



## **EXTRACTIVE SEPARATION OF RARE EARTH IONS BY USING CALIX[4]ARENE WITH ISOPROPYL HYDROGEN PHOSPHONATE AT UPPER RIM**

Keisuke OHTO\*, Tomomi YAMASAKI, Katsutoshi INOUE

Department of Applied Chemistry, Faculty of Science and Engineering,  
Saga University, 1-Honjo, Saga 840-8502, Japan  
e-mail: ohtok@cc.saga-u.ac.jp

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### **ABSTRACT**

5,11,17,23-Tetrakis(isopropyl hydrogen phosphonomethyl)- 25,26,27,28 - tetrapropoxycalix[4]arene in cone conformation has been synthesized to investigate extraction behavior for nine trivalent rare earth metal ions from chloride media into chloroform, together with isopropyl hydrogen (4-propoxyphenyl)methylphosphonate as a corresponding monomer. Although the aqueous distributions of the present extractants were greater than those of butyl ester type of the previous extractants, they were trace and slight amounts under the experimental condition for calix[4]arene and monomeric derivatives, respectively. From the result of pH dependency, extraction takes place by a simple ion-exchange mechanism for both extractants. The extraction ability between the present extractants for rare earth ions was comparable. Results of a Job plot and a loading test indicate that for calix[4]arene derivative, stoichiometry of the extraction is 1:1. The separation efficiency of a calix[4]arene derivative is less than that of a monomeric derivative. It is attributed to the offset by the size effect of a coordination site at the larger upper rim of calix[4]arene (for relatively larger light rare earth ions) and strong affinity of phosphonate group to heavy rare earth ions. Such result is similar to that of derivatives with butyl ester.

Keywords: Calix[4]arene, Phosphonate, Rare earth ions, Extraction, Selectivity

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### **INTRODUCTION**

Calixarenes are cyclic oligomers and the third host compounds with properties discriminating specific metal ions and organic compounds. Such

properties of calixarenes have been studied and their specific behavior has been reviewed [1,2]. The authors have focused on the use of calixarene compounds as solvent extraction reagents for metals separation. In our previous works, the specific extraction behavior was reported [3-8].

In the previous paper, we described the preparation of 5,11,17,23-tetrakis(butyl hydrogen phosphonomethyl)- 25,26,27,28- tetrapropoxycalix [4]arene and butyl hydrogen(4-propoxyphenyl) methylphosphonate. The compounds were synthesized to investigate their extraction behavior for trivalent rare earth metal ions [9]. Lower separation efficiency of the calix[4]arene derivative, as compared to a monomeric derivative, is attributed to the offset by high affinity of a ring-size of the upper rim side of calix[4]arene to light rare earth ions and the preference of heavy rare earth ions by phosphonate group. Introducing a steric alkyl chain, isopropyl group, instead of less steric n-butyl one, makes the calix[4]arene derivative effective for mutual separation of rare earth ions. The chemical structures of the extractants employed in the present and previous works are shown in Fig.1

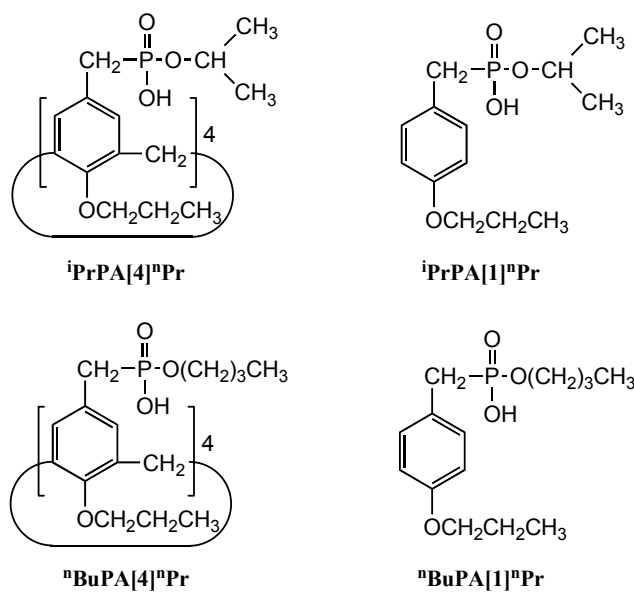


Fig. 1. Chemical structures of the present and the previous extractants.

