Extraction of Rare Earth Metals by Bis(2-Ethylhexyl)phosphoric Acid

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The extraction of lanthanum, samarium, and hydrogen ions from aqueous HNO_3 solutions by bis(2-etylhexyl)phosphoric acid solution in benzene has been studied. The distribution ratio dependence on the pH of the aqueous phase and concentration of extractant in the organic phase was investigated. The stoichiometric coefficients of the overall extraction reaction were determined as slopes of the logarithmic dependence of the distribution coefficients on the pH and the extractant concentration. The separation factors $\alpha_{Sm/La}$ ranging around the value of 10 decrease with addition of α-hydroxyisobutyric acid.

Bis(2-ethylhexyl)phosphoric acid (DEHPA) is an efficient extracting and separating agent for rare earth metal ions from acidic aqueous solutions. Several investigations were devoted to the mechanism of extraction during past 20 years [1—8]. They have shown that on extracting Eu and Am from aqueous solution of humic acid the organic phase contains LnA_3 $(HA)_3$ where HA is DEHPA and A^- is the corresponding anion [5]. Authors of papers [6, 7] studied the extraction of rare earth metals from aqueous solutions containing HNO_3 by DEHPA. It was shown [7] that the distribution ratio and the mechanism of extraction depended on the concentration of HNO_3 in the aqueous solution. At high HNO_3 concentrations the organic phase contains $Ln(NH_3)_3 \cdot 3HA$. At lower HNO_3 concentrations in the aqueous phase below 1 mol dm^{-3} the predominant type of associate is $Ln(HA_2)_{3-i}(NO_3)_i \cdot (HA)_j$ where the i and j values are between 0 and 3. Papers [4, 5, 8] describe the extraction of rare earth metals by DEHPA from the aqueous solutions of hydrochloric acid. The structure of associates that have been formed in the organic phase was studied in detail. The conclusions were very similar to the case of extraction from HNO_3 solutions, *i.e.* that the associates of the type $LnCl_3 \cdot 2m$ (HA) are created at high HCl concentrations whereas at lower concentrations of HCl the type of associates is $Ln_nA_{2(2n+1)}H_{n+2}$. Infrared and NMR spectra studied in [8] showed that DEHPA dissolved in kerosene enters the extraction reaction in the form of dimeric or polymeric molecules. Interesting results of investigation of the distribution ratios of rare earth metals extracted from the aqueous solutions containing 0.01 mol dm^{-3} HCl with 0.05 mol dm^{-3} DEHPA are published in [8]. They show that D_{Lm} increases with the atomic number from La to Ln but the curve is discontinuous. More exactly, one can observe the so-called “group of four” effect, *i.e.* the change of the slope of curve after each group of four rare earth metals, at Nd, Gd, and Ho.

Separation of rare earth metals by extraction with DEHPA at different pH of the aqueous phase was investigated in [9]. Based on these results the pilot plant has been designed.

The objective of the present paper is firstly the description of the extraction of some rare earth metals and H^+ ions from aqueous solutions with different concentrations of HNO_3 by DEHPA and secondly, the investigation of the effect of complexing agent, α-hydroxyisobutyric acid (HIBA) on the efficiency of separation.

EXPERIMENTAL

Organic phase consisting of DEHPA of 99.8 % purity was prepared by the Research Institute of Chemical Technology in Bratislava. DEHPA was diluted with benzene of anal. grade purity. The aqueous solution concentration was between 5×10^{-3}—10 mol dm^{-3}. The nitrates of La and Sm were prepared by dissolving the respective oxide of anal. grade purity (Ventron) in the nitric acid (anal. grade) solution. Their final concentration in the aqueous solution was 1×10^{-3}—5×10^{-3} mol dm^{-3}. Extraction experiments were carried out at room temperature, approximately 22 °C. The mass ratio of the organic and aqueous phases was 1 : 1. Both phases were in contact for 5 min by vigorous shaking of the flasks which were then left for 30 min in order to disengage the two phases.

The aqueous phase before and after extraction was analyzed either by spectrophotometric method with additions of Arzenazo III or by emission spectrometry with excitation in DCP plasma according to the Marinkovitch method. The pH of the solution was determined by pH-meter (Radelkis) OP 265/1.

RESULTS AND DISCUSSION

The effects of concentration of the bis(2-ethylhexyl)phosphoric acid and of pH of the aqueous solution on the distribution ratio of La and Sm were studied at constant temperature and constant initial concentration of $Ln(NO_3)_3$ in the aqueous solution.

