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EXTRACTION EQUILIBRIUM OF Ce(III), Pr(III) AND Nd(III) WITH ACIDIC ORGANOPHOSPHORUS EXTRACTANTS

YASUSHIGE MORI, HITOSHI OHYA, HARUHIKO ONO
AND WATARU EGUCHI

Department of Chemical Engineering, Kyoto University, Kyoto 606

Solvent extraction has recently attracted major interest for industrial-scale separation of lanthanoids, alike ion exchange. It is well known that di(2-ethylhexyl)phosphoric acid (henceforth D2EHPA) is an effective extractant for the mutual separation of lanthanoids, because of its high separation factor. 2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (henceforth EHPNA), which is similar in its chemical structure as D2EHPA, has a higher ability of back extraction at low acid concentration than D2EHPA.

In this paper, the extraction equilibrium of cerium, praseodymium and neodymium by EHPNA was investigated and was compared with that by D2EHPA.

It was found that the existence of two kinds of complexes should be considered in the region of high concentration of EHPNA, unlike the case of D2EHPA. The extraction of metals from the solution of mixed lanthanoids can be explained based on the extraction mechanism of individual elements.

Introduction

As lanthanoids have superior characteristics such as in their fluorescent, magnetic, optical and catalytic properties, demand for them is increasing. But the mutual separation and purification of lanthanoid elements is difficult because of the similarity in their chemical nature. Solvent extraction has recently attracted major interest for industrial-scale separation of lanthanoids, alike ion exchange.

It is well known that di(2-ethylhexyl)phosphoric acid (henceforth D2EHPA) is an effective extractant for the mutual separation of lanthanoids, because of its high separation factor. But D2EHPA has the disadvantage of difficulty in back extraction. 2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (henceforth EHPNA) has a higher ability of back extraction at low acid concentration than D2EHPA.

In this study, the extraction equilibrium of cerium, praseodymium and neodymium by EHPNA was investigated and was compared with that by D2EHPA.

1. Experimental

1.1 Reagents

EHPNA and D2EHPA were purified by washing the commercial extractants PC88A and DP8R kindly supplied by Daihachi Chemical Industry Co., Ltd., Japan, with 6 kmol/m³ hydrochloric acid solution, and then with deionized water several times. Toluene of guaranteed grade was used as the diluent without further purification. The organic solutions were prepared by diluting a desired amount of extractant with toluene.

The aqueous solution was prepared by dissolving the desired amount of lanthanoid chloride into deionized water. Ionic strength and pH of the aqueous solution were adjusted to $0.2\,kmol/m^3$ and at the desired level, respectively, by using lithium chloride and hydrochloric acid. The loading ratio, defined as the ratio of the total metal concentration in the organic phase to the supplied dimer extractant concentration, ranged from 0.07 to 22%.

1.2 Experimental procedure

Aqueous and organic solutions of known concentration were shaken vigorously in a stoppered glass flask for several minutes, then allowed to settle in a thermostat bath of 298 K for at least 24 h. The two solutions were then separated and analyzed.

1.3 Analysis

The concentration of extractant in the organic solution was determined by titration with a standard solution of sodium hydroxide in a mixture solution of ethyl alcohol and deionized water (volume ratios were 9 : 1) by using a pH meter.

The lanthanoid concentration in the aqueous solution was determined by EDTA titration with Arsenazo-I (Neo-Thorin) as an indicator. The concentration of cerium was also measured by a fluorophotometer. In the case of mixed lanthanoid solution, the absorptiometric method for praseodymium and neodymium and the fluorophotometric method for cerium were used. The concentration of lithium in the aqueous solution was measured by atomic absorptiometry.

The concentration of lanthanoid in the organic solution were determined by the same analytical methods as that in the aqueous solution, after back extraction with $6\,kmol/m^3$ hydrochloric acid solution.

2. Results and Discussion

2.1 Activity of hydrogen ion

The activity coefficient of hydrogen ion in the condition of the present work was calculated from the values measured by a pH meter and by titration. The results are shown in **Table 1**. From these results, the activity coefficient of hydrogen ion at $0.2\,kmol/m^3$ in ionic strength was taken to be 0.87 as mean value.

