

Separation of rare earth elements

I. Extraction of Sm, Pr, and Nd with tributylphosphate from nitrate solutions

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Dedicated to Professor E. Treindl, DrSc., in honour of his 60th birthday

The extraction of Sm, Pr, and Nd from an aqueous phase containing NaNO₃ and HNO₃ into the organic phase with tributylphosphate as an extractant and n-alkane as solvent was studied. The influence of the concentration changes of the individual extraction system components upon the distribution ratios and separation factors was investigated. It has been observed that the distribution ratio of each studied element increases with the increasing concentration of the salting out agent, NaNO₃ as well as of tributylphosphate. Increasing acidity, *i.e.* HNO₃ concentration, on the other hand, brings about decrease in the distribution ratio value. The separation factors Sm/Nd and Sm/Pr range from 1.2 to 3. The results obtained are discussed from the point of view of mutual solute—solvent interactions resulting in the change of activity coefficients in both phases.

Изучена экстракция Sm, Pr и Nd из водной фазы, содержащей NaNO₃ и HNO₃, в органическую фазу с трибутилфосфатом в качестве экстрактанта и n-алканом как растворителем. Исследовано влияние изменений концентрации отдельных компонентов экстракционной системы на распределительные отношения и факторы разделения. Наблюдалось, что распределительное отношение каждого изучаемого элемента возрастает при повышении концентрации высаливающего агента, NaNO₃, а также концентрации трибутилфосфата. Повышение кислотности, т.е. концентрации HNO₃, с другой стороны, приводит к снижению величины распределительного отношения. Факторы разделения Sm/Nd и Sm/Pr находятся в промежутке от 1,2 до 3. Полученные результаты обсуждаются с точки зрения взаимодействий растворимое вещество—растворитель, приводящих к изменению коэффициентов активности в обеих фазах.

The world consumption of rare earth elements has gradually been increasing during the last decade due to their widening utilization in various industrial branches, *e.g.* in metallurgy for alloys preparation, for production of permanent

magnets, catalysts, ceramic materials, as luminophores for screens, *etc.* Lately, much attention has been paid to the superconducting properties of some oxides of rare earth elements (REE) at relatively high temperatures.

Various organic extractants are used for REE extraction from aqueous solutions. Benzylalkylamines were used for REE extraction from neutral nitrate solutions [1]; for REE separation from americium benzyldimethyldodecylammonium nitrate was applied [2]. It is well known [3–7] that tributylphosphate (TBP) is a very suitable agent for REE extraction applicable also for solutions with very high HNO₃ concentration, *e.g.* 12–18 mol dm⁻³ in the extraction of Gd, Tb, Dy, Ho, and Y [3] or 6 mol dm⁻³ HNO₃ in the extraction of La, Sm, and Eu [4]. All REE are extracted by TBP from the acidic solutions prepared by leaching monazite concentrate and similar materials treatment [5]. If the acidity of the aqueous nitrate solutions is lower, a salting out agent must be added before applying TBP for REE extraction. For instance, 6 M-Al(NO₃)₃ was used for REE extraction with TBP at pH 1 [6]. *Chung-Hui Huang* and *Bautista* [7] studied the extraction of Sm and Gd from aqueous nitrate solutions by a mixture of TBP and Aliquat 336 with 4 M-NH₄NO₃ as salting out agent, and at pH 3.

In the present work, the extraction of Sm, Nd, and Pr from aqueous nitrate solution with HNO₃ and NaNO₃ as salting out agent and TBP in n-alkane solution as extractant was studied. The influence of HNO₃ and NaNO₃ concentration in the aqueous phase, and of TBP in the organic phase upon the distribution ratio and separation factors of REE extraction was investigated.

Theoretical

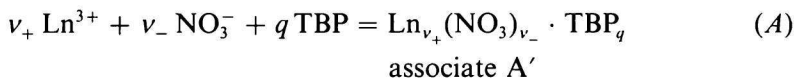
The equilibrium constant of the extraction of component *i* from aqueous to organic phase, *i.e.* the extraction constant is defined as follows

$$K_E = \frac{a'_i}{a_i} = \frac{c'_i \gamma_i}{c_i \gamma_{\pm}} \quad (1)$$

where a'_i , c'_i , and γ_i are activity, concentration, and activity coefficient, respectively, of the component *i* in the organic phase and a_i , c_i , and γ_{\pm} are the corresponding quantities in the aqueous phase.

