ACIDIC PHOSPHINATES WITH DIFFERENT ALKYL GROUPS AS EXTRACTANTS FOR RARE EARTHS

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Introduction

Solvent extraction has been a very useful and widely-used technique in hydrometallurgy. Production of rare earths has been, in the majority of cases, carried out using dialkylphosphonates such as EHPNA (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester), especially in chloride and nitrate media. The main advantage of EHPNA is that stripping is possible using mineral acids of lower concentration than for dialkylphosphates such as bis(2-ethylhexyl)phosphoric acid. However, 3 mol/l HCl or above is still needed to strip heavier rare earths in industrial production, and a large quantity of alkali is needed to precipitate rare earth oxalates from the stripping solution. A new series of phosphinic type extractants have been sought after which may have higher pH functionality as well as more favorable selectivity. At present, only bis(2,4,4-trimethylpentyl)phosphinic acid is commercially available with the trademark of "Cyanex 272" (Ritcey and Ashbrook, 1984).

The steric effect of the alkyl side chains in the extractant is reported to play an important role in the selectivity of solvent extraction, especially for the separation of rare earths with slightly different atomic radius (Yuan *et al.*, 1982). The alkyl side chain in the vicinity of the P(O)OH group is reported to increase the separation factor in rare earth extraction in the case of acidic phosphates (Takahashi *et al.*, 1995). Acidic phosphinates having steric alkyl side chains in the vicinity of the P(O)OH group are, therefore, expected to have better separation factors for the rare earths. The extraction constants of the rare earths of

various acidic organophosphorus compounds are governed chiefly by the charge of hydroxyl oxygen atom in grouping P(O)OH, owing to the direct influence of the charge density value on the pK_a of ligands (Yuan *et al.*, 1983). Dialkylphosphinic acids have the higher pK_a values than corresponding phosphates and phosphonates, and therefore, they may have better characteristics since the pH functionality of the phosphonates is higher than those of the other two extractants.

1. Experimental

1.1 Synthesis of acidic phosphinates

Figure 1 shows the structure of dialkylphosphinic acids, R₂P(O)OH, synthesized and used in this study. These phosphinates, PIA-226 (bis(2-ethylhexyl)phosphinic acid) for example, were synthesized as follows. 2-Ethylhexyl alcohol and phosphorus trichloride were mixed at 60–70°C for 8 h. 2-Ethylhexylchloride was isolated from bis(2-ethylhexyl)phosphite by vacuum distillation at 50°C (1.33 kPa) in 90% yield and 98% purity, which were determined by gas chromatography (GC).

Butyl alcohol (R'OH) and phosphorus oxychloride were mixed at 0°C for 8 h. The temperature was then slowly raised to 90°C to obtain monobutylphosphorusdichloride in good yield and 98% purity.

The reaction of 2-ethylhexylchloride with metallic magnesium suspended in diethylether was carried out

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Fig. 1 Structures, yield and purity of dialkylphosphinic acids, $\text{R}_2\text{P(O)OH}$

to give ether-soluble 2-ethylhexylmagnesiumchloride.

2-Ethylhexylmagnesiumchloride was mixed with monobutylphosphorusdichloride at 5°C, and the compound obtained was distilled under pressure (133 Pa) at 150°C to obtain bis(2-ethylhexyl)monobutylphosphinate in 85% yield and 96% purity by GC.

Monobutylphosphinate was hydrolyzed to give bis(2-ethylhexyl)phosphinate in 96% purity by GC.

All of the synthesized acidic phosphinates in this study have purity of about 95 wt%, as determined by potentiometric titration method.

1.2 Extraction of rare earths by acidic phosphinates

Aqueous chloride solutions of the rare earths were prepared by dissolving their oxides in heated hydrochloric acid. Practical aqueous solutions containing 0.01 mol/l rare earth chloride and NH_4OH and HCl as a pH adjustant were employed. The ionic strength of the aqueous solutions was not adjusted to a constant value, since the main purpose of the present work is the comparison of several acidic phosphinates as suitable extractants for rare earths. Extraction

Fig. 2 Relationship between distribution ratio of rare earths and pH with 1 mol/l PIA-226 in kerosene

was carried out by the following procedure. Equal volumes of a kerosene or toluene solution containing 1 mol/l dialkylphosphinic acid and an aqueous solution containing 0.01 mol/l rare earth were mechanically shaken at 25°C (60°C when PIA-n8 was used) for 60 min in a separation funnel. Stripping was carried out by shaking equal volumes of the metal-loaded organic solution and hydrochloric acid of various concentrations. After phase separation, the concentration of the rare earth metal ion in aqueous phase was measured by ICP-AES (Inductively coupled plasma atomic emission spectroscopy, Shimadzu Model ICP-1000II). The concentration of rare earth in the organic phase was determined by mass balance.

2. Results and Discussion

Dialkylphosphinic acids were obtained in reasonable yield and purity (Fig. 1). PIA-n8 is a white solid with a melting point of 82°C, and the other compounds are colorless or light yellowish liquids. Since diarylphosphinic acids having phenyl or 2-methylphenyl groups are barely soluble into typical solvents such as kerosene and toluene at 60°C, they were not used in this study.

