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Preorganized, cone-conformational calix[4]arene possessing four propylenephosphonic acids with high extraction ability and separation efficiency for trivalent rare earth elements

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Abstract *p-t*-Octylcalix[4]arene with tetraphosphonic acid at lower rim in cone conformation has been designed and synthesized as a new extraction reagent to investigate the extraction behavior of the nine trivalent rare earth elements: La, Pr, Nd, Sm, Eu, Gd, Ho, Y, and Er. The extraction of rare earth metals with the present extractant occurs by a simple ion-exchange mechanism. The stoichiometry of the extractant to rare earth metal ion was determined to be 2:1 based on the extraction equation, half pH values, $pH_{1/2}$, and the difference in the values of the extraction equilibrium constants of nine trivalent rare earth elements and separation factors between adjacent rare earth elements. This allowed for comparison of the estimated extraction efficiency and selectivity. The present extractant exhibited extremely high extractability and sufficiently high separation efficiency of rare earth metals, compared with calix[4]arene tetraphosphonic acid at upper rim, calix[4]arene tetraacetic acid at lower rim as previously reported and the commercial extraction reagent. This results was attributed to size and multidentate effects based on the preorganized cyclic structure of calix[4]arene and to the original selectivity of functional group for heavier rare earth elements.

This article paper is dedicated to Prof. Leonard F. Lindoy on the celebration of his 75th birthday.

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Introduction

The recovery and separation of metal resources in developing and preparing advanced materials and devices are essential. Among many techniques for recovery and separation of metals, solvent extraction has been extensively used due to its high separation efficiency, excellent versatility, and mass disposal potential. The role of extraction reagents is very important in solvent extraction method, and various extractant types have been prepared to date [1–11]. The requirements for extractant development are as follows: (1) high selectivity to a certain metal ion, (2) very low solubility in the aqueous phase, (3) highly soluble in aliphatic and aromatic diluents, (4) good kinetics of extraction, (5) easily stripped of the loaded metal, and (6) non-flammable, non-volatile, and non-toxic [12–14].

The family of rare earth metal is a typical metal group that is difficult to separate due to similar chemical properties and ionic size. These are key elements that support advanced industry and have been used as magnetic materials (i.e., magnetooptical recording materials and permanent magnets) luminescent materials (i.e., fluorescent dopants and luminescence center, YAG laser device) superconductors,

catalysts, polishers, and lasers. Separation techniques are necessary because high purity is generally required for use. Peppard et al. extensively investigated solvent extraction of rare earth elements with organophosphorus extractants for application in isolation from nuclear wastes and actinide [15–19]. Although a large number of novel extraction reagents for rare earth elements have been also prepared, higher-quality extractants for mutual separation of rare earth elements are still required. Calixarenes, which are macrocyclic oligomers, provide three-dimensional coordination sites and controlled cavities for attractive and interesting compounds [20, 21]. The ability to recognize and discriminate metal ions is a remarkable feature of these specific receptors and some review articles on these interesting ionophores have been published [22–28]. Extractive separation of rare earth elements has also been reported using carbamoyl methyl phosphine oxide (CMPO)-like neutral derivatives [29–38], neutral phosphonate derivatives [39], and carboxylic acid derivatives [40–46]. Although some CMPO-like extractants exhibit good separation efficiency in separating rare earth elements, most display larger light rare earth element selectivity due to introduction at larger upper rim. The calixarene derivatives also demonstrate poor separation efficiency for carboxylic acid derivatives, since metal ion selectivity is mostly dependent on stability constants between referential compounds with the same functionality and metal ions, and the functional group of carboxylic acid originally exhibits selectivity at the middle of rare earths with low separation efficiency.