For the present work, we synthesized the calix[4]arene derivative containing isopropyl phosphonic acid at the upper rim in order to investigate the extraction behavior for rare earth ions. The investigation considered steric hindrance and separation efficiency. The corresponding monomeric

analog was also synthesized to compare the extraction behavior and the separation efficiency with the calix[4]arene derivative.

## MATERIALS/METHODS/PROCEDURES

### Reagents

The precursors of 5,11,17,23-tetrakis(chloromethyl)-25,26,27,28-tetrapropoxycalix[4]arene (**1<sub>4</sub>**) and 2,6-dimethyl-4-chloromethylpropoxybenzene (**1<sub>1</sub>**) phosphonate compounds were synthesized in the same manner as described in the previous paper [9]. 5,11,17,23-Tetrakis(butyl hydrogen phosphonomethyl)-25,26,27,28-tetrapropoxycalix[4]arene and its monomeric analogue were also synthesized in a manner similar to the one presented in the previous paper [9]. The synthesis scheme of the present calix[4]arene type of the extractant is shown in Fig.2 as a typical example.

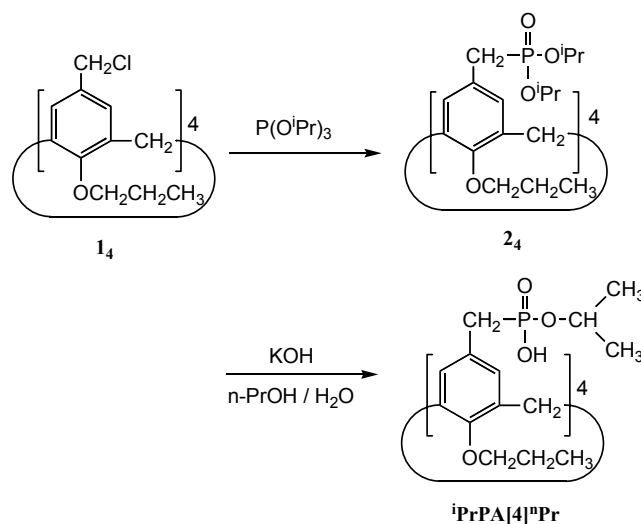


Fig. 2. Scheme of synthesis of the present calix[4]arene derivative.

### 5,11,17,23-tetrakis(dibutylphosphonomethyl)-25,26,27,28-tetrapropoxycalix[4]arene (cone conformation) (**2<sub>4</sub>**).

Tri(isopropyl)phosphite (127 g, 609 mmol) was added to **1<sub>4</sub>** (6.00 g, 7.63 mmol). The solution was stirred for 160 h at 100°C. The excess of the unreacted phosphite compound was removed *in vacuo*. The residue was further dried by a vacuum pump; highly viscous pale yellow liquid; 13.1 g (over 100%, still including tri(isopropyl)phosphite); tlc (SiO<sub>2</sub>, chloroform:methanol =5:1)  $R_f=0.63$ ; <sup>1</sup>H-NMR (270MHz, CDCl<sub>3</sub>, TMS, 27°C)  $\delta$  0.94 (12H, t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.12 (24H, d, OCH(CH<sub>3</sub>)<sub>2</sub>x2), 1.26 (24H, d, OCH(CH<sub>3</sub>)<sub>2</sub>x2), 1.84 (8H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.75 (8H, d (J=21.36 Hz), CH<sub>2</sub>P), 3.05 (4H, d, ArCH<sub>2</sub>Ar(*exo*)), 3.77 (8H, t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.35

(4H, d, ArCH<sub>2</sub>Ar(*endo*)), 4.52 (4H, q, OCH(CH<sub>3</sub>)<sub>2</sub> x2), 4.61 (4H, q, OCH(CH<sub>3</sub>)<sub>2</sub> x2), 6.50 (8H, s, ArH).

