CHEMICALLY BASED MODEL FOR THE EXTRACTION OF Pr(III) AND Nd(III) WITH MIXTURES OF VARIOUS ORGANOPHOSPHORUS COMPOUNDS

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Introduction

Mason *et al.*⁵⁾ have studied the extraction of trivalent lanthanides using mixtures of di(2-ethylhexyl) phosphoric acid (D2EHPA) and TBP or TOPO with small synergistic enhancement. With the higher lanthanides (atomic number $Z > 64$), Zangen⁷⁾ reported antagonistic effects with mixtures of D2EHPA and a series of neutral esters. However, he observed synergistic extraction in the case of lower lanthanides ($Z < 64$). Kandil and Farah⁴⁾ reported antagonistic effects in the extraction of terbium and europium with D2EHPA + TBP or D2EHPA + TOPO.

A survey of the literature shows that most extraction studies deal with mixtures of D2EHPA and neutral organophosphorus compounds at low concentrations of the rare earths. Although D2EHPA is an effective extractant for the mutual separation of lanthanides, it has the disadvantage of difficulty in back-extraction. EHPNA has a higher ability of back-extraction at low acid concentrations than D2EHPA. Hence it is of interest to investigate the synergism, if any, in the extraction of Pr(III) and Nd(III) with mixtures of EHPNA and TBP or TOPO.

Due to the difficulty in establishing the reaction mechanisms at high concentrations for the extraction of Pr(III) and Nd(III) with mixtures of EHPNA and TBP or TOPO by the usual slope analysis method,

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recourse was taken to nonlinear regression analysis using a computer. In this approach, plausible reaction mechanisms are assumed and the extraction constants are deduced by minimizing the root mean square fractional error between the experimental and calculated distribution coefficients.

1. Experimental

EHPNA was purified by washing the commercial extractant PC88A, supplied by Daihachi Chemical Industry Co., Ltd., Japan, with 6 mol dm⁻³ hydrochloric acid solution, and then with deionized water several times. TBP and TOPO were obtained from Fluka A. G. TBP was purified by multiple washing with a 10% NaOH solution and water¹⁾. TOPO⁵⁾ and kerosene used as diluent⁶⁾ were purified by the methods reported in the literature. The aqueous solution was prepared by dissolving the desired amount of praseodymium or neodymium chloride into deionized water. Ionic strength and pH of the aqueous solutions were adjusted to 0.1 mol dm⁻³ and at desired level respectively by using lithium chloride and hydrochloric acid.

Distribution coefficients were determined by the usual method. The concentration of lanthanoid in the aqueous phase was determined by titration with EDTA at pH=5 using xylenol orange as the indicator. The concentration of the lanthanoid in the organic solution was determined by the same methods after back-extraction with 6 mol dm⁻³ hydrochloric acid solution. The activity coefficient of the hydrogen ion under the conditions of the present work was calculated from the values measured by a pH meter and by titration.

2. Extraction Mechanism

The lanthanoid in the aqueous phase forms a variety of complexes in the presence of chloride ions, but under the conditions of the present work it is sufficient to consider only the first stability constant (β_1) defined by Eq. (1)³⁾.

$$\beta_1 = [\text{LnCl}^{2+}] / [\text{Ln}^{3+}][\text{Cl}^-] \quad (1)$$

β_1 is related to the dimensionless thermodynamic equilibrium constant, β_1° , which is a function of temperature only, as

$$\beta_1 = \frac{\beta_1^\circ \cdot \gamma_{\text{Ln}^{3+}} \gamma_{\text{Cl}^-}}{C_w \gamma_{\text{LnCl}^{2+}}} \quad (2)$$

where γ_x refers to the activity coefficient of ionic species x , which can be calculated by²⁾

$$-\log \gamma_x = 0.509 Z_x^2 [I^{0.5} / (1 + I^{0.5}) - 0.2 I] \quad (3)$$

The value of β_1° / C_w of the lanthanoid was calculated from β_1 values reported by Goto and Smutz³⁾. The

values of β_1 under the experimental conditions were calculated from Eqs. (2) and (3) and were found to be

$$\beta_{1,\text{Pr}} = 2.42; \quad \beta_{1,\text{Nd}} = 2.49.$$

When the lanthanoid ions are extracted from chloride solutions with mixtures of EHPNA ((HX)₂) and TBP (R) or TOPO (R), the ideal extraction equilibrium in the presence of antagonistic effects, as observed in the present study, can be written as

where (HX)₂ refers to the dimeric form of EHPNA, Ln(HX₂)₃ refers to the complex of the lanthanoid ion extracted into the organic phase and R refers to either TOPO or TBP. The formation of a complex between R and (HX)₂ appears to be a reasonable way of explaining the antisnergism observed in the present experiments. The extraction constants of the above reactions can be written as

$$K_1 = \frac{[\text{Ln}(\text{HX}_2)_3]_{\text{org}} [\text{H}^+]^3}{[\text{Ln}^{3+}]_{\text{aq}} [(\text{HX})_2]_{\text{org}}^3} \quad (6)$$

and

$$K_2 = \frac{[(\text{HX})_2\text{R}]_{\text{org}}}{[(\text{HX})_2]_{\text{org}} [\text{R}]_{\text{org}}} \quad (7)$$

where the subscript, org, designates the concentration of the chemical species in the organic phase at equilibrium. Then the distribution coefficient of the lanthanoid, D , can be represented as

$$D = \frac{[\text{Ln}(\text{HX}_2)_3]_{\text{org}}}{[\text{Ln}^{3+}]_{\text{aq}} + [\text{LnCl}^{2+}]_{\text{aq}}} \\ = \frac{K_1}{K_2^3} \frac{[(\text{HX})_2\text{R}]_{\text{org}}^3}{[\text{R}]_{\text{org}}^3 [\text{H}^+]^3 \{1 + \beta_1 [\text{Cl}^-]\}} \quad (8)$$

Hence a plot of $\log (D[\text{H}^+]^3 \{1 + \beta_1 [\text{Cl}^-]\})$ vs. $\log [(\text{HX})_2\text{R}] / [\text{R}]$ should give a slope of 3.

