out effect was verified on all rare-earth elements tested, *i.e.* La, Pr, Nd, and Sm. The results of experiments were evaluated according to the distribution ratios calculated from the formula $D = c_{\text{org}}/c_{\text{aq}}$. Each experiment was carried out twice. Results are summarized in Table 1. As it can be seen, the effect achieved by the addition of NH_4NO_3 is rather obvious. We can observe an enhancement of the extraction of Sm, Pr, and Nd ions if TBP is used as an extractant and this is to a slightly lesser extent observed when extracting La ions. On the contrary, extrac-

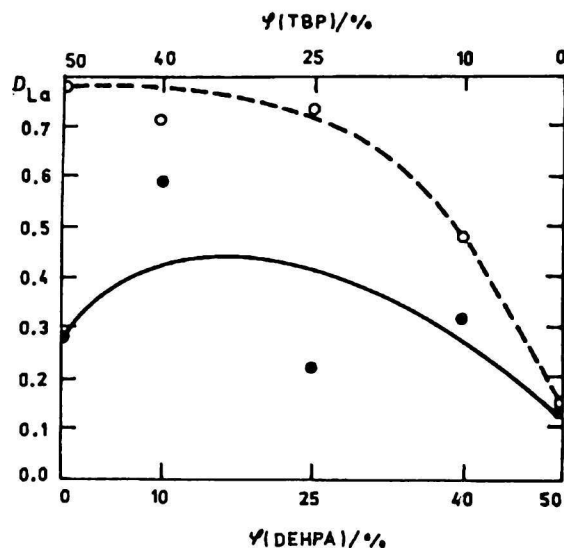


Fig. 1. Distribution coefficients of La vs. composition of DEHPA–TBP extracting agent. The initial composition of the aqueous phase: $c(\text{La}^{3+}) = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $c(\text{HNO}_3) = 0.5 \text{ mol dm}^{-3}$, — without NH_4NO_3 , ---- with $c(\text{NH}_4\text{NO}_3) = 8.5 \text{ mol dm}^{-3}$.

tion of Pr and Sm ions by DEHPA is suppressed by the addition of NH_4NO_3 to the aqueous solutions. Finally, only negligible change in the distribution ratio was observed by the addition of NH_4NO_3 when extracting La and Nd ions.

In another set of experiments we tried to establish if there was any change in distribution ratio brought about by the addition of TBP to DEHPA or, in other words, if there exists any synergetic effect in the extraction of rare-earth ions. Again, for comparison, extraction experiments were carried out with the aqueous phase containing NH_4NO_3 and without it. Results are illustrated in Fig. 1.

Fig. 1 shows the variation of D_{La} with the composition of the organic phase. The dashed line representing the variation in the case when salting-out agent was used in the aqueous phase is located above the full line representing experimental results obtained under identical experimental conditions but without the salting-out agent. This means that the salting-out agent enhances the removal of La into the organic phase at all compositions of the organic phase except for the one containing 50 vol. % DEHPA and 50 vol. % benzene. Furthermore, the plot of D_{La} vs. composition of extractant is not a straight line but a curve. By adding *e.g.* DEHPA to TBP (10 vol. % DEHPA and 40 vol. % TBP), the distribution ratio increases to 0.59 in comparison with 0.29 for pure TBP. Extraction of La ions from the aqueous phase which contained NH_4NO_3 was enhanced if some DEHPA was substituted by TBP in an organic phase. Again, the variation is not linear.

Table 1. Distribution Ratios of La, Pr, Nd, and Sm in TBP–DEHPA Mixed Extractant

$c(\text{NH}_4\text{NO}_3)$ in aqueous phase mol dm^{-3}	$\varphi(\text{Extractant})/\%$		D_{La}	D_{Pr}	D_{Nd}	D_{Sm}
	TBP	DEHPA				
0	50	0	0.28	0.04	0.05	0.01
0	40	10	0.59	0.25	0.005	0.37
0	25	25	0.22	0.98	0.03	1.30
0	10	40	0.32	2.05	0.21	3.56
0	0	50	0.13	5.45	0.03	11.10
8.5	50	0	0.79	3.59	3.60	9.74
8.5	40	10	0.59	0.25	2.90	12.12
8.5	25	25	0.73	5.88	0.96	15.90
8.5	10	40	0.47	6.20	0.05	13.20
8.5	0	50	0.14	4.58	0.04	7.34

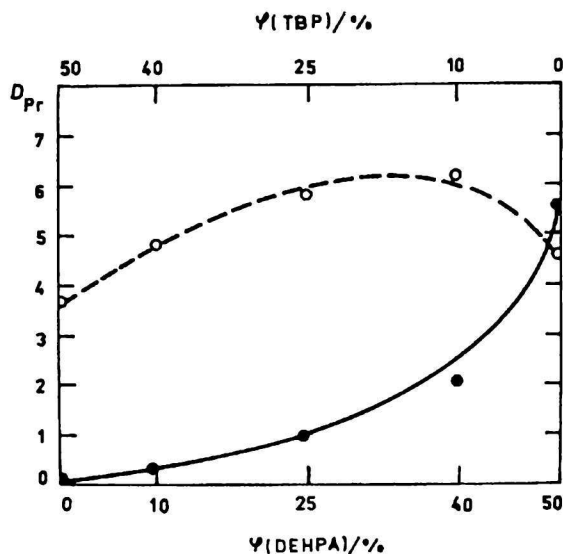


Fig. 2. Distribution coefficients of Pr vs. composition of DEHPA-TBP extracting agent. The initial composition of the aqueous phase: $c(\text{Pr}^{3+}) = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $c(\text{HNO}_3) = 0.5 \text{ mol dm}^{-3}$, — without NH_4NO_3 , ---- with $c(\text{NH}_4\text{NO}_3) = 8.5 \text{ mol dm}^{-3}$.