**5,11,17,23-tetrakis(isopropyl hydrogen phosphonomethyl)-25,26,27,28-tetrapropoxycalix[4]arene (cone conformation) (<sup>1</sup>PrPA[4]<sup>n</sup>Pr)**

Potassium hydroxide (27.6 g, 418 mmol), 400 cm<sup>3</sup> of n-propanol and 25 cm<sup>3</sup> of distilled water (1.39 mol) were added to crude **2<sub>4</sub>** (13.1 g, 7.63 mmol). The solution was refluxed over 18 h. The solvent was removed *in vacuo*. Chloroform and 6 M (M=mol dm<sup>-3</sup>) hydrochloric acid were added to the residue. After separation, the organic layer was independently washed three times with 1 M hydrochloric acid and then with distilled water. After drying over anhydrous magnesium sulfate, it was filtrated. The solvent was removed *in vacuo* and further dried by a vacuum pump; pale yellow powder; 9.36 g (quantitative); tlc (SiO<sub>2</sub>, chloroform:methanol=5:1) R<sub>f</sub>=0.00-0.20 (tailing); <sup>1</sup>H-NMR (270MHz, CDCl<sub>3</sub>, TMS, 27°C) δ 0.99 (12H, t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.34 (24H, d, OCH(CH<sub>3</sub>)<sub>2</sub>), 1.93 (8H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.97 (8H, d (J=21.36 Hz), CH<sub>2</sub>P), 3.08 (4H, d, ArCH<sub>2</sub>Ar(*exo*)), 3.83 (8H, t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.40 (4H, d, ArCH<sub>2</sub>Ar(*endo*)), 4.71 (4H, q, OCH(CH<sub>3</sub>)<sub>2</sub>), 6.71 (8H, s, ArH), 8.64 (4H, s(br), OH).

**Bis(isopropyl) (3,5-dimethyl-4-propoxy)phenylmethylphosphonate (**2<sub>1</sub>**)**

Tri(isopropyl)phosphite (27.9 g, 134 mmol) was added to **1<sub>1</sub>** (9.00 g, 42.3 mmol). The solution was stirred for 120 h at 100°C. The excess of the unreacted phosphite compound was removed *in vacuo* and further dried by vacuum pump; pale yellow liquid; 11.9 g (82.1%); tlc (SiO<sub>2</sub>, chloroform) R<sub>f</sub>=0.80; <sup>1</sup>H-NMR (270MHz, CDCl<sub>3</sub>, TMS, 27°C) δ 1.07 (3H, t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.22 (12H, d+d, OCH(CH<sub>3</sub>)<sub>2</sub>), 1.80 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.24 (6H, s, ArCH<sub>3</sub>), 3.00 (2H, d (J=21.36 Hz), CH<sub>2</sub>P), 3.70 (2H, t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.57 (2H, m, OCH(CH<sub>3</sub>)<sub>2</sub>), 6.94 (2H, s, ArH).

**Isopropyl hydrogen (3,5-dimethyl-4-propoxy)phenylmethylphosphonate (<sup>1</sup>PrPA[1]<sup>n</sup>Pr)**

Potassium hydroxide (20.0 g, 356 mmol), 250 cm<sup>3</sup> of n-propanol and 20 cm<sup>3</sup> (1.11 mol) of distilled water were added to **2<sub>1</sub>** (11.9 g, 34.7 mmol). The solution was refluxed over 24 h. All other procedures were similar to those used for <sup>1</sup>PrPA[4]<sup>n</sup>Pr preparation; pale yellow solid; 7.13 g (89.9%); tlc (SiO<sub>2</sub>, chloroform:methanol=5:1) R<sub>f</sub>=0.60 ; <sup>1</sup>H-NMR (270MHz, CDCl<sub>3</sub>, TMS, 27°C) δ 1.03 (3H, t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.20 (6H, d, OCH(CH<sub>3</sub>)<sub>2</sub>), 1.78 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.22 (6H, s, ArCH<sub>3</sub>), 2.88 (2H, d, CH<sub>2</sub>P), 3.64 (2H, t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.46 (1H, m, OCH(CH<sub>3</sub>)<sub>2</sub>), 6.90 (2H, s, ArH), 11.20 (1H, s(br), OH).

**Elution of the extractant into aqueous phase**

The organic solution was prepared by diluting each extractant in analytical grade chloroform, namely: to 5 mM and 20 mM for <sup>1</sup>PrPA[4]<sup>n</sup>Pr

and  ${}^i\text{PrPA}[1]^n\text{Pr}$ , respectively. Three kinds of aqueous solutions, each containing three kinds of rare earth ions, were prepared by dissolving rare earth chlorides (analytical grade) in 0.1 M hydrochloric acid or 0.1 M HEPES. The first solution contained La, Pr, and Nd, the second one Sm, Eu, and Gd, and the last one Ho, Er, and Y. The concentration of each rare earth ion in the solutions was adjusted to 0.1 mM. The pH values of aqueous solutions were adjusted by mixing the above two stock solutions (HCl-HEPES). Equal volumes (5 cm<sup>3</sup>) of the two phases were mixed and gently shaken at 303K for more than 4 h. After phase separation, the pH values and the phosphorus contents in the aqueous solutions were measured by a pH meter (Beckman  $\phi$ -45) and ICP-AES (Shimadzu ICPS-2000), respectively. The remained phosphorus contents were calculated from mass balance between the initial concentration of the extractant in the organic phase and the distributed concentration in the aqueous phase.