The equilibrium concentrations of all the species were calculated by using Eqs. (1), (6) and (7) and the conservation equations for (HX)₂, B and lanthanoid. The equilibrium concentrations of all the species thus obtained were substituted into Eq. (8). The values of constants K_1 and K_2 were determined by the Box method, so that these values might lead to a minimum root mean square fractional error, y , for all the experimental data.

$$y = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{D_{\text{cal},i} - D_{\text{expt},i}}{D_{\text{expt},i}} \right)^2} \quad (9)$$

3. Results and Discussion

In Fig. 1 and 2, the effects of the neutral

Fig. 1. Variation of $\log D$ with concentration of TBP in the presence of EHPNA in kerosene for the extraction of Pr(III). pH = 2.0, $[\text{Pr}] = 0.01 \text{ mol/dm}^3$

Fig. 2. Variation of $\log D$ with concentration of TOPO in the presence of EHPNA in kerosene for the extraction of Pr(III). pH = 2.0, $[\text{Pr}] = 0.01 \text{ mol/dm}^3$

Fig. 3. Variation of $\log D$ with concentration of TBP in the presence of EHPNA in kerosene for the extraction of Nd(III). pH = 2.0, $[\text{Nd}] = 0.01 \text{ mol/dm}^3$

Fig. 4. Variation of $\log D$ with concentration of TOPO in the presence of EHPNA in kerosene for the extraction of Nd(III). pH = 2.0, $[\text{Nd}] = 0.01 \text{ mol/dm}^3$

organophosphorus extractants TBP and TOPO upon the extractive power of EHPNA in kerosene for the extraction of Pr(III) are shown. Similarly **Fig. 3** and **4** show the effects on the extraction of Nd(III). These results indicate antagonistic effects. As is evident from Figs. 1–4, TBP is a more effective antisynnergist than TOPO.

These distribution data (Figs. 1–4) were analysed using Eq. (8) and the best fit between the experimental and calculated distribution coefficients was obtained when the formation of the species $\text{Ln}(\text{HX}_2)_3$ and $(\text{HX})_2 \cdot \text{R}$ was assumed. The extraction constants for the above data were determined by the procedure mentioned in the previous section and are shown in **Table 1**.

The plots (**Figs. 5** and **6**) of $\log (D_{\text{expt}}[\text{H}^+]^3 \{1 + \beta_1[\text{Cl}^-]\})$ vs. $\log[(\text{HX})_2\text{R}]/[\text{R}]$ have slopes of 3, further confirming the validity of the assumed reaction mechanisms, i. e., Eqs. (4) and (5). It is quite

Table 1. Equilibrium constants for the extraction of Pr(III) and Nd(III) with mixtures of EHPNA + TBP and EHPNA + TOPO

Element	System	K_1 [—]	K_2 [dm^3/mol]
Pr	EHPNA + TBP	0.0042	0.96
	EHPNA + TOPO	0.0047	4.14
Nd	EHPNA + TBP	0.0038	1.2
	EHPNA + TOPO	0.0048	6.9

reasonable to assume that complexes of the type $\text{EHPNA} \cdot \text{TBP}$ and $\text{EHPNA} \cdot \text{TOPO}$ are formed at higher concentrations of the synergists, which lowers the concentration of the free EHPNA and gives rise to the observed antagonistic effects. Such effects in these systems could also be explained by the structure of the Ln-HX complex formed as discussed by Kandil and Farah⁴⁾ for the extraction of europium and

Fig. 5. Log-Log plots for the extraction of Pr(III) and Nd(III) with mixtures of EHPNA + TBP in kerosene. pH = 2.0, [Pr] = [Nd] = 0.01 mol/dm³

Fig. 6. Log-Log plots for the extraction of Pr(III) and Nd(III) with mixtures of EHPNA + TOPO in kerosene. pH = 2.0, [Pr] = [Nd] = 0.01 mol/dm³

terbium with mixtures of D2EHPA and TBP.

Nomenclature

C_w	= molar concentration of pure water	[mol/dm ³]
D	= distribution coefficient	[—]
I	= ionic strength in aqueous phase	[mol/dm ³]
K_1	= extraction constant of the complex defined by Eq. (6)	[—]
K_2	= extraction constant of the complex defined by Eq. (7)	[dm ³ /mol]
γ	= root mean square fractional error defined by Eq. (9)	[—]
Z	= atomic number	[—]
Z_x	= ionic charge number of ion species x	[—]
β_1	= first stability constant of lanthanoid chlorocomplex	[dm ³ /mol]
β_1°	= dimensionless thermodynamic equilibrium constant	[—]
γ_x	= activity coefficient of species x	[—]

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