The relationship (1) holds if the temperature and pressure remain constant and the standard states chosen for both phases are the same. For the standard state, a hypothetical solution was chosen with concentration of the dissolved component equal to 1 mol dm⁻³ and with properties of infinitely diluted solution. Therefore, in the above equation the Henry's activity coefficients are applied.

The extraction reaction of lanthanide nitrates with TBP may be written in the form



The extraction constant of the reaction (A) is then expressed as

$$K_E = \frac{\gamma_{A'} c_{A'}}{\gamma_{\pm}^{\nu} c_{\text{Ln}}^{\nu_+} c_{\text{NO}_3}^{\nu_-} \gamma_{\text{TBP}}^q c_{\text{TBP}}^q} \quad (2)$$

γ_{\pm} , $\gamma_{A'}$, γ_{TBP} are the molar activity coefficients, c_{Ln} , c_{NO_3} , $c_{A'}$, c_{TBP} are the molar equilibrium concentrations of corresponding components in aqueous and organic phases; stoichiometric coefficient $\nu = \nu_+ + \nu_-$. The value $\nu_+ = 1$ was experimentally verified. The charges of particles in aqueous phase are omitted for the sake of simplicity.

The ratio of the concentrations of the component *i* in both phases is in such a case defined as the distribution ratio *D*. Eqn (2) can then be written as follows

$$D = K_E \frac{\gamma_{\pm}^{\nu} \gamma_{\text{TBP}}^q c_{\text{NO}_3}^{\nu_-} c_{\text{TBP}}^q}{\gamma_{A'}} \quad (3)$$

The distribution ratio is thus proportional to the ratio of the activity coefficients of the component, *i.e.* lanthanide in both phases. Accordingly, an enhancement of the extraction of component into the organic phase may be achieved by any intervention into the system bringing about either an increase in γ_{\pm} or decrease in $\gamma_{A'}$ or both. One of the methods of increasing γ_{\pm} is an increase in the ionic strength of the aqueous solution, which may be accomplished by increasing the concentration of nitrate ions by adding either HNO_3 or a soluble nitrate salt. In such a case, the nitrate ion concentration should be high.

The activity coefficient $\gamma_{A'}$ depends on the type of extractant and solvent as well as on the concentration of the component A' in the organic phase which, in turn, determines the composition of the particles in this phase.

Experimental

The organic phase contained 15, 25, 50, and 100 vol. % of TBP in n-alkane as a solvent. TBP (Soyuz Khim. Reaktiv) was used without any additional treatment, n-alkane was the fraction C₉ to C₁₂ (Slovnaft, Bratislava). The aqueous phase consisted of the REE nitrates (REE — Pr, Nd, Sm) of anal. grade (Ventron), nitric acid, and sodium nitrate as salting out agent, both anal. grade (Lachema, Brno).

Extractions were carried out at room temperature (22 ± 2°C). The volume ratio of the organic to aqueous phases was 1 : 2. The mixing period took 5 min, which has proved to be sufficient for attaining the equilibrium; the phase disengagement was carried out for 20 min.

For analysis, the aqueous phase before and after the extraction was used. Contents of one individual REE or of all REE were determined by molecular absorption spectrometry with Arsenazo III at pH 4.7 and the wavelength $\lambda = 652$ nm. The emission spectrometry with inductively coupled plasma was used for determination of more than one REE in the solution.

Results and discussion

The dependence of distribution ratio for Sm, Pr, and Nd upon the TBP content in the organic phase, shown in Fig. 1 points to the feasibility of separation of Sm from the other two elements. With increasing concentration of TBP the increase of the distribution ratio is more remarkable: at 15 and 25 vol. % of TBP the value of D is relatively low in all three cases whereas the extraction with 50 % TBP gives much better values of D . Although the highest value of D was obtained in case of 100 % TBP as extractant, in further experiments 50 % TBP was used.

The influence of the acid concentration in the aqueous phase upon the distribution ratio of Sm at constant ionic strength ($I = 6 \text{ mol dm}^{-3} \text{ NaNO}_3$) is presented in Fig. 2. It shows that D_{Sm} is remarkably reduced by a decrease in the pH value; at the HNO_3 concentration 0.7 mol dm^{-3} its value is negligible.