Fig. 1 shows the variation of the logarithm of the distribution ratio D_{H+} with equilibrium pH of the aqueous phase at constant temperature and constant concentration of DEHPA, $c(\mathrm{DEHPA}) = 0.15\ \mathrm{mol\ dm^{-3}}$ in the organic phase. The equation calculated by the linear regression from the experimentally determined values of D_{H+} is of the following form

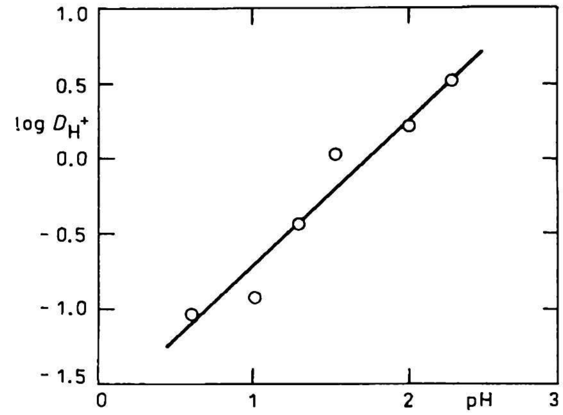

Fig. 1. Variation of log D_{H+} with pH at equilibrium of the aqueous solution; $c(\mathrm{DEHPA}) = 1.5 \times 10^{-1}\ \mathrm{mol\ dm^{-3}}$.

$$\log D_{H+} = -1.86 + 0.98\ \mathrm{pH} \qquad (1)$$

The slope of the line $\delta(\log D_{H+})/\delta(\log \mathrm{pH})$ is equal to the stoichiometric coefficient n and this in eqn (*1*) is 0.98 which rounded gives the value $n = 1$. Solvent extraction under these experimental conditions takes place in accordance with the following reaction

$$(HA)_2 = HA_2^- + H^+ \qquad (A)$$

Supposing that the chemical reaction

$$Ln^{3+} + 3\ NO_3^- + m\ HA = Ln(NO_3)_3A_n(HA)_{m-n} + n\ H^+ \qquad (B)$$

of extraction of Ln^{3+} reaches its equilibrium state, we can express the equilibrium constant based on equilibrium concentrations

$$K_e = D_{Ln}\frac{[H^+]^n}{[HA]^m} \qquad (2)$$

As the equilibrium constant remains constant at fixed temperature we obtain by its derivation, taking the logarithm and using the formulae $\mathrm{pH} = -\log\{[H^+]\}$ the corresponding stoichiometric coefficient of the reaction (*B*)

$$\left|\frac{\delta(\log D_{Ln})}{\delta(\mathrm{pH})}\right|_{[HA]} = n \qquad (3)$$

$$\left|\frac{\delta(\log D_{Ln})}{\delta(\log [HA])}\right|_{\mathrm{pH}} = m \qquad (4)$$

Therefore the slope of lines which represent the variation of log D_{Ln} with pH (Fig. 2) at constant concentration of the bis(2-ethylhexyl)phosphoric acid gives actually the stoichiometric coefficient n whereas the slope of the line that represents the variation of log D_{Ln} with concentration of the bis(2-ethylhexyl)phosphoric acid at constant pH of the aqueous phase (Fig. 3) corresponds to the stoichiometric coefficient m.

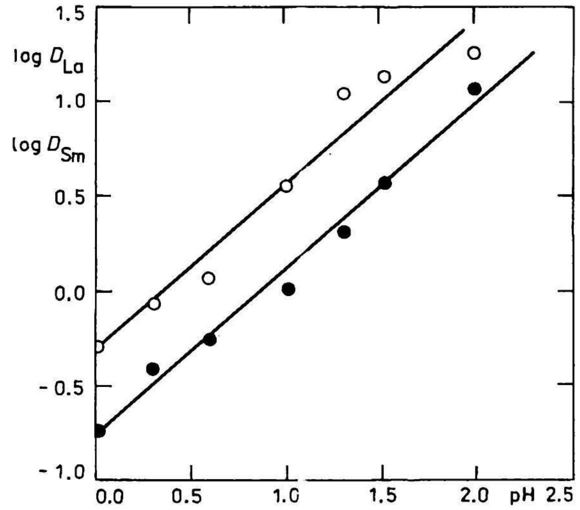

Fig. 2. Variation of log D_{La} and log D_{Sm} with pH. Initial concentration of lanthanoids: $c(Ln(NO_3)_3) = 5 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$, $c(\mathrm{DEHPA}) = 1.5 \times 10^{-1}\ \mathrm{mol\ dm^{-3}}$. ○ log D_{La}, ● log D_{Sm}.