Organophosphorus acid compounds are some of the most effective extractants including 2-ethylhexyl 2-ethylhexylphosphonic acid, di-2-ethylhexylphosphoric acid, and calixarene derivatives [47–49]. However, these also exhibit light rare earth selectivity or have poor separation efficiency with heavy rare earth selectivity, because some derivatives were bibasic and others were disubstituted derivatives with unsubstituted phenol fragments. In our previous work, the calix[4]arene derivative with tetraphosphonic acid at upper rim was prepared, and the extraction behavior of rare earths was investigated [50, 51]. Although calixarene exhibited much higher separation efficiency than the carboxylic acid derivative due to the associated functionality, the separation efficiency was lower compared with the corresponding monomeric derivative. This result was attributed to the offset between the size recognition effect at the upper rim of calix[4]arene for larger light rare earth elements and the affinity of the phosphonic acid group for smaller heavy rare earth ones.

In the present work, we have synthesized calix[4]arene derivatives containing phosphonate groups at lower rim to investigate the extraction behavior for rare earth metals (La, Pr, Nd, Sm, Eu, Gd, Ho, Y, and Er) including both extraction ability and mutual separation efficiency.

Experimental

Reagents

The present extractant **5** has been prepared in four steps of cyclization, diphosphonation at the distal position, the complete tetraphosphonation on the remaining phenol oxygen atoms, and final hydrolysis with base from the corresponding phenol. 5,11,17,23-Tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene-25,26,27,28-tetol **1** was synthesized in a similar manner as previously described [43]. Regardless of introduction of the same groups, the stepwise synthesis was performed for extractant **5**, since the direct tetraphosphonation from tetrol **1** failed. The synthetic scheme for extractant **5** is shown in Fig. 1.

Dibutyl 3-bromopropylphosphonate (**2**) [52]

Propylene dibromide (121 g, 599 mmol) was added to tributyl phophite (50.0 g, 200 mmol). The mixture was stirred and heated at 140 °C for 20 h. The desired compound was collected by distillation in vacuo (1 mmHg) at 115 °C; colorless liquid; bp 115 °C/1 mmHg, 30.6 g (yield 53.9%), ^{1}H-NMR (300 MHz, CDCl$_3$, TMS, 30 °C) δ 0.54 (6H, t, 2CH$_3$), 1.40 (4H, m, 2CH$_2$CH$_3$), 1.65 (4H, m, 2CH$_2$CH$_2$CH$_3$), 1.87 (2H, m, CH$_2$CH$_2$Br), 2.20 (2H, m, PCH$_2$), 3.48 (2H, t, BrCH$_2$), (4H, m, 2POCH$_2$).

25,27-Dihydroxy-26,28-bis{3-(dibutylphosphoryloxy)propoxy}-5,11,17,23-tetrkis(1,1,3,3-tetramethylbutyl)calix[4]arene (**3**)

Under a nitrogen stream, **1** (1.01 g, 1.15 mmol), sodium carbonate (2.43 g, 23.0 mmol, 20 eq) was added to 60 cm^3 of dry acetonitrile and the mixture was refluxed for an hour. After cooling, **2** (0.785 g, 2.49 mmol, 2.2 eq) was added to the mixture and the mixture was refluxed for 138 h. After filtration, the solvent was removed in vacuo. The residue was extracted with chloroform and the organic solution was washed twice with 1 M (M = mol dm^{-3}) hydrochloric acid and three times with distilled water. After drying over anhydrous magnesium sulfate, the solution was filtered and the solvent was then removed in vacuo; pale yellow viscous liquid, the crude compound included reactant **2** as an impurity, TLC (SiO$_2$, CHCl$_3$: MeOH = 30:1, R_f = 0.54); IR (KBr) v_{O-H} 3,429 cm^{-1} (br), v_{P-O-R} 1,024 cm^{-1}; ^{1}H-NMR (300 MHz, CDCl$_3$, TMS, 30 °C) δ 0.20 (18H, s, 2(CH$_3$)$_3$), 0.75 (18H, s, 2(CH$_3$)$_3$), 0.92 (18H, t, 4CH$_3$), 1.08 (18H, s, 2(CH$_3$)$_2$), 1.40 (12H + 8H + 4H, s + m + s, 2(CH$_3$)$_2$ + 4CH$_2$CH$_3$ + 2CCH$_2$C), 1.65 (8H + 4H + 4H, m + m + s, 4CH$_2$CH$_2$CH$_3$ + 2CH$_2$CH$_2$P + 2CCH$_2$C), 2.27 (4H, m, 2CH$_2$P), 3.30 (4H, d, *exo*-CH$_2$), 4.05 (4H + 8H, t + m,

