Solvent Extraction of Trivalent Rare Earth Metal Ions with Carboxylate Derivatives of Calixarenes

Keisuke Ohto*, Masayuki Yano*, Katsutoshi Inoue*, Takehisa Yamamoto**,
Masahiro Goto**, Fumiyuki Nakashio**, Seiji Shinkai** and Takeshi Nagasaki***

**Department of Applied Chemistry, Faculty of Science and Engineering, Saga University,*
Honjo, Saga 840, Japan
***Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University,*
Hakozaki, Fukuoka 812, Japan
****Department of Bioapplied Chemistry, Faculty of Engineering, Osaka City University,*
Sugimoto, Osaka 558, Japan

As novel calixarene or macrocyclic types of extractants, 37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexakis(1,1,3,3-tetramethylbutyl)calix[6]arene and 25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene as well as p-(1,1,3,3-tetramethylbutyl)phenoxy acetic acid, as their monomeric analog, and 2,6-bis[2-carboxymethoxy-5-(1,1,3,3-tetramethylbutyl)benzyl]-4-(1,1,3,3-tetramethylbutyl)phenoxyacetic acid as a linear trimer analog, have been synthesized in order to investigate their extraction abilities of rare earth metal ions, RE^{3+} (RE=Y, La, Pr, Nd, Sm, Eu, Gd, Ho, Er), from an aqueous nitrate solution. It was found that the calixarene derivatives provide much higher extractability and greater separation efficiency than do the monomeric analog and the other acidic carboxylate extractants. The selectivity for rare earth elements in this system is not affected by the ring size. In extraction from an aqueous mixture of nitric acid–glycine, the stoichiometry of the extracted species was determined and the extraction equilibrium constants as well as the separation factors were evaluated for each extractant. A stripping test was also performed and the stripping of rare earths was found to be successfully achieved with diluted hydrochloric acid.

Keywords Solvent extraction, rare earth, calixarene carboxylate, aggregation, stripping, solubility

Calixarenepolyols and their derivatives have been attracting much attention as novel types of interesting host compounds.[1-3] Their recognition ability for metal ions can be one of the remarkable features as a specific receptor.

They have plural phenolic hydroxyl groups which can be relatively easily chemically modified. It is expected that the introduction of ion-exchangeable functional groups into them will make them effective extractants, due to a chelating effect, and also that the cyclic structures and their rigid skeletons contribute to a high selectivity, owing to their size-discriminating ability for metal ions with different ionic radii.

A number of studies have been conducted on calixarenes or their derivatives as receptors for metal ions. Izatt *et al.* carried out extraction of alkali metal ions with 5,11,17,23-tetra-t-butylcalix[4]arene-25,26,27,28-tetrol and 5,11,17,23,29,35-hexa-t-butylcalix[6]arene-37,38,39,40,41,42-hexol.[4] Shinkai *et al.* found that 37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexa-t-butylcalix[6]arene and 37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexahexylcalix[6]arene extract uranyl ion (UO_2^{2+}) efficiently and selectively as a complex with a pseudo planar penta- or hexacoor-

dinate geometry.[5] Yoshida *et al.* reported that 5,11,17,23,29,35-hexa-t-butylcalix[6]arene-37,38,39,40,41,42-hexol can extract copper(II) ions from an alkaline ammoniacal solution.[6] Masuda *et al.* reported on the extraction of silver(I), palladium(II), and nickel(II) ion with 5,11,17,23,29,35-hexa-t-butylcalix[6]arene-37,38,39,40,41,42-hexol.[7] Nagasaki *et al.* carried out extraction of transition metal cations by the derivatives of calixarenepolyols with carboxymethoxyl groups, N-hydroxycarbamoylmethoxyl groups, and N-[2-(dimethylamino)ethyl]carbamoylmethoxyl groups.[8] Ludwig *et al.* reported on the extraction of lanthanide ions with 37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexa-t-butylcalix[6]arene and 25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetra-t-butylcalix[4]arene.[9]

However, the calixarene derivatives with t-butyl groups as alkyl radicals so far investigated have poor solubility in ordinary organic diluents, such as kerosene, benzene or toluene, and, consequently, are not necessarily suitable as extractants.