Extraction of Pr ions is represented by a diagram plotted in Fig. 2. In case that no NH_4NO_3 is added to the aqueous phase the best results are obtained with the extractant consisting of 50 vol. % DEHPA ($D_{\text{Pr}} = 5.45$); any substitution ratio of DEHPA to TBP, hence no synergetic effect. With the application of the salting-out agent the situation changed dramatically. The distribution ratios are higher (except for extraction with 50 vol. % DEHPA) and there exists a synergetic effect. For example, the organic phase consisting of 40 vol. % DEHPA and 10 vol. % TBP extracted praseodymium with $D_{\text{Pr}} = 6.2$.

Extraction of Nd by TBP or a mixed extractant is rather inefficient as can be deduced from the diagram illustrated in Fig. 3 in case that the aqueous phase was without NH_4NO_3 . The addition of the salting-out agent brought about a dramatic change of the situation, the distribution ratio increased from 0.005 to 3.6 (for 50 vol. % TBP) and from 0.04 to 2.9 (for the mixture of 40 vol. % TBP and 10 vol. % DEHPA). The synergetic effect occurs in the extraction of Nd only in the case that NH_4NO_3 has been added into the aqueous phase. Also the addition of the salting-out agent only negligibly affects the distribution ratio if the extractant was either 50 vol. % DEHPA or 40 vol. % DEHPA and 10 vol. % TBP.

According to the results depicted in Fig. 4 it can be seen that the application of NH_4NO_3 has a positive effect on extraction of Sm. Another important conclusion is that the synergetic effect occurs only in the case when the aqueous phase

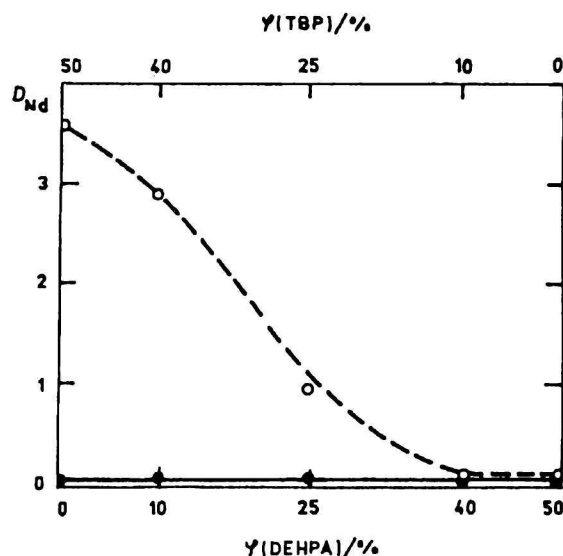


Fig. 3. Distribution coefficients of Nd vs. composition of DEHPA-TBP extracting agent. The initial composition of the aqueous phase: $c(\text{Nd}^{3+}) = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $c(\text{HNO}_3) = 0.5 \text{ mol dm}^{-3}$, — without NH_4NO_3 , ---- with $c(\text{NH}_4\text{NO}_3) = 8.5 \text{ mol dm}^{-3}$.

contained the salting-out agent. The maximum magnitude of the distribution ratio, 15.9, was determined when extracting with 25 vol. % TBP and 25 vol. % DEHPA. Organic extractants with other compositions removed Sm with relatively high distribution ratios which were, however, always below 15.9.

The separation factors of rare-earth elements were theoretically calculated from the relevant distribution ratios of separating elements A and

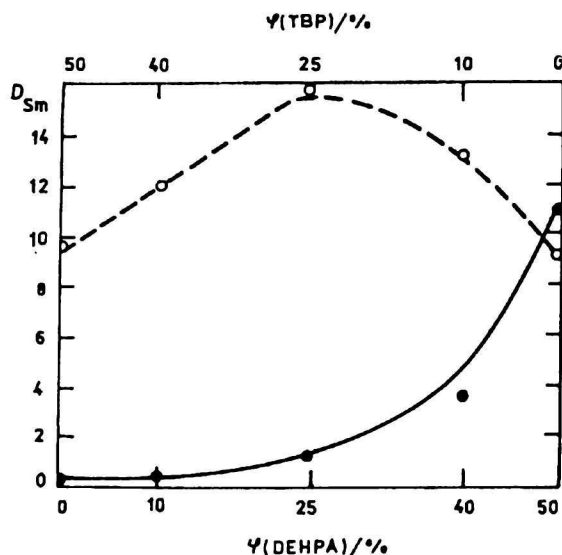


Fig. 4. Distribution coefficients of Sm vs. composition of DEHPA-TBP extracting agent. The initial composition of the aqueous phase: $c(\text{Sm}^{3+}) = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $c(\text{HNO}_3) = 0.5 \text{ mol dm}^{-3}$, — without NH_4NO_3 , ---- with $c(\text{NH}_4\text{NO}_3) = 8.5 \text{ mol dm}^{-3}$.