2.2 Stability constants of the lanthanoid chloro-complexes

The lanthanoid in the aqueous phase takes a variety of complex forms in the presence of chloride ions, but under the conditions of the present work it is sufficient to consider only the first stability constant defined by Eq. (1).[2]

$$\beta_1 = \frac{[LnCl^{2+}]}{[Ln^{3+}][Cl^-]} \qquad (1)$$

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

Table 1. Activity coefficient of hydrogen ion

$[H^+]$ by titration	a_H by pH meter	$a_H/[H^+]$
0.161	0.1288	0.800
0.101	0.08128	0.805
0.0797	0.09761	0.848
0.0404	0.03631	0.899
0.0202	0.01862	0.918
0.0101	0.00912	0.903
0.00202	0.001862	0.918
	av.	0.870

Note: Ionic strength is approximately $0.2\,kmol/m^3$ in all experiments.

Table 2. First stability constants of lanthanoid chloro complexes[2,5]

		Ce	Pr	Nd
β_1	$I = 0.6\,kmol/m^3$	1.25	—	—
	1.0	1.73	1.58	1.62
β_1°/c_w		12.9	13.0	13.4

temperature only as

$$\beta_1 = \frac{\beta_1^\circ}{c_w} \cdot \frac{\gamma_{Ln}\gamma_{Cl}}{\gamma_{LnCl}} \qquad (2)$$

where γ_X refers to the activity coefficient of ionic species X, which can be calculated by[1]

$$-\log\gamma_X = 0.509z_X^2[I^{0.5}/(1+I^{0.5})-0.2I] \qquad (3)$$

where z_X stands for ionic charge of X. Moreover, c_w is the molar concentration of pure water, which was used to adjust the unit.

The value of β_1°/c_w of the lanthanoid were calculated from β_1 values reported by Goto et al.[2] and by Robert et al.[5] at two ionic strengths. **Table 2** shows their values of β_1 and the calculated β_1°/c_w. The values of β_1 under the experimental conditions were calculated from Eqs. (2) and (3) together with β_1°/c_w shown in Table 2.

2.3 Extraction equilibrium of lanthanoid

The extraction mechanism of lanthanoid by D2EHPA in aromatic diluents has been reported as follows:[4]

$$Ln^{3+} + 3\overline{(HR)_2} \rightleftharpoons \overline{LnR_3(HR)_3} + 3H^+ \qquad (4)$$
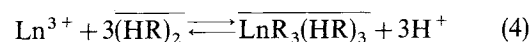
where Ln stands for lanthanoid element and $\overline{(HR)_2}$ refers to the dimer of the extractant in the organic phase. The extraction constant can be written as

$$K_{ex} = \frac{[\overline{LnR_3(HR)_3}][H^+]^3}{[Ln^{3+}][\overline{(HR)_2}]^3} \qquad (5)$$

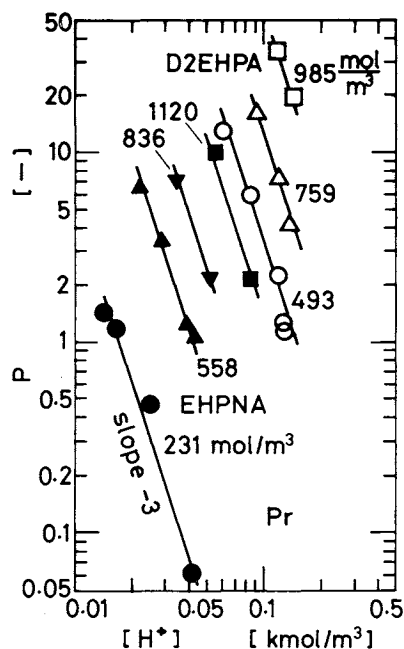The partition equilibrium ratio is derived from Eqs. (1) and (5) as

Fig. 1. Distribution ratio against hydrogen ion concentration in the range of low praseodymium loading. Solid lines are straight lines with a slope of -3

$$P = \frac{\overline{[LnR_3(HR)_3]}}{[Ln^{3+}] + [LnCl^{2+}]}$$

$$= \frac{K_{ex}\overline{[(HR)_2]}^3}{(1 + \beta_1[Cl^-])[H^+]^3} \tag{6}$$

It is satisfactory to consider that the extraction of lanthanoid by EHPNA follows the same mechanism as D2EHPA, because the two extractants are similar in their chemical structures. **Figure 1** shows the relationship between the partition equilibrium ratio of praseodymium and the concentration of hydrogen ion, changing the extractant concentrations as a parameter, under the conditions of nearly constant chloride ion concentration and of much higher concentration of the extractants than the initial praseodymium concentration in the aqueous phase. The partition equilibrium ratio is inversely proportional to the third power of the hydrogen ion concentration for both extractants.