In order to overcome this drawback, compounds possessing longer branched alkyl chains were designed to enhance their lipophilicity in the present work. That is,
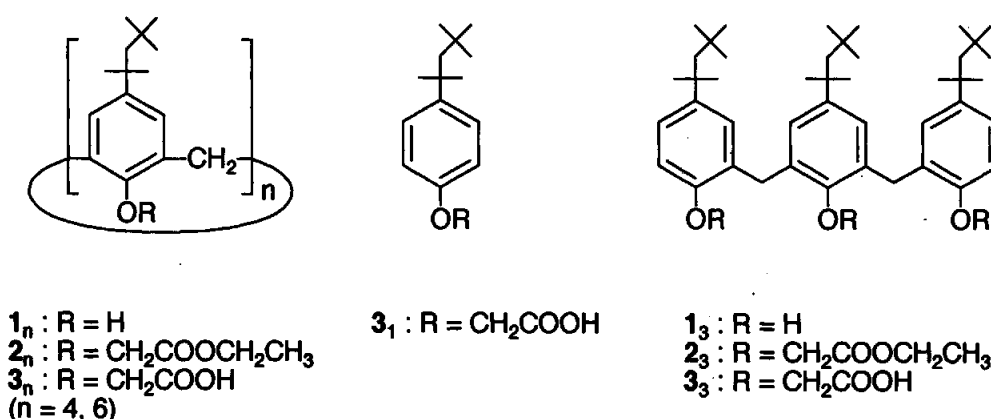
Fig. 1   Chemical structures of the extractants.

37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17, 23,29,35-hexakis(1,1,3,3-tetramethylbutyl)calix[6]arene and 25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene as new solvent extraction reagents as well as *p*-(1,1,3,3-tetramethylbutyl)phenoxyacetic acid as their monomeric analog and 2,6-bis[2-carboxymethoxy-5-(1,1,3,3-tetramethylbutyl)benzyl]-4-(1,1,3,3-tetramethylbutyl)-phenoxyacetic acid as a linear trimer analog were synthesized in order to investigate their aggregation in toluene or chloroform and their extraction behavior for rare earth metal ions, such as their discriminating ability. The mutual separation among adjacent rare earth metal ions is one of the most difficult problems in the separation of metal ions due to their similar chemical properties. In the present work, we attempted to investigate the possibility of mutual separation by making use of the subtly different ionic radii of rare earth ions. The stripping possibility for rare earth metal ions was also investigated with varying concentrations of hydrochloric acid.

Experimental

Reagent

The chemical structures of the extractants used in the present work are shown in Fig. 1.   The syntheses of the extractants were carried out according to similar manners to those for calixarene derivatives with *t*-butyl groups.

5,11,17,23,29,35-Hexakis(1,1,3,3-tetramethylbutyl)calix[6]-
arene-37,38,39,40,41,42-hexol (1_6)[10]

Under a nitrogen atmosphere to 500 cm³ of *p*-xylene were added *p*-(1,1,3,3-tetramethylbutyl)phenol (60.00 g, 276 mmol), paraformaldehyde (20.00 g, 633 mmol) and 43 cm³ of 5 mol dm⁻³ potassium hydroxide aqueous solution.   The solution was stirred at 110°C for 2 h, then refluxed at 140°C for 2 h, while removing the water by a Dean–Stark trap.   After cooling, to the solution was