The values of the distribution ratio, D , were plotted against pH value for the extractant PIA-226 in Fig. 2, in which the concentration of the extractant and feed concentration of the metal were 1 mol/l and 0.01 mol/l, respectively. A straight line with slope of about 3 was obtained for all metals, as expected. The extractant concentrations were then varied in the range $[(\text{HL})_2] = 0.1 - 1$ mol/l, and the plots of the value of $D[\text{H}^+]^3$ against the extractant concentration

Table 1 Separation factor of adjacent rare earths with dialkylphosphinic acid and EHPNA

Extractant	La/Pr	Pr/Nd	Nd/Sm	Sm/Eu	Eu/Gd	Gd/Tb	Tb/Dy	Dy/Ho	Ho/Y	Y/Er	Er/Tm	Tm/Yb	Yb/Lu
PIA-n8	2.1	1.7	1.9	2.2	3.2	1.5	5.3	3.1	2.4	1.0	3.9	4.6	2.2
PIA-215	6.9	1.9	1.6	1.9	3.3	2.5	1.8	3.8	2.5	1.7	2.0	4.8	5.2
PIA-226	1.6	1.9	2.0	1.5	3.5	2.7	2.0	4.4	2.4	1.6	2.2	4.1	6.0
PIA-117	1.2	4.2	2.2	2.9	1.1	3.2	4.6	4.8	1.6	2.0	2.6	3.6	5.0
PIA-126	2.7	1.4	10.7	4.1	1.3	2.9	3.4	5.1	1.6	2.0	3.5	3.4	4.7
EHPNA	1.4	1.9	5.8	1.6	2.3	1.9	5.2	2.7	4.4	1.9	2.6	2.0	4.0

Fig. 3 Effect of concentration of PIA-226 in kerosene on extraction equilibria of rare earths

gave straight lines with slope of about 3, as shown in **Fig. 3** for the case using PIA-226. This leads to

where Ln^{3+} is a rare earth ion and HL is dialkylphosphinic acid, which is assumed to dimerize in non-polar diluents, as judged from its $\text{P}(\text{O})\text{OH}$ structure. This formulation with the present extractant is identical to those obtained for dialkylphosphonic acids and dialkylphosphoric acids, as expected (Yuan *et al.*, 1982). The extraction constant is thus expressed by the following equation.

$$K_{\text{ex}} = D[\text{H}^+]^3 / [(\overline{\text{HL}})_2]^3 \quad (7)$$

The extraction constants obtained are shown in **Fig. 4**, in which only the data obtained employing kerosene as a diluent are cited. The constants increase continuously with increasing atomic number

Fig. 4 Extraction constants of rare earths with 1mol/l acidic phosphinates and EHPNA

as seen for the dialkylphosphinates and EHPNA. With established extractants such as acidic phosphates and phosphonates, extraction constants are known to consist of four curved lines when the constants are plotted against the elements from La to Lu (Inoue *et al.*, 1995; Sato, 1989). This is called a tetrad effect. With the present extractants, however, the tetrad effect is only slightly visible, especially for α position-substituted phosphinates by methyl or ethyl group (PIA-117 and PIA-126), compared with β position-substituted phosphinates (PIA-226 and PIA-215).

The position of the side chain in the alkyl groups of the acidic phosphates is important to control the separation factors of rare earths, especially for the lighter rare earths (Ishida *et al.*, 1995). Separation factors were thus obtained as the ratio of extraction constant of the adjacent rare earths. The values obtained with phosphinates are shown in **Table 1**, together with those with EHPNA for comparison.

The separation factors obtained with the present dialkylphosphinic acids are superior to those of EHPNA for heavier rare earths. The steric crowding around P(O)OH group of the α -substituted dialkylphosphinic acids is more bulky than that of β -substituted acids. The former may weaken the coulombic interaction between P(O)O and metal ions to decrease the formation of metal complex (Ishida *et al.*, 1995). The decrease in extractability is more apparent for the case of lighter rare earths than the heavier ones as shown in Fig. 4. In addition to the steric hindrance effect in the vicinity of the P(O)OH group, it is expected that an introduction of effective substituents will increase the separation factor which is closely related to pK_a value of extractant (Yuan *et al.*, 1982).

As shown in Fig. 4, the extraction constants obtained with dialkylphosphinic acids are smaller than those of acidic phosphate and phosphonate. This means that stripping can be done using hydrochloric acid of lower concentrations. In the case of EHPNA, 0.25 mol/l HCl and 3 mol/l HCl are needed to strip lighter and heavier rare earths, respectively. In the present extractants, 1 mol/l HCl is found to be enough to strip completely the heaviest rare earth, Lu.

Conclusion

Several dialkylphosphinic acids were synthesized and used for extraction and separation of rare earths. With respect to PIA-117 and PIA-126 having substituents in the α -position, some improvement in the separation factors for the adjacent elements were

seen compared with EHPNA, especially for heavier group elements. This is attributed to the steric hindrance arising from two branched alkyl groups directly linked to the coordinating group. It is possible to strip using hydrochloric acid of lower concentration, as expected from the equilibrium relationship.

Nomenclature

D	= distribution ratio	[—]
HL	= acidic phosphinate extractant	
K_{ex}	= extraction constant	[—]
[]	= concentration of species in brackets	[mol/l]

<Superscript>

—	= organic phase
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