Fig. 2 shows the experimentally determined distribution ratios of lanthanum and samarium between aqueous and organic phase as log *D vs.* pH at constant concentration of the bis(2-ethylhexyl)phosphoric acid in the organic phase, $c(\mathrm{DEHPA}) = 0.15\ \mathrm{mol\ dm^{-3}}$ and at constant initial concentration of lanthanum and samarium in the aqueous phase $5 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$.

The linear regression method was applied to calculate the coefficient of the equations describing the variation of D_{La} and D_{Sm} with the pH of the solution

$$\log D_{La} = -0.75 + 0.86\ \mathrm{pH} \qquad (5)$$

$$\log D_{Sm} = -0.31 + 0.87\ \mathrm{pH} \qquad (6)$$

It follows from Fig. 2 and eqns (*5*) and (*6*) that the

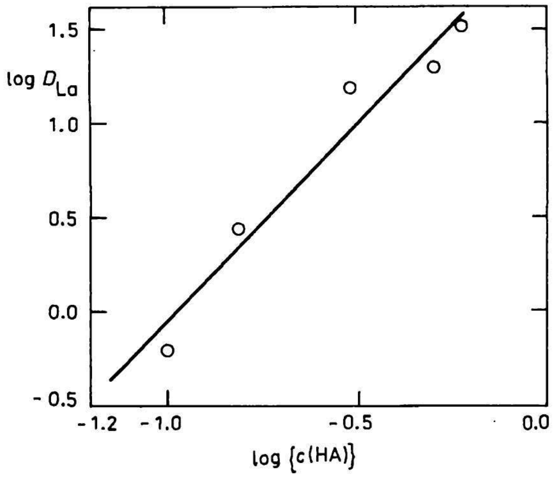

Fig. 3. Variation of log D_{La} with log c(HA). Initial concentrations: $c(La(NO_3)_3)$ = 5.5 × 10^{-3} mol dm^{-3}, $c(HNO_3)$ = 0.5 mol dm^{-3}.

slopes of the two lines are the same. Their rounding to the nearest integer gives the stoichiometric coefficient $n = 1$ in the reaction (B).

When determining the stoichiometric coefficient m only lanthanum ion was used for experiments. It has been assumed that other lanthanoids in solvent extraction process behave similarly.

Fig. 3 shows the experimentally determined values of the distribution coefficients of lanthanum in log D_{La} – log {c(La)} coordinates. The linear function calculated by the linear regression method is: log D_{La} = 2.03 + 2 log {c(HA)}. The slope of the line is

$$\frac{\delta(\log D_{La})}{\delta(\log\{c(HA)\})} = 2$$

which means that the stoichiometric coefficient m equals 2. The obtained stoichiometric coefficients enable to write the chemical reaction in which the associate is being formed

$$Ln^{3+} + 2\,NO_3^- + 2\,HA = Ln(NO_3)_2AHA + H^+ \quad (C)$$

It was shown already [10] that the separation factors $\alpha_{Sm/La}$ are low, their values are in the vicinity of one. By applying the α-hydroxyisobutyric acid as a complexing agent the separation factors $\alpha_{Sm/La}$ do not increase as shown in Fig. 4. In these experiments the aqueous phase consisted of nitric acid solution with pH values between 3.5 and 4, lanthanoids concentration $c(Ln(NO_3)_3)$ = 5 × 10^{-3} mol dm^{-3}, the complexing agent HIBA was added so that its concentration would be between 0 and 0.02 mol dm^{-3}, the organic phase comprised DEHPA with the concentration 1.5 × 10^{-1} mol dm^{-3} dissolved in benzene. The measured and calculated values are summarized in Table 1.

Previous results [10, 11] on the investigation of extraction with amines showed that the addition of a complexing agent brought about the increase of the separating factors. In the presented case of extraction with DEHPA La was extracted to a lesser extent than Sm which is also evident from the position of the curves in Fig. 3. The addition of the complexing agent suppresses the separating effect because HIBA forms with samarium stronger complex than with lanthanum [12]. This means that Sm which can be easier extracted is being blocked by the addition of the complexing agent thus reducing the separation of La and Sm.

