Extraction of Lanthanoids from Hydrochloric and Nitric Acid Solutions by Di(2-ethylhexyl)phosphoric Acid[†]

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Di(2-ethylhexyl)phosphoric acid[†] (D2EHPA or HX) extracts lanthanoids (Ln) from a moderately acidic solution by cation exchange reaction: $Ln^{3+}+m(HX)_n \rightleftarrows LnX_3\cdot 3HX+3H^+$. From the mode of extraction *m* is estimated to be 3 in benzene diluent, and smaller than 3 in heptane diluent. The change of the relative extractability with the atomic number of lanthanoids is in line with what is expected from the concept of the tetrad effect proposed by Peppard *et al.* When the hydrogen ion concentration is very high, the main reaction is solvation: $Ln^{3+}+3A^-+q(HX)_n \rightleftarrows LnA_3\cdot 4HX$. In benzene diluent *q* is 2 and *n* is 2, while *q* is 1.6—1.7 in heptane diluent. It can be attributed to the difference in the association degree of D2EHPA that *m* or *q* is smaller in heptane than in benzene.

Di(2-ethylhexyl)phosphoric acid[†] (D2EHPA or HX) extracts a lanthanoid by a cation exchange reaction expressed by

$$Ln^{3+}{}_{(aq)} + 3(HX)_{2(org)} \rightleftarrows LnX_3\cdot 3HX_{(org)} + 3H^+{}_{(aq)}, \qquad (1)$$

where the subscripts (aq) and (org) represent the aqueous and organic phase, respectively.[1,2] In a saturated aliphatic hydrocarbon, however, the extraction behavior of the lanthanoids differs slightly from what is expected from Eq. 1.[3,4] The association degree of D2EHPA is higher than 2 in such a solvent.[5] Sato and Ueda assumed that the extracted species is different from that described in Eq. 1.[4] Assuming that a lanthanoid is extracted only by a cation exchange reaction, the distribution ratio of the lanthanoid is expected to decrease with the increase in acid concentration in aqueous phase. However, in the extraction of metals by a dialkyl phosphoric acid the distribution ratio increases with the acid concentration in the region in which acid concentration is very high.[6-8] This suggests that some other reactions occur. We have studied the distribution equilibria of some lanthanoids with D2EHPA.

Experimental

Materials. D2EHPA (Union Carbide Corporation) was purified[9] and then diluted with heptane or benzene to the desired concentration. The lanthanoid salt solutions were prepared as described for chloride solutions.[3]

Procedure. Equal volumes of organic D2EHPA solution and the aqueous lanthanoid solution were placed in an Erlenmeyer flask with a glass stopper. The flask was shaken vigorously for 15 min, allowed to stand for 30 min, and again shaken for 10 min. After the flask had been allowed to stand for 30 min or longer, the glass stopper was replaced by the glass stopcock used for separation of the two liquids, and the two phases were separated. All the equilibration procedures were carried out at 20.0±0.2 °C.

Determination of Equilibrium Data. The lanthanoids and yttrium extracted into the organic phase were recovered by back-extracting four times with equal volumes of 6M hydrochloric or nitric acid solution. The concentrations of lanthanoids and yttrium were determined by EDTA titration with Xylenol Orange as an indicator. The concentration of hydrogen ion in the aqueous solution was determined by titration with a standard solution of sodium hydroxide with Bromophenol Blue as an indicator. The concentration of D2EHPA in organic solution was determined by titration with a standard sodium hydroxide solution in an ethanol–water (4: 1 volume ratio) solvent with a pH meter. The concentration of D2EHPA was determined as the monomer unit. The distribution ratio of a lanthanoid is defined to be the ratio of the concentration of the lanthanoid in the organic phase to that in the aqueous phase.