#### Distribution study of rare earth ions

Both solutions were prepared using the methods described above. Equal volumes (5 cm<sup>3</sup>) of the both phases were mixed and gently shaken at 303K for more than 4 h. After phase separation, the pH and the concentrations of metals in the aqueous solutions were measured by a pH meter (Beckman  $\phi$ -45) and ICP-AES (Shimadzu ICPS-2000), respectively. The concentrations of metal ions extracted were calculated from the mass balance.

### RESULTS AND DISCUSSION

#### Elution of the extractant into aqueous phase

From the practical point of view, no leakage of the extractant into aqueous phase is required. The effect of pH on the aqueous distribution of the both extractants into the aqueous phase is shown in Fig.3, where percentage elution is defined by eq.(1):

$$\% \text{ elution} = [\text{L}]_{\text{aq}} / [\text{L}]_{\text{ini}} \times 100 \quad (1)$$

where  $[\text{L}]_{\text{ini}}$  and  $[\text{L}]_{\text{aq}}$  are the initial extractant concentrations in the organic phase and the equilibrium extractant concentration in the aqueous phase, respectively.

The result shows that only trace (less than 0.5%) or slight (less than 3%) distribution are observed for  ${}^i\text{PrPA}[4]^n\text{Pr}$  or  ${}^i\text{PrPA}[1]^n\text{Pr}$  at the extraction pH region, i.e. 1.5 - 3.9. The aqueous distribution of the high molecular calix[4]arene derivative was found to be significantly lower than that of the monomeric derivative at high pH. It is attributed to the fact that undissociated neutral  ${}^i\text{PrPA}[4]^n\text{Pr}$  is fundamentally less than  ${}^i\text{PrPA}[1]^n\text{Pr}$ . The ratio between lipophilicity to ionic charge for calix[4]arene compound (mono to tetravalent species) is much higher than that of the monomeric one (only monovalent species). That is, the former has much higher molecular

weight than the latter, only monovalent species for both extractants should exist at experimental low pH region

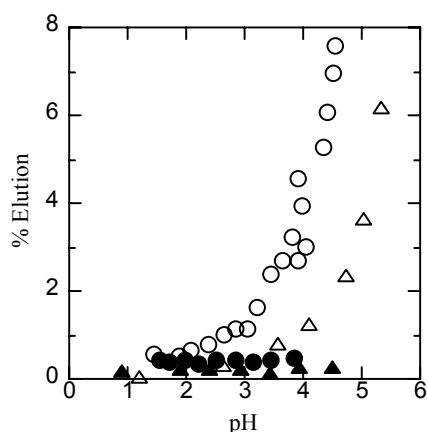
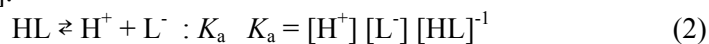


Fig. 3. Effect of percentage distribution of the extractants into aqueous phase. Close circle: <sup>1</sup>PrPA[4]<sup>n</sup>Pr, open circle: <sup>1</sup>PrPA[1]<sup>n</sup>Pr, close triangle: <sup>n</sup>BuPA[4]<sup>n</sup>Pr, open triangle: <sup>n</sup>BuPA[1]<sup>n</sup>Pr.

The effect of pH on the distribution ratio of for <sup>1</sup>PrPA[1]<sup>n</sup>Pr into the aqueous phase is shown in Fig.4, together with the previous extractant, <sup>n</sup>BuPA[1]<sup>n</sup>Pr. The acid dissociation of the extractant in the aqueous phase is expressed by eq.(2). where distribution ratio,  $D_a$ , and the partition coefficient of the undissociated species  $K_D$ , are expressed by eq.(3) and (4), respectively [10]:



$$D_a = [HL]_{org} ([HL] + [L^-])^{-1} \quad (3)$$

$$K_D = [HL]_{org} [HL]^{-1} \quad (4)$$

where HL and the subscript <sub>org</sub> represent the monomeric extractants and the species in the organic phase, respectively.