Fig. 1 Synthetic scheme of the extractant **5**
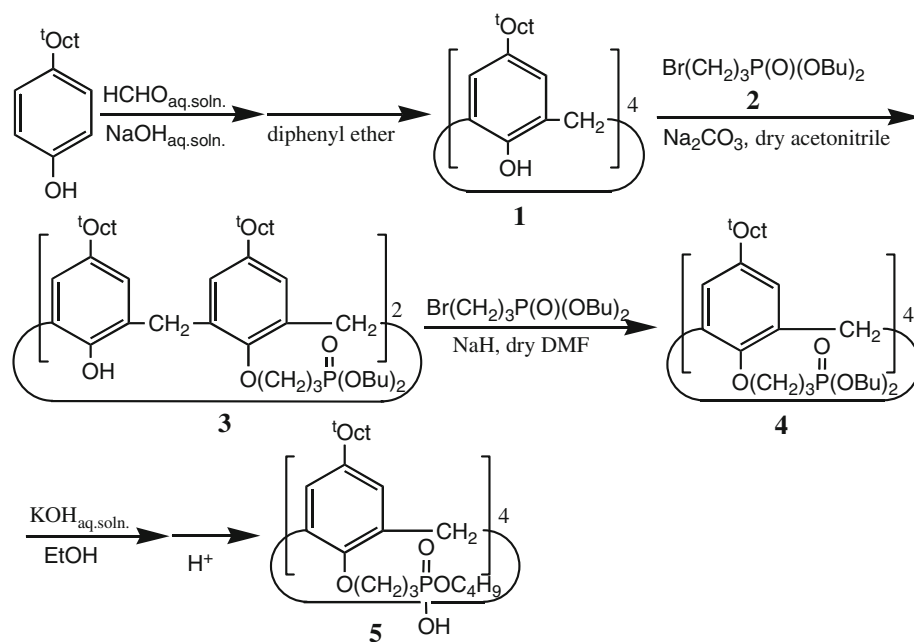
2CH$_2$CH$_2$CH$_2$P + 4POCH$_2$), 4.28 (4H, d, *endo*-CH$_2$), 6.81 (4H, s, ArH), 7.00 (4H, s, ArH), 7.62 (2H, s, OH).
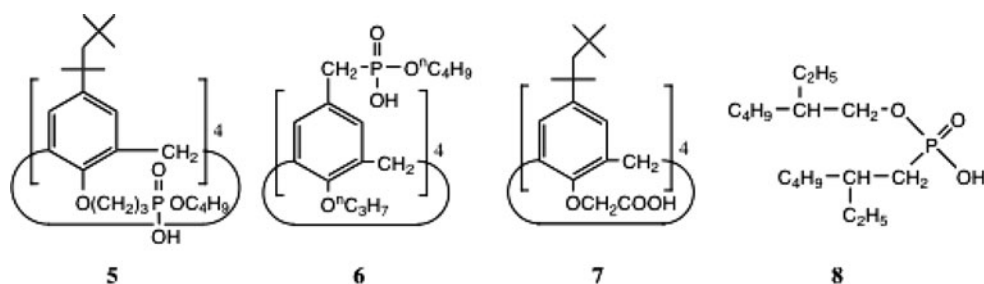
25,26,27,28-Tetrakis{3-(dibutylphosphoryloxy)propoxy}-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (**4**)