Figures 2–7 show the effect of extractant concentration on the partition equilibrium ratio. The abscissa in these figures is the calculated concentration of free dimer extractant at equilibrium. In the case of D2EHPA (Figs. 2, 3 and 4), the partition equilibrium ratio is proportional to the third power of the free dimer extractant concentration over the whole range, as is expected from Eq. (6). In the case of EHPNA (Figs. 5, 6 and 7), however, the partition equilibrium ratio is proportional to the third power of the free dimer extractant concentration in the lower extractant concentration range, but deviates in the higher range of the free dimer extractant.
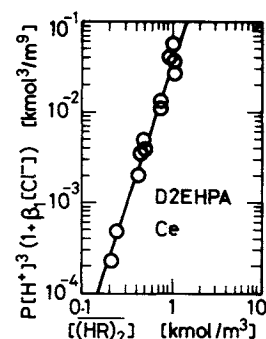

Fig. 2. Effect of concentration of D2EHPA on partition equilibrium ratio of cerium. The solid line is a straight line with a slope of 3. The broken line, which cannot be distinguished from the solid line, is the calculated line when $j = 1$
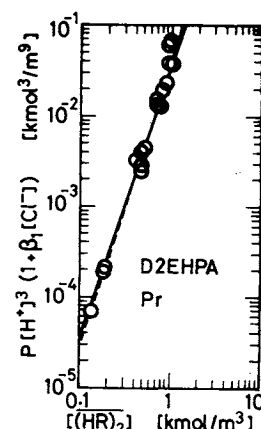

Fig. 3. Effect of concentration of D2EHPA on partition equilibrium ratio of praseodymium. The solid line is a straight line with a slope of 3. The broken line is the calculated line when $j = 1$
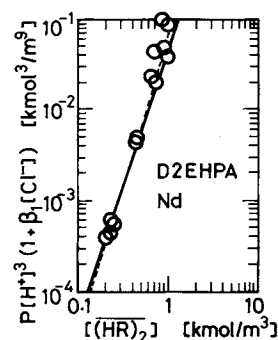

Fig. 4. Effect of concentration of D2EHPA on partition equilibrium ratio of neodymium. The solid line is the straight line with slope 3. The broken line is the calculated line when $j = 1$

For the values shown in these figures, the activity coefficients of chemical species in the organic phase were assumed to be unity, because of the lack of an estimation method for the activity in the organic phase. However, it is difficult to think that the deviation from the relation of Eq. (6) in the case of EHPNA is due to the change of activity in the organic
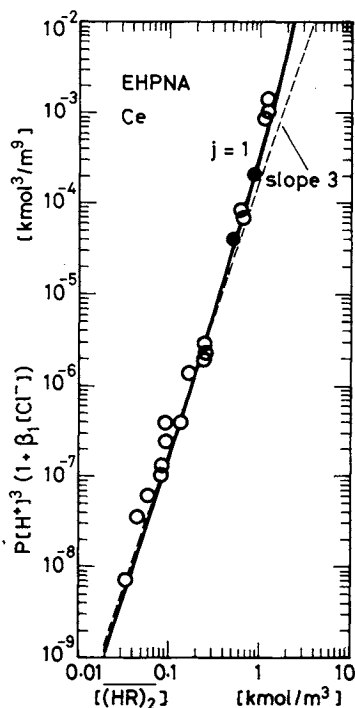
Fig. 5. Effect of concentration of EHPNA on partition equilibrium ratio of cerium. The broken line is a straight line with a slope of 3. The solid line is the calculated line when $j = 1$
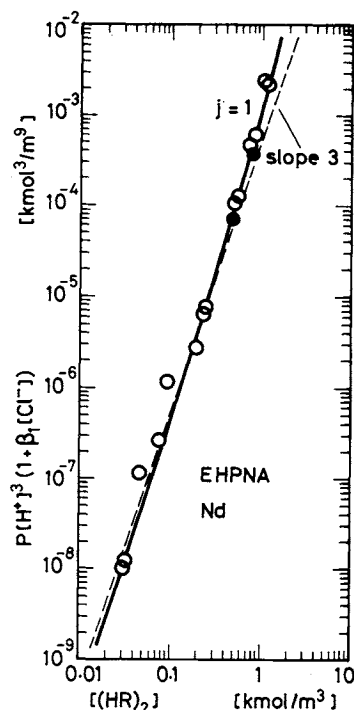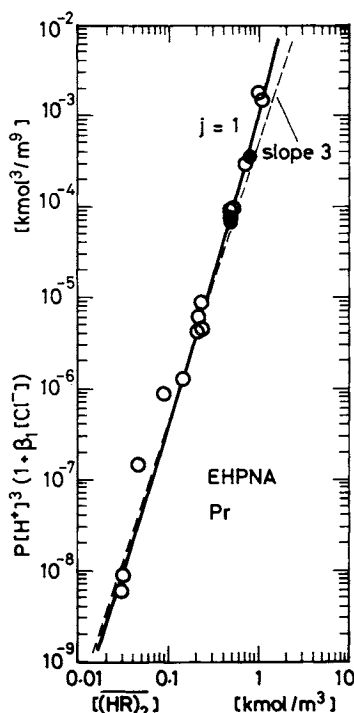