Results and Discussion

Figure 1 shows the variation of the distribution ratios of dysprosium and europium with the concentration of

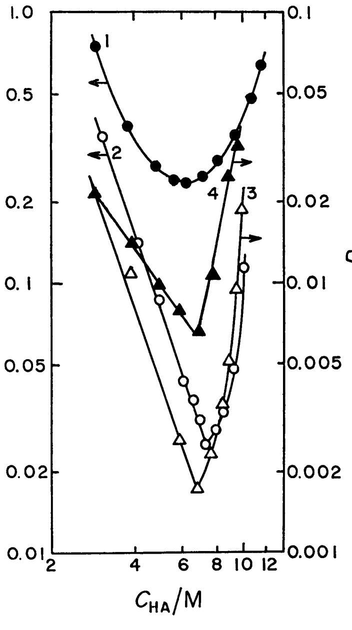

Fig. 1. Relationship between the distribution ratio, *D*, and the concn of the acid or the anion in the aq phase in the extraction of Eu or Dy by 1 M D2EHPA in heptane.
1: 0.05 M $Dy(NO_3)_3$–HNO_3 system, HA: HNO_3, 2: 0.05 M $DyCl_3$–HCl system, HA: HCl, 3: 0.05 M $EuCl_3$–HCl system, HA: HCl, 4: 0.05 M $EuCl_3$–HCl–LiCl system, C_{HCl}=2.88 M, $C_{HA}=C_{HCl}+C_{LiCl}$. 1M= 1 mol/dm^3.

[†] Bis(2-ethylhexyl) hydrogenphosphate in IUPAC notation.

hydrochloric or nitric acid in aqueous phase. With the increase in the concentration of acid the distribution ratio decreases in the lower acid concentration region and increases in the higher concentration ragion, exhibiting a minimum at acid concentration 6—8 M. Similar data were obtained in other systems. From the extraction behavior we see that D2EHPA extracts a lanthanoid mainly by a cation exchange reaction in the low acid concentration region and by some other reactions in the high acid concentration region.[6]

Low Acid Concentration Region. The cation exchange reaction for the extraction of a trivalent lanthanoid by D2EHPA can be expressed as follows, taking into account the association degree of D2EHPA, *n*.

$$\mathrm{Ln^{3+}}_{(\mathrm{aq})} + m(\mathrm{HX})_{n(\mathrm{org})} \rightleftarrows \mathrm{LnX_3}\cdot x\mathrm{HX}_{(\mathrm{org})} + 3\mathrm{H^+}_{(\mathrm{aq})}, \tag{2}$$

where the ratio of D2EHPA to the lanthanoid in the extracted species is $(3+x)$, and $m\times n$ is equal to $(3+x)$. Three hydrogen ions are transferred into the aqueous phase per each lanthanoid extracted.[3]

It was confirmed that Eq. 1 is valid in benzene diluent. The association degree of D2EHPA was found cryoscopically to be nearly equal to 2. The plot of log *D vs.* log C_{HX} shows that the distribution ratio of the lanthanoid is of third power with respect to D2EHPA concentration.

Table 1. Extractant dependency of the extraction of Eu by D2EHPA in heptane

Series	$C_{\mathrm{HA,i}}$ a) / M f)	$C_{\mathrm{Eu,i}}$ b) / M f)	Extractant dependency c) estimated for $x=3$	$x=2$
1 d)	0.50	0.05	2.16	2.17
2 d)	0.40	0.05	2.12	2.20
3 d)	0.40	0.14	2.25	2.25
4 d)	0.076	0.208	2.28	2.73
5 e)	0.194	0.05	2.23	2.38

a) The initial concentration of hydrochloric or nitric acid in aq phase. b) The initial concentration of Eu in aq phase. c) Estimated from the slope of the plot of lg D_{Eu} *vs.* lg C_{HX} (C_{HX}: 0.1—1.0 M). d) $\mathrm{EuCl_3}$–HCl system. e) $\mathrm{Eu(NO_3)_3}$–$\mathrm{HNO_3}$ system. f) 1 M=1 mol/dm^3.