added 30 cm³ of concentrated hydrochloric acid; it was then stirred for 8 h.   After removing the solvent *in vacuo*, the residue was extracted with chloroform.   The solution was washed three times with 1 mol dm⁻³ hydrochloric acid, and once with brine.   After drying with anhydrous magnesium sulfate, the solution was dried *in vacuo*; to the residue was added hexane.   The resulting crude powder was filtrated and purified by washing with carbon tetrachloride several times until a white powder was obtained, or by recrystallization with hot acetone to a boiling chloroform solution; white powder, mp (decomp)>267°C, yield 16%, TLC (SiO₂, chloroform:hexane=1:2 v/v, R_f=0.43); IR (KBr) ν_{O-H} 3180(br) cm⁻¹, $\nu_{C=C}$ 1600 and 1490 cm⁻¹; ¹H NMR (250 MHz, CDCl₃, TMS, 30°C) δ 0.71 (54H, s, C(CH₃)₃), 1.28 (36H, s, C(CH₃)₂), 1.69 (12H, s, C–CH₂–C), 3.88 (12H, s(br), Ar–CH₂–Ar), 7.11 (12H, s, ArH), 10.17 (6H, s, OH). m/z M⁺ 1311, Found: C, 73.14; H, 8.89%. Calcd for C₉₀H₁₃₂O₆·1/2CCl₄: C, 73.29; H, 8.90%.

37,38,39,40,41,42-Hexakis(ethoxycarbonylmethoxy)-
5,11,17,23,29,35-hexakis(1,1,3,3-tetramethylbutyl)calix[6]-
arene (2_6)[11]

Under a nitrogen atmosphere to 500 cm³ of *N,N*-dimethylformamide were added 1_6 (10.00 g, 7.6 mmol), ethyl bromoacetate (27.90 g, 167 mmol) and cesium carbonate (25.00 g, 76.5 mmol).   The solution was stirred at 50°C for 23 h.   After cooling, excess cesium carbonate was filtrated off, and the solvent was removed *in vacuo*.   The residue was dissolved in chloroform. The solution was washed three times with 1 mol dm⁻³ hydrochloric acid, and once with brine.   After drying with anhydrous magnesium sulfate, the solution was dried *in vacuo*, and then recrystallized with ethanol; white powder, mp 184 – 186°C, yield 50%, TLC (SiO₂, chloroform:methanol=5:1 v/v, R_f=0.48); IR (KBr) disappeared peak ν_{O-H} 3180 cm⁻¹, $\nu_{C=O}$ 1770 cm⁻¹; ¹H NMR (250 MHz, CD₃COCD₃, TMS, 30°C) δ 0.70 (54H, s, C(CH₃)₃), 1.12 (54H, s(br), C(CH₃)₂ and COOCH₂CH₃), 1.56 (12H, s, C–CH₂–C), 4.03 (24H, s(br), Ar–CH₂–Ar and COOCH₂CH₃), 4.30 (12H, s,

OCH_2COO), 6.95 (12H, s, ArH). Found: C, 75.00; H, 9.29%. Calcd for $C_{114}H_{168}O_{18}$: C, 74.96; H, 9.27%.

37,38,39,40,41,42-Hexakis(carboxymethoxy)-5,11, 17,23,29,35-hexakis(1,1,3,3-tetramethylbutyl)calix[6]arene (3₆)¹²

To 200 cm³ of tetrahydrofuran were added 2₆ (4.20 g, 2.3 mmol) and tetramethylammonium hydroxide aqueous solution (15%, 125.00 g, 206 mmol). The solution was refluxed for 22 h. After cooling, to the solution was added chloroform and the organic layer was separated. The solvent was removed *in vacuo*. The residue was extracted in chloroform. The solution was washed three times with 1 mol dm⁻³ hydrochloric acid, and four times with distilled water. After drying with anhydrous magnesium sulfate, the solution was dried *in vacuo*, and then recrystallized with methanol; white powder, mp 243 - 246°C, yield 89%, TLC (SiO₂, chloroform : methanol=5 : 1 v/v, R_f=0.01 - 0.11, tailing); IR (KBr) ν_{O-H} 3440(br) cm⁻¹, $\nu_{C=O}$ 1740 cm⁻¹; ¹H NMR (250 MHz, CD_3SOCD_3, TMS, 100°C) δ 0.73 (54H, s, $C(CH_3)_3$), 1.07 (36H, s, $C(CH_3)_2$), 1.57 (12H, s, $C-CH_2-C$), 3.97 (12H, s(br), $Ar-CH_2-Ar$), 4.23 (12H, s, OCH_2COO), 6.98 (12H, s, ArH). Found: C, 72.94; H, 8.82%. Calcd for $C_{102}H_{144}O_{18} \cdot CH_3OH$: C, 73.19; H, 8.83%.