The combination of eqs.(2), (3), and (4) gives eq.(5).

$$D_a = K_D ( 1 + K_a [H^+]^{-1} )^{-1} \quad (5)$$

Taking a logarithm,

$$\log D_a = \log K_D - \log ( 1 + K_a [H^+]^{-1} ) \quad (6)$$

Equation (6) is approximated by eq.(7) at pH sufficiently lower than  $pK_a$ , while it is approximated by eq.(8) at pH sufficiently greater than  $pK_a$ . The pH at the intersection of two straight lines corresponds to  $pK_a$  of <sup>1</sup>PrPA[1]<sup>n</sup>Pr and <sup>n</sup>BuPA[1]<sup>n</sup>Pr. The  $pK_a$  values for <sup>1</sup>PrPA[1]<sup>n</sup>Pr and <sup>n</sup>BuPA[1]<sup>n</sup>Pr are almost the same and are evaluated to be 3.97 and 4.15, respectively.

$$\log D_a = \log K_D \quad (7)$$

$$\log D_a = \log K_D - \log K_a [H^+]^{-1} \quad (8)$$

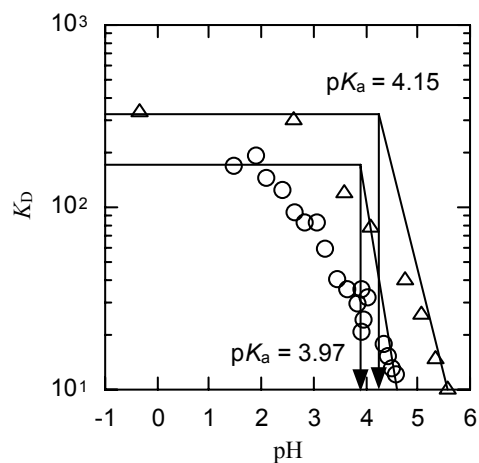


Fig. 4. Effect of pH on distribution ratio of monomeric derivatives into aqueous phase. Open circle:  ${}^1\text{PrPA}[4]^n\text{Pr}$ , open triangle:  ${}^n\text{BuPA}[1]^n\text{Pr}$ .

#### Distribution study of rare earth ions

The time required to reach equilibrium for yttrium extraction as a representative example among rare earth ions was examined. The influence of shaking time on % extraction of yttrium at pH=2.0 with  ${}^1\text{PrPA}[4]^n\text{Pr}$  and  ${}^1\text{PrPA}[1]^n\text{Pr}$  is shown in Fig.5. The % extraction is defined as eq. (9):

$$\% \text{ extraction} = \frac{[\text{RE}]_{\text{org}}}{[\text{RE}]_{\text{ini}}} \times 100 \quad (9)$$

where  $[\text{RE}]_{\text{org}}$  and  $[\text{RE}]_{\text{ini}}$  represent the extracted and the initial rare earth (yttrium) concentrations, respectively. Yttrium extraction with both extractants is sufficiently fast and reaches equilibrium within 4 h.

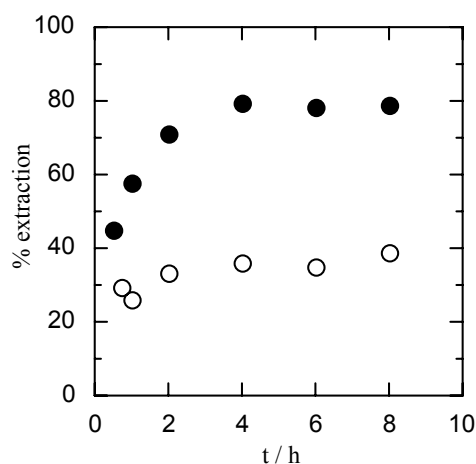
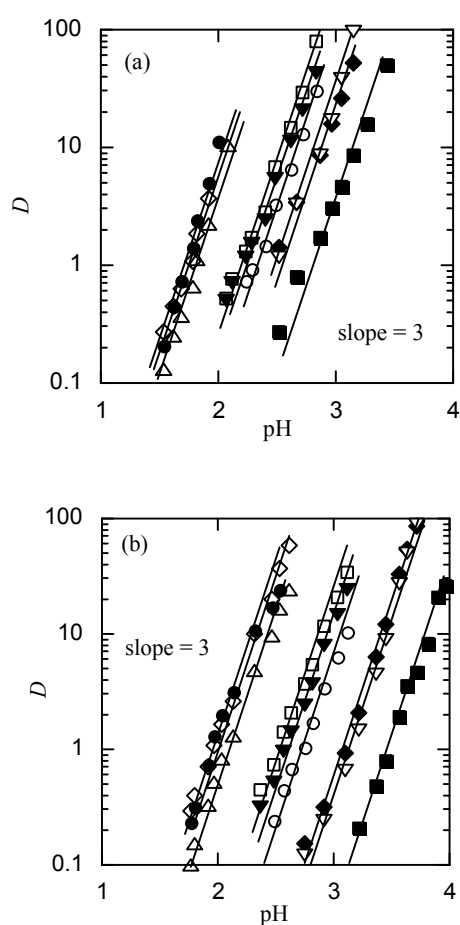