Under a nitrogen stream, sodium hydride (2.35 g, 61.4 mmol, 14 eq, washed with heptane for oil removal before use) was added to crude **3** (5.86 g, 4.37 mmol) in 50 cm^3 dry DMF in a salt ice bath and the mixture was stirred for an hour. The reactant **2** (6.85 g, 21.7 mmol, 5 eq) was added to the mixture and the mixture was stirred for 3 h in an ice bath and then for 72 h at room temperature. 1-Butanol (80 cm^3) was added to deactivate excess sodium hydride in an ice bath. Solvent and excess amount of **2** were removed in vacuo. The residue was extracted with chloroform, and the organic solution was washed twice with 1 M hydrochloric acid and three times with distilled water. After drying over anhydrous magnesium sulfate, the solution was filtered, and the solvent was then removed in vacuo again; dark brown viscous liquid, the crude compound still included the reactant **2** as an impurity, TLC (SiO$_2$, CHCl$_3$: MeOH = 30: 1, R_f = 0.34); IR (KBr) disappeared peak v_{O-H} 3,429(br) cm^{-1}, ^{1}H-NMR (300 MHz, CDCl$_3$, TMS, 30 °C) credible peaks at δ 3.12 and 4.35 (8H, dd, *exo*- and *endo*-CH$_2$) and 6.73 (8H, s, ArH), and the disappeared peak at 7.62 (2H, s, OH) and no peaks for D$_2$O-exchange around 5–7 ppm.

25,26,27,28-Tetrakis[3-{hydroxy(butyl)phosphoryloxy}propoxy]-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (**5**)

Potassium hydroxide (2.85 g, 43.2 mol) in water (5.07 g, 282 mmol) was added to crude **4** (3.51 g, 61.4 mmol as consecutive from synthesis of **4**) in 60 cm^3 ethanol and the mixture was refluxed for 192 h. Solvent was removed in vacuo, and the residue was extracted with chloroform. The organic solution was washed once with 6 M hydrochloric acid, twice with 1 M hydrochloric acid and four times with distilled water. After drying over anhydrous magnesium sulfate, the solution was filtered, and the solvent was then removed in vacuo. The residue was recrystallized from acetonitrile, heptane, and chloroform; white powder, 1.11 g (Yield 26%), TLC (SiO$_2$, CHCl$_3$: MeOH = 10: 1, R_f = 0.00–0.18 [tailing]); IR (KBr) $v_{P(O)OH}$ 2,690 (br), 2,249(br), and 1,681 (br) cm^{-1}; ^{1}H-NMR (300 MHz, CDCl$_3$, TMS, 30 °C) δ 0.69 (36H, s, 4(CH$_3$)$_3$), 0.94 (12H, t, 4CH$_3$), 1.11 (24H, s, 4(CH$_3$)$_2$), 1.40 (8H + 8H, m + m, 4CH$_2$CH$_3$ + 4CH$_2$CH$_2$P), 1.52 (8H, s, 4CCH$_2$C), 1.68 (8H, m + m + s, 4CH$_2$CH$_2$CH$_3$), 2.40 (8H, m, 4CH$_2$P), 3.12 (4H, d, *exo*-CH$_2$), 3.95 (8H, t, 4POCH$_2$), 4.08 (8H, t, 4CH$_2$CH$_2$CH$_2$P), 4.36 (4H, d, *endo*-CH$_2$), 6.59 (4H, s, POH), 6.73 (8H, s, ArH); Found: C, 68.12; H, 9.43%. Calcd for C$_{88}$H$_{148}$O$_{16}$P$_4$ + C$_7$H$_{16}$: C,67.67, H, 9.80%. From the ^{1}H-NMR spectral data, the impurities in the previous step were determined to be nearly removed and compound **5** was fixed in cone conformation.

The chemical structures of the present extraction reagents together with referential ones are shown in Fig. 2. In detail, calix[4]arene derivatives with tetraphosphonic acid at upper rim, **6** and with tetraacetic acid at lower rim, and **7** were also shown for the comparison.

The commercial extractant **8**, 2-ethylhexyl 2-ethylhexylphosphonic acid, PC-88A, was kindly supplied from Daihachi Chemical Industry Co., Ltd. and was used without further purification. The other chemicals were purchased and also used without further purification.