5,11,17,23-Tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene-25,26,27,28-tetol (1₄)¹⁰

Under a nitrogen atmosphere to p-(1,1,3,3-tetramethylbutyl)phenol (100.00 g, 460 mmol) were added a formaldehyde aqueous solution (50.0 cm³, 37%, 665.5 mmol) and 8 cm³ of 4 mol dm⁻³ sodium hydroxide aqueous solution. The solution was refluxed for 2 h. To the viscous solution was added 650 cm³ of diphenyl ether. The solution was first stirred at 110°C for 2 h, then at 250°C for 9 h, while the water was removed. After cooling, to the solution was added 5 cm³ of concentrated hydrochloric acid; it was then stirred for 2 h. The solvent was removed *in vacuo*. The residual viscous oil underwent Soxhlet extraction with toluene to remove over salt. After cooling, the resulting precipitate was recrystallized again with toluene; pale-yellow prism, mp 250°C, yield 31%, TLC (SiO₂, carbon tetrachloride R_f=0.61); IR (KBr) ν_{O-H} 3150(br) cm⁻¹, $\nu_{C=C}$ 1600 and 1490 cm⁻¹; ¹H NMR (250 MHz, CDCl₃, TMS, 30°C) δ 0.54 (36H, s, $C(CH_3)_3$), 1.23 (24H, s, $C(CH_3)_2$), 1.57 (8H, s, $C-CH_2-C$), 3.50 (4H, s(br), $Ar-CH_2-Ar(exo)$), 4.36 (4H, s(br), $Ar-CH_2-Ar(endo)$), 6.99 (8H, s, ArH), 9.95 (4H, s, OH). m/z M⁺ 873, Found: C, 82.72; H, 10.06%. Calcd for $C_{60}H_{88}O_4$: C, 82.52; H, 10.16%.

25,26,27,28-Tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (cone conformation) (2₄)¹¹

Under a nitrogen atmosphere to 40 cm³ of dry acetone were added 1₄ (1.01 g, 1.1 mmol), ethyl bromoacetate (2.62 g, 15.7 mmol) and potassium carbonate (2.88 g, 20.8 mmol). The solution was refluxed for 20 h. After

cooling the excess of potassium carbonate was filtered off; the solvent was then removed *in vacuo*. The residue was dissolved in chloroform. The following procedures were similar to the method used for preparing 2₆; colorless crystal, mp 133 - 135°C, yield 71%, TLC (SiO₂, chloroform : methanol=5 : 1 v/v, R_f=0.57); IR (KBr) disappeared peak ν_{O-H} 3150 cm⁻¹, $\nu_{C=O}$ 1760 cm⁻¹; ¹H NMR (250 MHz, CDCl₃, TMS, 30°C) δ 0.69 (36H, s, $C(CH_3)_3$), 1.09 (24H, s, $C(CH_3)_2$), 1.27 (12H, t, $COOCH_2CH_3$), 1.54 (8H, s, $C-CH_2-C$), 3.17 (4H, d, $Ar-CH_2-Ar(exo)$), 4.18 (8H, q, $COOCH_2CH_3$), 4.79 (8H, s, OCH_2COO), 4.81 (4H, d, $Ar-CH_2-Ar(endo)$), 6.74 (8H, s, ArH). Found: C, 74.27; H, 9.11%. Calcd for $C_{76}H_{112}O_{12}$: C, 74.96; H, 9.27%.