Fig. 5. Effect of shaking time on % extraction of yttrium at initial pH = 2.0. Close circle:  ${}^1\text{PrPA}[4]^n\text{Pr}$ , open circle:  ${}^1\text{PrPA}[1]^n\text{Pr}$ .

The influence of pH on the distribution ratio of rare earth ions with the extractants  ${}^i\text{PrPA}[4]^n\text{Pr}$  and  ${}^i\text{PrPA}[1]^n\text{Pr}$  is shown in Figs. 6(a) and (b), respectively. All points in both figures lie on straight lines with the slope of 3, equivalent to the charge of trivalent rare earth ions. The extraction order is as follows:  $\text{Er} > \text{Y} > \text{Ho} > \text{Gd} > \text{Eu} > \text{Sm} > \text{Nd} > \text{Pr} > \text{La}$ . Heavy rare earth ions are extracted preferentially to light ones, as observed in the extraction with other phosphorus-based acidic extractants. (It is well-known that the position of yttrium is placed between holmium and erbium when organophosphorus extractants are employed [11].)



Figs. 6. Effect of pH on distribution ratio of rare earths with (a)  ${}^i\text{PrPA}[4]^n\text{Pr}$  and (b)  ${}^i\text{PrPA}[1]^n\text{Pr}$ . Close circle: Er, open rhombus: Y, open triangle: Ho, open square: Gd, close inverted circle: Eu, open circle: Sm, close rhombus: Nd, open inverted circle: Pr, open square: La.



Next, in order to elucidate the stoichiometry between  ${}^i\text{PrPA}[4]^n\text{Pr}$  and rare earth ions, the continuous variation method was applied and the loading test was carried out. The Job plot for Er(III) and  ${}^i\text{PrPA}[4]^n\text{Pr}$  is shown in Fig.7. The stoichiometry of erbium and  ${}^i\text{PrPA}[4]^n\text{Pr}$  is found to be 1 : 1, since it was extracted mostly at 1 : 1 ratio with  ${}^i\text{PrPA}[4]^n\text{Pr}$ .

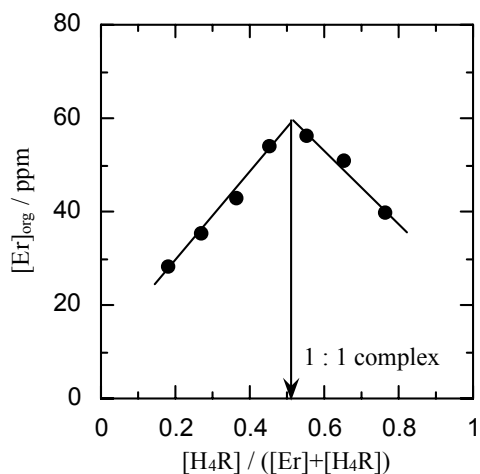


Fig. 7. Job plot for Er(III) and  ${}^i\text{PrPA}[4]^n\text{Pr}$ .

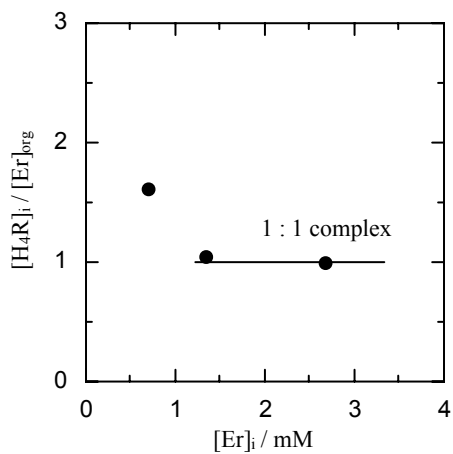


Fig. 8. Loading test of Er(III) with  ${}^i\text{PrPA}[4]^n\text{Pr}$ .