Distribution study of rare earth metals

The extraction was performed in a similar manner as previously described [43, 46]. An organic solution was prepared by diluting each extractant into an analytical grade of chloroform at 5.0 mM. The following three kinds of aqueous solutions, which each contained three kinds of rare earth ions, were prepared by dissolving analytical grade rare earth chloride (Some of them were prepared by dissolving rare earth oxide into hydrochloric acid.) into 0.1 or 1.0 M to dilute the hydrochloric acid to 0.1 mM: the first solution contained La, Pr, and Nd, the second was Sm, Eu, and Gd, and the last was Ho, Er, and Y. For extractant **5**, 0.1 M diluting hydrochloric acid and 0.1 M HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid) aqueous solutions were also used as aqueous media. The pH of the aqueous solutions was adjusted by arbitrarily mixing the above three hydrochloric acid stock solutions (HCl-HEPES). Equal volumes (3 cm^3) of both phases were mixed and vigorously shaken at 303 K for more than an hour. After phase separation, the metal concentrations in the aqueous solutions were measured by ICP-AES (Shimadzu ICPS-8100), respectively. The extracted metal ion concentrations were calculated from the differences in the metal concentrations of the aqueous phase before and after the equilibration. Proton concentrations were calculated from the mixing ratio of hydrochloric acid solutions. Then, the proton activities were estimated using activity coefficients [53]. The equilibrium pH was assumed to be the same as the initial pH because the pH was low enough to ignore the change before and after the extraction.

For commercial extractant **8**, PC-88A, a similar extraction experiment was performed; except for the extractant concentration was 20.0 mM to generate the same amount of the functional group for **8** as the tetrameric extractants **5–7**.

Results and discussion

For distribution of the extractant into the aqueous phase, calix[4]arene with phosphonic acid at upper rim, extractant **6** showed only negligible distribution at pH 1.4–4.2 in the previous work because of the large molecular weight, the significant localization of polar groups based on cone conformation, and the stepwise acid dissociation constants till the fourth [50, 51]. The present extractant **5** with higher carbon number was expected to exhibit more lipophilicity and less hydrophilicity than the previous lower **6**; the aqueous distribution of **5** is also negligible under the extraction conditions, because the present extractant **5** has a greater carbon number than the previous **6**, and both extractants have the same phosphonic acid groups and basicity.

The extraction time was first investigated. The effect of shaking time on the percentage extraction of trivalent lanthanum, europium, and erbium ions with **5** is shown in Fig. 3. As expected from the Eigen mechanism [54], the extraction equilibrium of rare earth elements is fast. Although the extraction samples were mildly shaken in the present work at 130 rpm, extraction of rare earth metal ions was fast and reached equilibrium within half an hour.