Fig. 6. Effect of concentration of EHPNA on partition equilibrium ratio of praseodymium. The broken line is a straight line with a slope of 3. The solid line is the calculated line when $j = 1$

phase, because the activity of EHPNA should be almost the same as that of D2EHPA due to the similarity in their chemical structures.

Fig. 7. Effect of concentration of EHPNA on partition equilibrium ratio neodymium. The broken line is a straight line with a slope of 3. The solid line is the calculated line when $j = 1$

To consider the reason for the deviation mentioned above, let us assume the presence of a single additional complex expressed by

$$\overline{LnR_3(HR)_3} + j\overline{(HR)_2} \rightleftharpoons \overline{LnR_3(HR)_{2j+3}} \qquad (7)$$
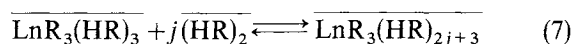
$$K_c = \frac{[\overline{LnR_3(HR)_{2j+3}}]}{[\overline{LnR_3(HR)_3}][\overline{(HR)_2}]^j} \qquad (8)$$

The partition equilibrium ratio is expressed as follows, rather than by Eq. (6):

$$P = \frac{[\overline{LnR_3(HR)_3}] + [\overline{LnR_3(HR)_{2j+3}}]}{[Ln^{3+}] + [LnCl^{2+}]}$$

$$= \frac{K_{ex}[\overline{(HR)_2}]^3}{[H^+]^3} \cdot \frac{(1 + K_c[\overline{(HR)_2}]^j)}{(1 + \beta_1 [Cl^-])} \qquad (9)$$

It can safely be assumed that hydrochloric acid and lithium chloride dissociate completely under the present experimental conditions. Thus the following mass balance equations are effected.
For lanthanoid,

$$[LnCl_3]_s = [Ln^{3+}] + [LnCl^{2+}]$$

$$+ V_r([\overline{LnR_3(HR)_3}] + [\overline{LnR_3(HR)_{2j+3}}]) \qquad (10)$$

For chloride,

$$3[LnCl_3]_s + [HCl]_s + [LiCl]_s = [LnCl^{2+}] + [Cl^-] \qquad (11)$$

Table 3. Estimated K_{ex}, K_c, and Err

Metal	j	D2EHPA			EHPNA		
		K_{ex} [—]	K_c [(m³/mol)^j]	Err	K_{ex} [—]	K_c [(m³/mol)^j]	Err
Ce	0	2.85×10^{-2}	—	0.0611	1.71×10^{-4}	—	0.224
	1	2.78	4.24×10^{-5}	0.0610	1.26	2.24×10^{-3}	0.157
	2	2.84	9.16×10^{-9}	0.0611	1.48	2.63×10^{-6}	0.129
Pr	0	3.11×10^{-2}	—	0.0961	3.81×10^{-4}	—	0.282
	1	2.12	1.04×10^{-3}	0.0764	2.80	2.13×10^{-3}	0.167
	2	2.47	1.03×10^{-6}	0.0765	3.14	2.42×10^{-6}	0.189
Nd	0	4.39×10^{-2}	—	0.136	4.44×10^{-4}	—	0.259
	1	3.12	1.06×10^{-3}	0.118	3.14	2.96×10^{-3}	0.124
	2	3.79	7.83×10^{-7}	0.127	3.73	3.33×10^{-6}	0.126

For lithium,

$$[LiCl]_s = [Li^+] \tag{12}$$

And for extractant,

$$\overline{[(HR)_2]_s} = \overline{[(HR)_2]} + 3\overline{[LnR_3(HR)_3]}$$
$$+ (j+3)\overline{[LnR_3(HR)_{2j+3}]} \tag{13}$$

where subscript s means the intial value in the feed solutions. We also consider the dissociation of water and the electric charge balance in the qsueous phase.