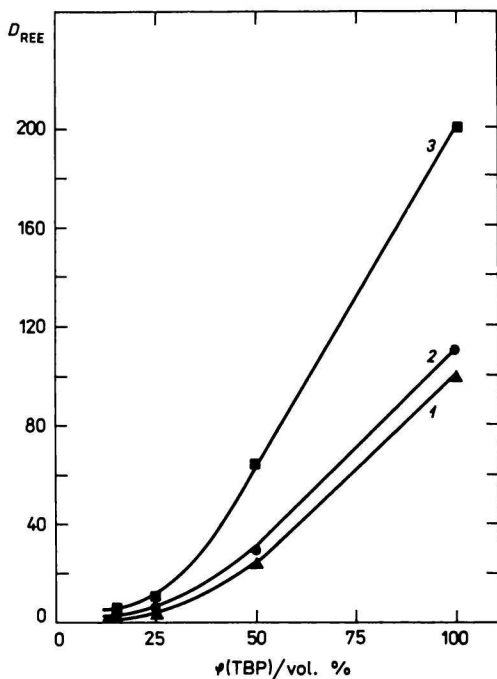
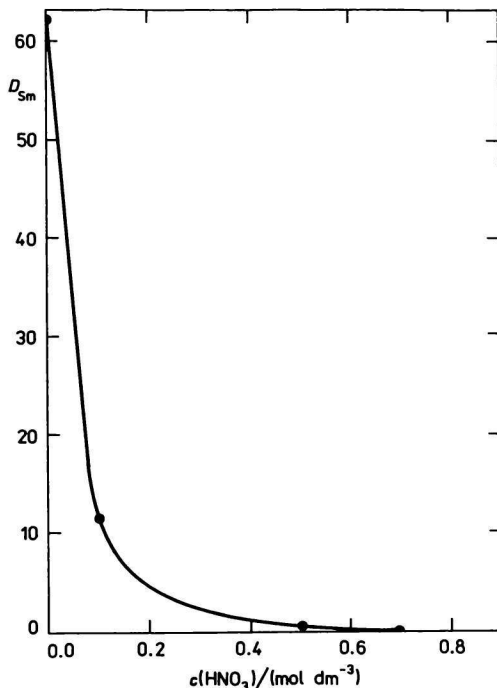


Fig. 1. Plot of the distribution ratio D of various REE vs. TBP content. $c(\text{NaNO}_3) = 6.0 \text{ mol dm}^{-3}$, $c(\text{HNO}_3) = 10^{-3} \text{ mol dm}^{-3}$, $c(\text{Ln}^{3+}) = 10^{-3} \text{ mol dm}^{-3}$. 1. Pr; 2. Nd; 3. Sm.

Fig. 2. Plot of the distribution ratio for Sm vs. concentration of HNO_3 in the aqueous phase.

$$\begin{aligned} c(\text{Sm}^{3+}) &= 10^{-3} \text{ mol dm}^{-3}, \\ c(\text{NaNO}_3) &= 6.0 \text{ mol dm}^{-3}, \\ c(\text{TBP}) &= 1.858 \text{ mol dm}^{-3}. \end{aligned}$$



In Fig. 3 the dependence of D_{Sm} upon the concentration of salting out agent at constant pH is demonstrated. It is obvious that increasing NaNO_3 concentration in the aqueous phase leads to a remarkable increase in the value of D_{Sm} . The effect is the highest at concentration between 5 and 6 mol dm^{-3} NaNO_3 : at the former NaNO_3 concentration the $D_{\text{Sm}} = 13$ whereas at the latter one it increases to the value $D_{\text{Sm}} = 64$. The highest NaNO_3 concentration used is very close to the solubility limit of the salt.

The experimental results may be interpreted by help of eqn (3). Assuming all other parameters constant, D increases with the increase in the extractant, TBP concentration. The same is true for the increase in NO_3^- concentration realized by increasing the salting out agent, NaNO_3 , concentration. The latter influence, however, is reflected not solely in the increase of $c(\text{NO}_3^-)$ value. With increasing salting out agent concentration the activity of H_2O in aqueous phase decreases from the value $0.9845 \text{ mol dm}^{-3}$ for 1 mol dm^{-3} NaNO_3 solution to the value $0.896 \text{ mol dm}^{-3}$ for 6.2 mol dm^{-3} NaNO_3 solution. (The calculation of the activity of water has been carried out by help of the Gibbs—Duhem equation, with data from [8].) The solute—solvent interaction in the aqueous phase is weakened and, consequently, an increase in the activity coefficient γ_{\pm} results. According to eqn (3) an increase in D should occur and it is in fact observed in Fig. 3.