The pH dependency of trivalent rare earths with the present extractant was next investigated. Effect of pH on the distribution ratio of rare earth metals with **5** is shown in Fig. 4. All points in Fig. 4 lie on straight lines with slopes of 3, which is equivalent to the charge of rare earth metals. This result indicates that all trivalent metal ions are ion-exchanged with three protons from the extractants even in such low pH region, where the acid dissociation of the ion-exchangeable type of extractant is not easy. As expected from the previous result of time to reach extraction equilibrium, the extraction ability of **5** is extremely high.
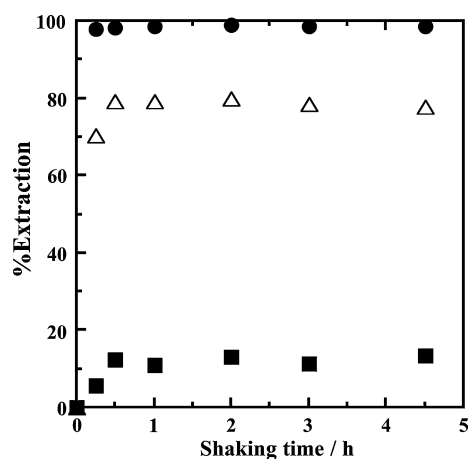
Fig. 3 Effect of shaking time on the percentage extraction of trivalent lanthanum, europium, and erbium ions with extractant **5**. *Filled square*: La, *open triangle*: Eu, *filled circle*: Er, [metal] = 0.1 mmol dm^{-3}, [extractant] = 5 mmol dm^{-3}, 0.1 mol dm^{-3} HNO$_3$—0.1 mol dm^{-3} HEPES
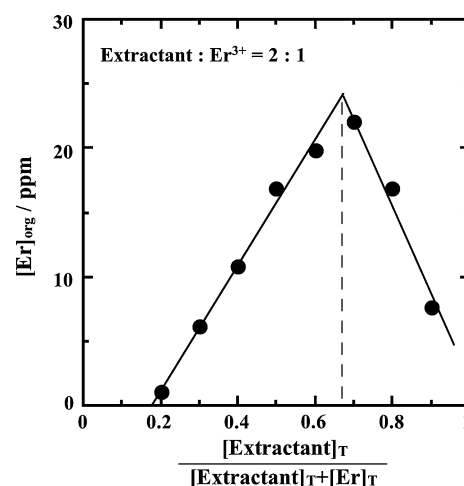
Fig. 5 Job's plots for trivalent erbium with **5**. [**5**] + [Er^{3+}] = 1 m-mol dm^{-3}, 0.1 mol dm^{-3} HCl (Initial pH = 1.1)
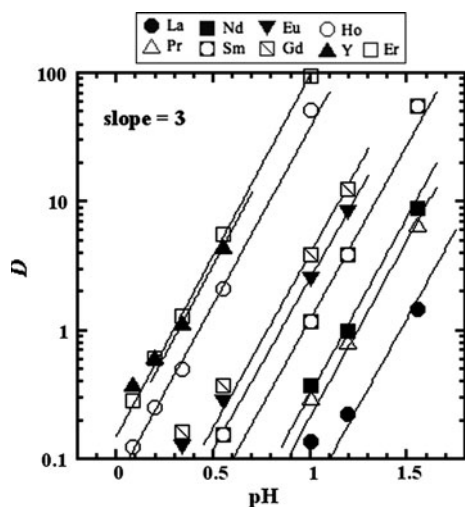

Fig. 4 Effect of pH on distribution ratio of rare earth metals with the extractant **5**. [metal] = 0.1 mmol dm^{-3} each, [extractant] = 5 mmol dm^{-3}, 1.0 mol dm^{-3} HCl—0.1 mol dm^{-3} HCl or 0.1 mol dm^{-3} HCl—0.1 mol dm^{-3} HEPES buffer solution

The extraction selectivity is as follows: Er > Y > Ho > Gd > Eu > Sm > Nd > Pr > La. Heavy rare earth metals are preferentially extracted over light ones. The tendency of the selectivity to rare earth metals is similar to conventional acidic phosphorus extractants, although relatively poor. For acidic phosphorus extractants, yttrium is placed between holmium and erbium [55].

A further experiment using Job's method was performed to confirm the stoichiometry of the extraction reaction. The Job's plots for Er(III) with **5** are shown in Fig. 5 as a typical result. Trivalent erbium was found to form 1:2 metal: extractant complexes with extractant **5**.
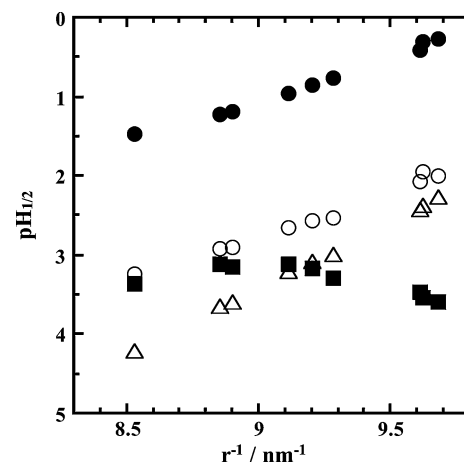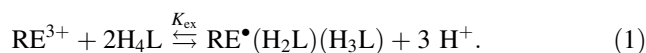

Fig. 6 Relationship between half pH value, pH$_{1/2}$ and reciprocal number of ionic radii for trivalent rare earths, r^{-1}, for the extractants **5**–**8**