$$K_w = [H^+][OH^-] \tag{14}$$

$$3[Ln^{3+}] + 2[LnCl^{2+}] + [H^+] + [Li^+]$$
$$= [Cl^-] + [OH^-] \tag{15}$$

If values of K_{ex} and K_c are assumed for each value of j, the concentrations of all species in this system can be obtained by using Eqs. (1) to (3), (5), (8), and (10) through (15), and P_{calc} can be calculated from Eq. (9). The evaluation function is defined as follows:

$$Err = (1/N)\sum_{}^{N} \{(P_{obs} - P_{calc})/P_{obs}\}^2 \tag{16}$$

where N denotes the number of experimental data and P_{obs} is the value defined as the ratio of lanthanoid concentrations observed in both organic and aqueous phases. The most suitable combinations of the values of K_c and K_{ex} are obtained when Err is minimum at each value of j. Table 3 shows these values.

The value of Err was small and also hardly dependent on the value of j, in the case of D2EHPA. The broken lines in Figs. 2, 3 and 4 is the calculated lines for $j=1$, and are nearly same as the solid straight line with a slope of 3. The broken line is especially consistent with the solid line in the case of cerium in Fig. 2. However, in the case of EHPNA, the value of Err was dependent on j and was smaller when $j=1$ than when the additional complex was neglected, that is, when $j=0$. The solid lines for $j=1$ agree with the experimental data better than the broken lines for

$j=0$, as can be seen in Figs. 5, 6 and 7. Kazuoka et al.[3] reported that the coordination number for a lanthanoid element was eight rather than six when it was extracted by a weakly acidic extractant such as Versatic Acid 911. We concluded that the additional complex should be considered for EHPNA, but can be neglected for D2EHPA, because EHPNA is a weaker acid than D2EHPA.

The solid circles in Figs. 5, 6 and 7 show the experimental results of extraction from a solution of mixed lanthanoids, i.e. the mixture of cerium, praseodymium and neodymium. The extraction of mixed lanthanoids can be explained satisfactorily, considering change of the free extractant and the hydrogen ion concentration, by the extraction equilibrium of the three metal ions.

Conclusion

The extraction equilibrium of cerium, praseodymium and neodymium with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) and di(2-ethylhexyl)phosphoric acid (D2EHPA) dissolved in toluene from hydrochloric acid solution was examined at 298 K.

The following results were obtained:

1) In the case of EHPNA, the existence of two kinds of complexes should be considered. One is the usual complex having six as the coordination number. The other is the complex still added by one molecule of free dimer extractant, which is considered to have eight as the coordination number.

2) In the case of D2EHPA, the additional complex need not be considered, as reported earlier.

3) The extraction from a solution of mixed lanthanoids can be explained based on the extraction mechanism of the individual elements.

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Nomenclature

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REMOVAL OF H₂S, CH₃SH AND (CH₃)₃N FROM AIR BY USE OF CHEMICALLY TREATED ACTIVATED CARBON

HIROSHI IKEDA, HIDEKI ASABA AND YASUSHI TAKEUCHI

Department of Industrial Chemistry, Meiji University, Kawasaki 214

Removal of H₂S, CH₃SH and (CH₃)₃N, mixed with air in a concentration range from 10 to 800 ppm at 303 K, by use of activated carbon impregnated with NaOH or Na₂CO₃ (IAC) or sulfonated activated carbon (SAC) was studied to obtain the basic data useful for design of a deodorization process.

For the system of IAC–H₂S or CH₃SH, the adsorption equilibrium was of rectangular type and adsorption capacity could be increased as much as about 40 to 60 times of that of original carbon. For the system of SAC–(CH₃)₃N, the adsorption equilibrium obeyed the Freundlich equation and the effect of sulfonation was much larger when the concentration of (CH₃)₃N was lower in comparison with the original carbon.

Intraparticle effective diffusivity, D_{ic} or D_{iq}, was determined by curve-fitting of calculated breakthrough curves with experimental ones. The value of D_{ic} or D_{iq} decreased with the increase of the amount impregnated or the amount of acidic functional groups (–SO₃H and –COOH) introduced by sulfonation.

Introduction

It is said that there are about three hundred kinds of ill-smelling compounds, whose molecular weights are mostly less than two hundred, in our environment. Their sources are various plants, such as excrements works, sewage treatment works, petrochemical plants, pharmaceuticals plants, food-processing plants, semiconductor plants, paint plants and so on.

Accordingly, effluent gases from such plants have been treated by washing followed by neutralizing with chemicals, adsorption onto activated carbon and the like, condensation, masking, direct or catalytic combustion and so on. Among these treatment methods, the washing method and/or the adsorption method have been used most frequently, and many kinds of impregnated . activated carbon and sulfonated acti-