The extractant dependency estimated for the extraction of europium with D2EHPA in heptane is given in Table 1. The equilibrium concentration, C_{HX}, was estimated by the equation $C_{\mathrm{HX}}=C_{\mathrm{HX,i}}-(3+x)C_{\mathrm{Eu(org)}}$, derived from Eq. 2, where $C_{\mathrm{HX,i}}$ and $C_{\mathrm{Eu(org)}}$ are the initial concentration of D2EHPA and the equilibrium concentration of europium in the organic phase, respectively. In the estimation the cases $x=3$ and $x=2$ were assumed.[3,10] Mason *et al.* proposed an equation in which *x* is 2 and *m* is 2.5 regarding D2EHPA as dimeric in heptane. When *x* is 3, the estimated dependency is nearly equal for all the series. On the other hand, when *x* is 2 the dependency differs a great deal for series 4 from those for the others. Thus it is reasonable to assume *x* to be 3 rather than 2. Eq. 2 can be rewritten as

$$\mathrm{Ln^{3+}}_{(\mathrm{aq})} + m(\mathrm{HX})_{n(\mathrm{org})} \rightleftarrows \mathrm{LnX_3}\cdot 3\mathrm{HX}_{(\mathrm{org})} + 3\mathrm{H^+}_{(\mathrm{aq})}. \tag{3}$$

The extractant dependency for the nitrate system (series 5) is nearly equal to that for chloride systems (Table 1) suggesting that there is no serious difference in the extraction reaction between the two systems. The values of the extractant dependency are considerably smaller than 3, the value obtained for the benzene system. The difference in value of the two systems may be explained in terms of the difference of the association degree of D2EHPA, since the ratio of D2EHPA to a lanthanoid in the extracted species is 6 in both systems, though the effect of the activity coefficient should be taken into account for discussion. The extractant dependency for several lanthanoids and yttrium is given in Table 2.

Table 2. Extractant dependency of the extraction of lanthanoids (Ln) and yttrium

	Extractant dependency
La	2.40
Pr	2.26
Nd	2.22
Sm	2.15
Eu	2.16
Gd	2.18
Tb	2.12
Dy	2.06
Er	2.05
Yb	2.11
Y	2.11

Extraction conditions: C_{HX}=0.1—1.0 M, $C_{\mathrm{Ln,i}}$=0.02—0.05 M, C_{HCl}=0.15—2 M. 1 M=1 mol/dm^3.

Figure 2 shows the relative extractability of several lanthanoids and yttrium. The relative extractability was estimated from the difference of the distribution ratios normalized to an identical condition. The average separation factor for the adjacent lanthanoids is evaluated to be 2.28, which is in rough accord with that reported by Pierce *et al.*[11] The relative extractability is not a smooth function of the atomic number, *Z*, of the lanthanoid. The shape of the curve is in fair agreement with that expected from the concept of the tetrad effect proposed by Peppard *et al.*[12] A tendency similar to the concept was also reported by Siekierski.[13] The relative extractability of yttrium seems to be between holmium and erbium; that of holmium was not determined in this study.

In order to check the validity of the relations stated above with regard to the distribution equilibrium, the equilibrium values calculated by the use of the following equations were compared with the actual extraction isotherms.[3]

$$D = K' \times \frac{C^{a}_{\mathrm{HX}}}{C^{3}_{\mathrm{H^+}}},\quad C_{\mathrm{HX}} = C_{\mathrm{HX,i}} - 6C_{\mathrm{Ln(org)}},\ \text{and}$$

$$C_{\mathrm{H^+}} = C_{\mathrm{H^+,i}} + 3C_{\mathrm{Ln(org)}}$$

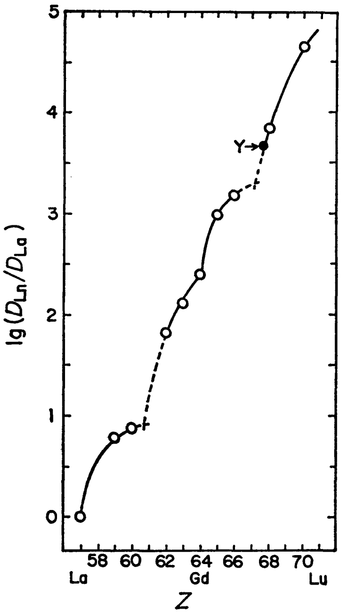

Fig. 2. Variation of the distribution ratio, *D*, with the atomic number, *Z*, of lanthanoids in the extraction from the chloride solutions by 1M D2EHPA in heptane. $C_{LnCl_3,i}$=0.02—0.05M, C_{HCl}=1M, C_{HX}=0.5 M. 1M=1 mol/dm³.