Therefore, the stoichiometric relation of the extraction reaction of trivalent erbium with extractant **5** is proposed by the Eq. 1:

$$RE^{3+} + 2H_4L \overset{K_{ex}}{\leftrightarrows} RE^{\bullet}(H_2L)(H_3L) + 3\ H^+. \tag{1}$$

where RE and H$_4$L represent rare earth metals and tetrameric phophonic acid **5**, and K_{ex} is the extraction equilibrium constant. The above-mentioned stoichiometric relationship yields the equilibrium relationship expressed as follows:

$$K_{ex} = [RE^{\bullet}(H_2L)(H_3L)][H^+]^3 \big/ \big([RE^{3+}][H_4L]_2\big). \tag{2}$$

Eq. 2 is rewritten by Eq. 3.

$$\log D = 3pH + 2\log[H_4L] + \log K_{ex}. \tag{3}$$

The D value is the distribution ratio defined by Eq. (3).

$$D = \left[RE^{3+}\right]_{org} \Big/ \left[RE^{3+}\right]_{aq} = [RE^{\bullet}(H_2L)(H_3L)]/\left[RE^{3+}\right]. \tag{4}$$

The subscripts org and aq represent the species in the organic and aqueous phases, respectively. The concentration difference before and after extraction is negligible, and the equilibrium extractant concentration can be regarded as the

Table 1 Half pH values, $pH_{1/2}$, difference of half pH values, $-\Delta pH_{1/2}$, extraction equilibrium constants, K_{ex}, and separation factors, β for each extrantant

Extractant No.	Extractant 5				Extractant 6			
Concentration	5 mM				5 mM			
Stoichiometry	2:1 (Extractant:RE)				1:1 (Extractant:RE)			
Rare earth metals		$-\Delta pH_{1/2}$	K_{ex}	β	$pH_{1/2}$	$-\Delta pH_{1/2}$	K_{ex}	β
La	1.46		1.67E+00		3.23		4.08E−08	
		0.24		5.25		0.31		8.51
Pr	1.22		8.75E+00		2.92		3.48E−07	
		11.04		1.32		0.03		1.23
Nd	1.18		1.15E+01		2.89		4.28E−07	
		0.23		4.90		0.24		5.25
Sm	0.95		5.65E+01		2.65		2.24E−06	
		0.10		2.00		0.09		1.86
Eu	0.85		1.13E+02		2.56		4.18E−06	
		0.09		1.86		0.03		1.23
Gd	0.76		2.10E+02		2.53		5.14E−06	
		0.35		11.22		0.46		23.99
Ho	0.41		2.36E+03		2.07		1.23E−04	
		0.10		2.00		0.13		2.45
Y	0.31		4.70E+03		1.94		3.03 E−04	
		0.05		1.41		−0.06		0.66
Er	0.26		6.64E+03		2.00		2.00E−04	

Extractant No.	Extractant 7				Extractant 8			
Concentration	5 mM				20 mM			
Stoichiometry	1:1 (Extractant:RE)				3:1 (Extractant*:RE)			
La	3.36		1.66E−08		3 91		1.80E−06	
		0.26		6.03		0.47		26.28
Pr	3.10		1.00E−07		3.44		4.73E−05	
		−0.04		0.76		0.05		1.42
Nd	3.14		7.60E−08		3.39		6.74E−05	
		0.02		1.15		0.34		10.36
Sm	3.12		8.73E−08		3 05		6.98E−04	
		−0.06		0.66		0.15		2.83
Eu	3.18		5.77E−08		2.90		1.98E−03	
		−0.11		0.47		0.05		1.41
Gd	3.29		2.70E−08		2.85		2.79E−03	
		−0.16		0.33		0.47		25.00
Ho	3.45		8.93E−09		2.39		6.98E−02	
		−0.14		0.38		0.11		2.13
Y	3.59		3.40E−09		2.28		1.48E−01	
		0.05		1.41		0.02		1.17
Er	3.54		4.80E−09		2.25		1.73E−01	

*Extractant as dimer species

initial, because the initial extractant concentration is sufficiently higher than the total metal concentrations. Consequently, Eq. 3 is rewritten using Eq. 5.

$$\log D = 3\mathrm{pH} + \text{constant}. \tag{5}$$

The slope of pH dependency in Fig. 4 is 3 derived from the charge of rare earth elements, and the result satisfies this equation and the extraction reaction (1).