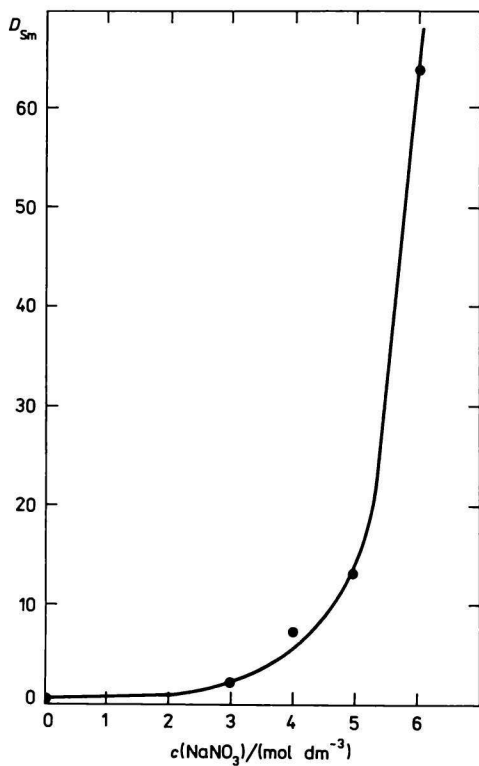


Fig. 3. Plot of the distribution ratio for Sm vs. concentration of NaNO_3 in the aqueous phase.

$$c(\text{Sm}^{3+}) = 10^{-3} \text{ mol dm}^{-3},$$

$$c(\text{HNO}_3) = 10^{-3} \text{ mol dm}^{-3},$$

$$c(\text{TBP}) = 1.858 \text{ mol dm}^{-3}.$$

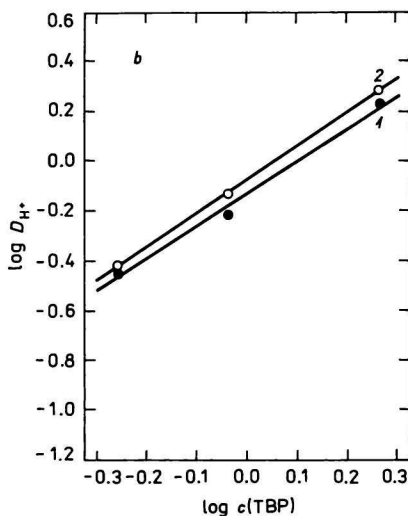
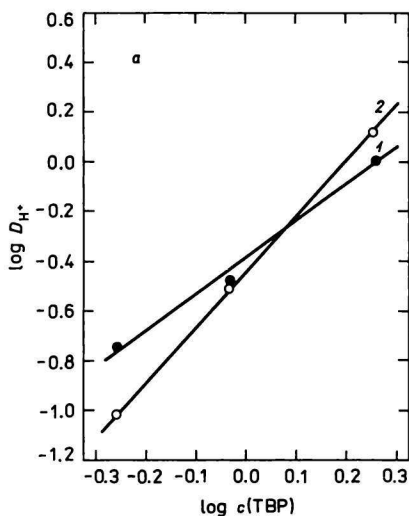


Fig. 4. Logarithmic plot of the distribution ratio D_{H^+} vs. TBP concentration. $c(\text{NaNO}_3) = 6 \text{ mol dm}^{-3}$, $c(\text{HNO}_3)/(\text{mol dm}^{-3})$: 1. 10^{-1} , 2. 10^{-3} . $c(\text{Sm}^{3+})$: a) 0, b) $10^{-3} \text{ mol dm}^{-3}$.

Table 1

The calculated separation factors α for separation of Sm from Pr or Nd for various concentrations of REE in the aqueous phase and TBP in the organic phase