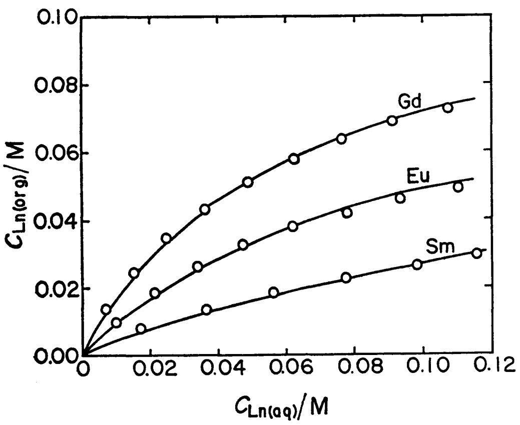

Fig. 3. Distribution equilibria for $SmCl_3$-HCl-, $EuCl_3$-HCl-, and $GdCl_3$-HCl-1M D2EHPA in heptane systems.
[H⁺]=1M. The solid curves represent the calculated values. 1M=1 mol/dm³.

In the calculation the constant *K′* was evaluated from the equilibrium data observed for the system where $C_{Ln,i}$=0.1 M†† and C_{H^+}=1 M.†† $C_{H^+,i}$ represents the initial concentration of hydrogen ion. For the value of *a*, the extractant dependency given in Table 2 was used. Figure 3 shows the extraction isotherms for the $SmCl_3$-HCl-, $EuCl_3$-HCl-, and $GdCl_3$-HCl-D2EHPA in heptane systems. The calculated values are denoted by three curves and the experimental values by open circles. The validity of the relations is demonstrated by the agreement between the calculated and observed values.

High Acid Concentration Region. Solvation is a predominant reaction at high acidity, which is expressed by

$$Ln^{3+} + 3A^- + q(HX)_n \rightleftharpoons LnA_3 \cdot qnHX, \qquad (4)$$

where A^- represents an anion.[4,7] This indicates that the effect of the concentration of a mineral acid on the extraction by solvation is essentially attributed to the corresponding anion. It is demonstrated by the similarity in shape of curves 3 and 4 (Fig. 1), though a little difference can be attributed to the difference in HCl concentration. The shapes of the curves can be explained as follows. (i) Increase in HCl concentration causes decrease in the amount of the extraction of europium by the cation exchange reaction, since the extraction reaction is of inverse third power dependence on the hydrogen ion concentration. (ii) Increase in chloride concentration depresses the extraction of a lanthanoid by the cation exchange reaction, since the concentration of the trivalent lanthanoid ion, one reactant in Eq. 2, decreases by complexing between the lanthanoid and chloride. (iii) Increase in chloride concentration increases the amount of the extraction of the lanthanoid by the solvation expressed by Eq. 4. The extractant dependency of the extraction of lanthanoids from highly acidic solutions where the lanthanoids are extracted almost only by solvation is given in Table 3. The extractant dependency is about 2.0 both for the nitrate and the chloride systems when benzene is a diluent, and Eq. 4 can be rewritten for such systems as follows since D2EHPA is practically dimeric in benzene.

Table 3. Extractant dependency of the extraction of lanthanoids

Ln	HA	$C_{HA,i}$[a)] / M[b)]	Diluent	Extractant dependency[c)]
Er	HNO_3	12.0	Benzene	2.15
Er	HCl	10.5	Benzene	2.10
Eu	HCl	10.0	Benzene	2.08
Er	HNO_3	12.0	Heptane	1.60
Er	HCl	10.5	Heptane	1.68
Dy	HNO_3	12.0	Heptane	1.63
Dy	HCl	10.5	Heptane	1.73
Eu	HCl	10.0	Heptane	1.70

a) The initial concentration of the acid in aq phase. b) 1 M=1 mol/dm³. c) Estimated from the slope of the plot of lg D_{Ln} *vs.* lg C_{HX} ($C_{Ln,i}$=0.05 M, C_{HX}=0.1—1.0 M).

$$LnA_3 + 2(HX)_2 \rightleftharpoons LnA_3 \cdot 4HX \qquad (5)$$

On the other hand the dependency is smaller in heptane diluent as in the case of the cation exchange reaction.

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†† Throughout this paper, 1M=1 mol/dm³.

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