The relationship between half pH value, $\mathrm{pH}_{1/2}$ and the reciprocal number of ionic radii for trivalent rare earth metals with 6 as the coordination number, r^{-1}, for tetraphosphonic acid extractant of 5 is shown in Fig. 6 with plots of the extractant with tetraphosphonic acid at upper rim 6, tetraacetic acid extractant 7 and commercial extractant 8. The half pH value, $\mathrm{pH}_{1/2}$ is defined as the pH value that half of the metal ions are extracted under the present experimental condition.

The y-axis is inverted such that the plots for extractants with high extraction efficiency or easily extracted metals are upside down. Although the stoichiometries for each extractant are not the same the extraction ability and the separation efficiencies can be compared because the amounts of functional group under the experimental conditions for all extractants are the same. The extraction ability of extractants 5 is much greater than extractants 6–8 because the plots are obviously higher which is attributed to the highly pre-organized structure for rare earth metals by size-fitting and the converging effect of four phosphonic acids due to cone conformation. The difference between adjacent plots corresponds to the separation efficiency. The plots for 5 do not also exactly lie on the straight lines as demonstrated by the 'tetrad' [56] similarly to 6–8. However, the presumable slope of the plots can roughly indicate metal selectivity and the separation efficiency. As described in the results or pH dependency, 5 exhibits high heavy rare earth metal selectivity with an extraction selectivity of Er > Y > Ho > Gd > Eu > Sm > Nd > Pr > La. The separation efficiency for 5 is much higher than for 7 and comparable to that for 6, and slightly lower than that for 8, which exhibited the best extractant during separation among the stable commercial extractants. Changing alkyl branches to 2-ethylhexyl groups would result in more effective mutual separation of rare earth metals.

From the data in Fig. 6 and Eq. 3, half pH values, $\mathrm{pH}_{1/2}$, the difference in half pH values, $-\Delta\mathrm{pH}_{1/2}$ from the value of the heavier to lighter metal, and the extraction equilibrium constants, K_{ex}, and separation factors, β for each extractant were estimated. The values are listed in Table 1. The difference in half pH values, $-\Delta\mathrm{pH}_{1/2}$ is calculated from the difference in the $\mathrm{pH}_{1/2}$ values between heavier and lighter metal ions (the negative $\Delta\mathrm{pH}_{1/2}$ value means that the heavier metal ion is more easily extracted compared to the

lighter metal ion). The separation factor, β, is defined by Eq. 6:

$$\begin{aligned} \beta &= D_{\text{Heaviermetal}} \big/ D_{\text{Lighter metal}} \\ &= K_{\text{ex,Heavier metal}} \big/ K_{\text{ex,Lighter metal}}. \end{aligned} \tag{6}$$

The values of K_{ex} for each extractant are not directly comparable due to different stoichiometries whereas the values of $\mathrm{pH}_{1/2}$, $-\Delta\mathrm{pH}_{1/2}$, and β are directly comparable. As described in Fig. 6, the present extractant 5 shows extremely high extraction ability and reasonable separation efficiency to rare earth metals.

Conclusions

Tetraphosphonic acid derivative of calix[4]arene in cone conformation has been designed and synthesized as a new type of extractant for trivalent rare earth metals. The present extractant exhibits a fast extraction rate. The extraction ability of the present extractant is much greater and selectivity is slightly less than that of the extractants with tetraphosphonic acid at upper rim, tetraacetic acid used previously, and the commercial extractant 2-ethyl-hexyl 2-ethylhexylphosphonc acid. The high extraction ability is attributed to the highly pre-organized structure for rare earth metals by size-fitting and converging of four phosphonic acids due to cone conformation. Changing alkyl branches to steric 2-ethylhexyl groups, controlling stoichiometry and drastic depressing of the extraction ability would result in more effective mutual separation of rare earth metals.

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