c_{Sm}	c_{Pr} OR c_{Nd}	$\varphi(\text{TBP})/\text{vol. \%}$					
		15		25		50	
		$\alpha_{\text{Sm/Pr}}$	$\alpha_{\text{Sm/Nd}}$	$\alpha_{\text{Sm/Pr}}$	$\alpha_{\text{Sm/Nd}}$	$\alpha_{\text{Sm/Pr}}$	$\alpha_{\text{Sm/Nd}}$
10^{-3}	10^{-3}	4.12	1.84	2.63	1.86	2.62	2.24
	5×10^{-3}	4.32	2.26	3.05	1.99	3.19	2.43
	10^{-2}	5.67	2.66	3.18	2.46	3.39	3.29
	5×10^{-2}	8.42	4.80	6.88	3.90	5.87	4.40
5×10^{-3}	10^{-3}	3.30	1.66	2.15	1.52	1.95	1.47
	5×10^{-3}	3.46	1.81	2.48	1.62	2.37	1.80
	10^{-2}	4.54	2.13	2.59	2.00	2.52	2.45
	5×10^{-2}	6.74	3.84	5.61	3.19	4.36	3.27
10^{-2}	10^{-3}	2.96	1.32	1.90	1.35	1.77	1.51
	5×10^{-3}	3.10	1.63	2.20	1.44	2.16	1.64
	10^{-2}	4.00	1.92	2.29	1.77	2.29	2.22
	5×10^{-2}	6.05	3.45	4.97	2.83	3.96	2.97
5×10^{-2}	10^{-3}	1.80	0.81	1.07	0.75	1.15	0.99
	5×10^{-3}	1.89	0.99	1.24	0.81	1.41	1.07
	10^{-2}	2.48	1.17	1.29	1.00	1.49	1.45
	5×10^{-2}	3.68	2.10	2.80	1.60	2.58	1.99

From the above said it follows that a decrease in D value caused by HNO_3 concentration increase — as shown in Fig. 2 — may be ascribed to the increase in H^+ and not NO_3^- concentration. Fig. 4 offers confirmation that HNO_3 is extracted by TBP into the organic phase. This competitive extraction is probably the most significant effect causing suppression of lanthanide extraction at such a high HNO_3 concentration as 0.7 mol dm^{-3} , shown for Sm in Fig. 2. Another effect may, however, not be excluded: with increasing HNO_3 concentration the strengthening of the solute—solvent interaction in the aqueous phase takes place by forming hydrogen bridge-type bondings between the HNO_3 hydrogen and water molecules in the solvation sphere of lanthanide which would result in the decrease of the activity coefficient γ_{\pm} , and, accordingly in D values.

The distribution ratios D_i obtained for individual REE enabled to calculate the theoretical values of separation factors according to the formula

$$\alpha_{i/j} = \frac{D_i}{D_j} \quad (4)$$

Table 2

The determined separation factors α for separation of Sm from Pr or Nd for various concentrations of REE in the aqueous phase and TBP in the organic phase

c_{Sm} mol dm ⁻³	c_{Pr} OR c_{Nd} mol dm ⁻³	$\varphi(\text{TBP})/\text{vol. \%}$			
		15		50	
		$\alpha_{\text{Sm/Pr}}$	$\alpha_{\text{Sm/Nd}}$	$\alpha_{\text{Sm/Pr}}$	$\alpha_{\text{Sm/Nd}}$
10 ⁻³	10 ⁻³	7.81		2.06	
	5 × 10 ⁻²	3.08		1.71	
	10 ⁻³		3.15		1.54
	5 × 10 ⁻²		2.01		1.25

Values of separation factors calculated according to formula (4) for the pairs of REE $\alpha_{\text{Sm/Pr}}$ and $\alpha_{\text{Sm/Nd}}$ are summarized in Table 1. The following may be stated:

— with increasing initial concentration of Sm in the aqueous phase both separation factors decrease;

— with increasing initial Pr or Nd concentration in the aqueous phase both separation factors increase;

— the $\alpha_{\text{Sm/Pr}}$ value is in all measured cases higher than $\alpha_{\text{Sm/Nd}}$;

— the influence of increasing TBP concentration in the organic phase is not explicit. At low initial Sm concentrations the values $\alpha_{\text{Sm/Pr}}$ decrease with increasing TBP concentration whereas at higher initial Sm concentration value (5 × 10⁻² mol dm⁻³) the value $\alpha_{\text{Sm/Pr}}$ attains minimum at 25 % TBP. The separation factor $\alpha_{\text{Sm/Nd}}$ shows minimum value at 25 % TBP for all initial concentrations of Sm.

The practical consequence is that separation of small amounts of Sm from higher amounts of Pr or Nd is feasible; separation of Sm from Pr is better than separation of Sm from Nd. Relatively high values of $\alpha_{\text{Sm/Pr}}$ in the extraction with 15 % TBP point out to the suitability of such extraction agent. The corresponding distribution ratio values presented in Fig. 1 however, show that the extraction with 15 % TBP is applicable in practice only in case of a multistage extraction process.

Table 2 summarizes some of the determined values of the separation factors. Comparison of these results with the corresponding calculated separation factor values in Table 1 shows that all determined separation factors are lower than the calculated ones with the exception of values obtained for the lowest REE concentration in the aqueous phase and TBP in the organic phase.

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