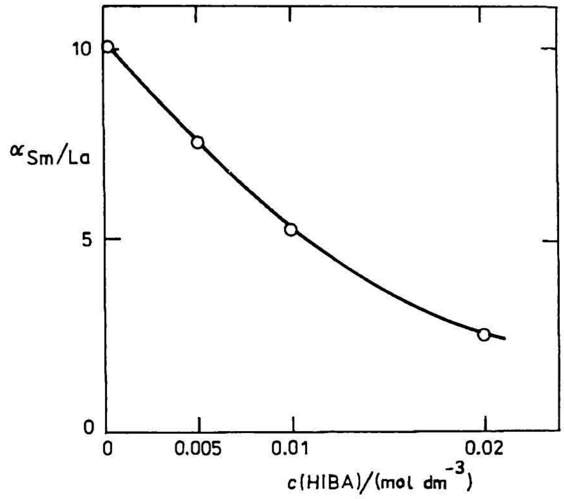

Fig. 4. Variation of the separation factor $\alpha_{Sm/La}$ with the concentration of α-hydroxyisobutyric acid. c(DEHPA) = 1.5 × 10^{-1} mol dm^{-3}, $c(Ln(NO_3)_3)$ = 5 × 10^{-3} mol dm^{-3}, pH 3.5—4.

Table 1. Separation Factors ($\alpha_{Sm/La}$) in Dependence on the Concentration of α-Hydroxyisobutyric Acid

c(HIBA) / mol dm^{-3}	D_{La}	D_{Sm}	$\alpha_{Sm/La}$
0	1.59	16.21	10.2
5 × 10^{-3}	3.99	30.11	7.55
10^{-2}	4.54	23.99	5.28
5 × 10^{-2}	11.15	28.23	2.53

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Synthesis of $BaFe_{12}O_{19}$ Powders in Molten Alkali Metal Chlorides

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Very fine powders of barium ferrite $BaFe_{12}O_{19}$ were prepared by the reaction of iron(III) oxide and barium carbonate in the medium of molten alkali metal chlorides. The effect of the temperature and the time of the isothermal heating on the conversion degree and the size of the $BaFe_{12}O_{19}$ crystals was studied. $BaFe_{12}O_{19}$ originates already at the temperature of 800 °C, however it becomes to be the dominating reaction product above the temperature of 850 °C and the heating time of 1 h. It was found that at the temperature of 850 °C and the reaction time of 0.5—2 h the rate of the $BaFe_{12}O_{19}$ crystal growth is controlled by surface chemical reaction. The activation energy of the $BaFe_{12}O_{19}$ formation has the value ΔE = 300 kJ mol^{-1} corresponding to the reaction in the liquid medium as the rate-limiting process.

Barium ferrite $BaFe_{12}O_{19}$ is a typical representative of the ferrites with high magnetic remanence, widely used in the production of the permanent magnets. It is produced from commercial iron(III) oxide and barium carbonate by the solid-state reaction at about 1100 °C [1].

Very fine powders of mixed oxides may be prepared with advantage by precipitation in molten salt medium [2]. In the present work the experimental conditions for the $BaFe_{12}O_{19}$ barium ferrite preparation by precipitation in the molten alkali metal chloride mixture were studied.

EXPERIMENTAL

Barium ferrite $BaFe_{12}O_{19}$ was prepared by the reaction of iron(III) oxide with barium carbonate in the medium of molten alkali metal chlorides according to the equation

$$BaCO_3(l) + 6\,Fe_2O_3(s) = BaFe_{12}O_{19}(s) + CO_2(g) \quad (A)$$

The heating temperatures in the interval of 750—950 °C and the exposure times of 0.5—2 h were chosen for the preparation. The equimolar mixture NaCl + KCl in the three-fold mass surplus was used as a flux. After the isothermal heating at the desired temperature the samples were cooled and dissolved in boiling distilled water. The composition of insoluble remainder was determined by means of the X-ray powder diffraction analysis. The diffraction line at 0.277 nm was used for the semiquantitative analysis of $BaFe_{12}O_{19}$.

The crystal diameters in terms of the temperature and time of heating were measured. On the basis of the statistical analysis of the time dependence of the average crystal diameters the probable control mechanism of the isothermal crystal growth of $BaFe_{12}O_{19}$ as well as the activation energy of its formation was determined using the procedure described in [3].