The result is supported by the loading test, which shows that the plots approach to 1 with the increase of the extractant concentration shown in Fig.8. From the result shown in Figs. 6 - 8: since the extraction occurs due to simple ion-exchange and stoichiometry is 1 : 1, the reaction scheme is suggested as eq.(10):



where  $\text{H}_4\text{L}$  represents  ${}^i\text{PrPA}[4]^n\text{Pr}$ . The coordination number of rare earth ions is greater than 6. The coordination number of a single phosphonic acid is generally 1, but for the saturation of rare earth ions coordination, it must be 2 with both phosphoryl oxygen and phosphonic acid involved.

Finally, separation efficiency is discussed. The relation between the  $\text{pH}_{1/2}$  values and reciprocal numbers of ionic radii for rare earth ions is shown in Fig.9, together with the data for buty butyl ester derivatives of calix[4]arene,  ${}^n\text{BuPA}[4]^n\text{Pr}$  and  ${}^n\text{BuPA}[1]^n\text{Pr}$ .

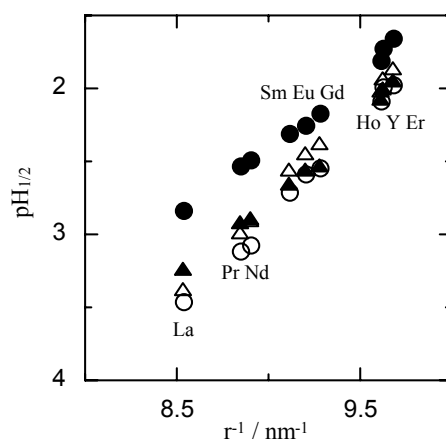


Fig. 9. Relation between  $\text{pH}_{1/2}$  value and reciprocal numbers of ionic radii of rare earths. Close circle:  ${}^i\text{PrPA}[4]^n\text{Pr}$ , open circle:  ${}^i\text{PrPA}[1]^n\text{Pr}$ , close triangle:  ${}^n\text{BuPA}[4]^n\text{Pr}$ , open triangle:  ${}^n\text{BuPA}[1]^n\text{Pr}$ .

Since the mutual separation efficiencies for rare earths are evaluated from the slope of the plots (or the difference of the  $\text{pH}_{1/2}$  values between La and Er), the efficiency of calix[4]arene extractant with isopropyl ester is slightly lower than that of the monomeric one. Isopropyl hydrogen alkylphosphonate compounds well investigated by Yuan *et al.* [12] are quite effective extractants due to the steric hindrance of isopropyl group close to the coordination site. The result may be attributed to the fact that the coordination site of calix[4]arene phosphonate at the upper rim is much larger than lanthanum size, that is, to offset of two effects between the size and functional group. The former is related to the coordination site for upper

rime side of calixarene desirable to larger light rare earths, while the latter is related to the preferable affinity of phosphonate group for heavy rare earth. The result is similar to the previous one [9]. Consequently, the separation efficiency of  ${}^1\text{PrPA}[4]^n\text{Pr}$  is less than not only that of  ${}^1\text{PrPA}[4]^n\text{Pr}$ , but also that of  ${}^n\text{BuPA}[4]^n\text{Pr}$ .

### CONCLUSION

The cone conformational phosphonate derivative of calix[4]arene and its corresponding monomeric analog were synthesized and the extraction behavior for nine trivalent rare earth ions from chloride media into chloroform was investigated. The extractants were found to be distributed into the aqueous phase in small amount under the present experimental condition. The extraction ability of both extractants was nearly the same. The lower separation efficiency of calix[4]arene extractant with isopropyl ester is attributed to the offset by the size effect of the coordination site at the larger upper rim of calix[4]arene for relatively larger light rare earth ions and strong affinity of phosphonate group to heavy rare earth ions, together with a much larger coordination site provided by the upper rim than required for lanthanum. Multiplication of the both effects which would be achieved by the introduction of phosphonate groups onto the lower rim of calix[4]arene makes the separation ability effective.

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