Table 2. Separation Factors of Rare-Earth Ions

$\varphi(\text{Extractant})/\%$		$\alpha_{\text{Sm/La}}(\text{calc.})$	$\alpha_{\text{Sm/Pr}}(\text{calc.})$	$\alpha_{\text{Sm/Nd}}(\text{calc.})$	$\alpha_{\text{La/Nd}}(\text{calc.})$	$\alpha_{\text{Pr/Nd}}(\text{calc.})$	$\alpha_{\text{Pr/La}}(\text{calc.})$
TBP	DEHPA	$\alpha_{\text{Sm/La}}(\text{exp.})$	$\alpha_{\text{Sm/Pr}}(\text{exp.})$	$\alpha_{\text{Sm/Nd}}(\text{exp.})$	$\alpha_{\text{La/Nd}}(\text{exp.})$	$\alpha_{\text{Pr/Nd}}(\text{exp.})$	$\alpha_{\text{Pr/La}}(\text{exp.})$
25	25	21.8	2.7	15.6	0.8	6.1	8.0
		6.3	3.2	2.0	0.5	0.8	3.6
0	50	52.4	1.6	183.0	3.5	114.0	32.7
		6.6	4.1	2.0	1.0	1.0	3.8

B, i.e. $\alpha_{A/B} = D_A/D_B$. In order to find out if the elements may be separated by the application of the mixed organic phases, several tests have been carried out with the aqueous phase containing $5 \times 10^{-2} \text{ mol dm}^{-3}$ of each lanthanoid tested and NH_4NO_3 . Results are summarized in Table 2. We can see that the separation of Sm and La is most effective with the separation factor above 6 and it does not seem to be greatly affected by the composition of the extractant. The organic phase

individual extractants of the same concentration as it has been in the mixed phase. Table 3 summarizes the synergetic coefficients of La, Pr, Nd, and Sm. For comparison, the coefficients were calculated for systems with and without the salting-out agent. In case of La, the synergetic coefficients are higher if the aqueous phase contained NH_4NO_3 . Samarium exhibits antagonism which seems to be independent of the additions of the salting-out agent. The synergetic coefficients of

Table 3. Synergetic Coefficients of Rare-Earth Ions in TBP–DEHPA System

$\varphi(\text{Extractant})/\%$		S_{La}		S_{Pr}		S_{Nd}		S_{Sm}	
TBP	DEHPA	A	B	A	B	A	B	A	B
40	10	0.22	1.08	1.26	1.26	0.50	1.00	0.37	0.16
25	25	0.35	1.57	1.43	1.12	1.71	0.52	0.21	0.22
10	40	0.47	1.70	1.41	1.46	1.60	0.06	0.40	0.40

A without and B with the salting-out agent.

consisting of 50 vol. % DEHPA is not suitable for separating Sm and Pr. The separation factors of Sm/Nd are always around 2 and do not seem to be greatly affected by the composition of the organic phase. La/Nd separation with the organic phase consisting of 25 vol. % DEHPA and 25 vol. % TBP is more efficient than with the phase consisting of 50 vol. % DEHPA. The same applies to Pr/Nd separation. Pr/La separation is successful with both organic phases tested here. It was, however, rather unexpected to see that the actual separation factors were in each case much lower than the theoretically calculated, except $\alpha_{\text{Sm/Pr}}$.

The synergetic coefficients of each rare-earth metal were evaluated according to the formula $S = D_{AB}/(D_A + D_B)$ where D_{AB} is the distribution ratio of an element in the mixed extracting agent, D_A , D_B are the distribution ratios of an element in

Pr are approximately the same if the aqueous solution was with or without NH_4NO_3 .

REFERENCES

1. Yagodin, G. A., Segyevskii, V. V., Evdokimova, L. V., and Babenko, L. M., *Dokl. Akad. Nauk SSSR* 258, 695 (1981).
2. Torres, R. A. and Choppin, G. R., *Radiochim. Acta* 35, 143 (1984).
3. Mikhailichenko, A. Yu. and Pimenova, R. M., *Zh. Neorg. Khim.* 17, 1907 (1973).
4. Mikhailichenko, A. Yu. and Pimenova, R. M., *Radiokhimiya* 11, 8 (1969).
5. Scargill, D., Alcock, K., Fletchen, J. M., Hesford, E., and McKay, H. A. C., *J. Inorg. Nucl. Chem.* 4, 304 (1957).
6. Shigeto Nakamura and Nobuo Suzuki, *Polyhedron* 5, 1805 (1986).
7. Huang, Chung-Hui and Bautista, R. G., *Sep. Sci. Technol.* 1983, 18.

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