25,26,27,28-Tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (cone conformation) (3₄)¹²

To 300 cm³ of tetrahydrofuran were added 2₄ (7.00 g, 5.8 mmol) and a tetramethylammonium hydroxide aqueous solution (15%, 250.01 g, 411 mmol). The following procedures were similar to the method used for preparing 3₆; white powder, mp 246 - 247°C, yield 93%, TLC (SiO₂, chloroform : methanol=5 : 1 v/v, R_f=0.01 - 0.30, tailing); IR (KBr) ν_{O-H} 3400(br) cm⁻¹, $\nu_{C=O}$ 1740 cm⁻¹; ¹H NMR (250 MHz, CD_3COCD_3, TMS, 30°C) δ 0.57 (36H, s, $C(CH_3)_3$), 1.24 (24H, s, $C(CH_3)_2$), 1.58 (8H, s, $C-CH_2-C$), 3.35 (4H, d, $Ar-CH_2-Ar(exo)$), 4.74 (8H, s, OCH_2COO), 4.81 (4H, d, $Ar-CH_2-Ar(endo)$, 7.11 (8H, s, ArH). Found: C, 73.65; H,8.62%. Calcd for $C_{68}H_{96}O_{12}$: C, 73.88; H, 8.75%.

p-(1,1,3,3,-Tetramethylbutyl)phenoxyacetic acid (3₁)

This preparation was based on a paper by Bartsch *et al.*¹³ Under a nitrogen atmosphere to sodium hydride (10.01 g, 95%, 396 mmol) was added dropwise 100 cm³ of dry tetrahydrofuran; the solution was then stirred for half an hour at room temperature. To the solution was added dropwise 300 cm³ of tetrahydrofuran containing p-(1,1,3,3-tetramethylbutyl)phenol (40.22 g, 195 mmol) for 5.5 h; the solution was then stirred for 1 h at room temperature. To the solution was added dropwise 200 cm³ of dry tetrahydrofuran containing bromoacetic acid (40.75 g, 293.3 mmol) for 4 h. To the solution was added 220 cm³ of dry tetrahydrofuran and sodium hydride (95%, 2.02 g, 84 mmol); the solution was then stirred for 1 h. To this solution was added dropwise methanol to deactivate any excess of sodium hydride in an ice bath; then, 6 mol dm⁻³ and 1 mol dm⁻³ hydrochloric acid were added. After stirring, the organic layer was separated. The organic layer was removed *in vacuo*. To the residue was added chloroform; the solution was then washed three times with 1 mol dm⁻³ hydrochloric acid and four times with distilled water. The solution was dried with anhydrous magnesium sulfate. After the solution was dried *in vacuo*, the residue was recrystallized from hexane; white needle, mp 102 - 104°C, yield 60%, TLC (SiO₂, chloroform, R_f=0.03); IR (KBr) ν_{O-H} 3040(br) cm⁻¹, $\nu_{C=O}$ 1740 cm⁻¹,

$\nu_{C=C}$ 1610 and 1510 cm⁻¹; ¹H NMR (270 MHz, CDCl₃, TMS, 30°C) δ 0.71 (9H, s, C(CH₃)₃), 1.34 (6H, s, C(CH₃)₂), 1.71 (2H, s, C-CH₂-C), 4.66 (2H, s, OCH₂COO), 6.83 (2H, d, C-C-ArH), 7.30 (2H, d, C-O-ArH). Found: C, 72.62; H, 9.04%. Calcd for C₁₆H₂₄-O₃: C, 72.69; H, 9.15%.

2,6-Bis(hydroxymethyl)-4-(1,1,3,3-tetramethylbutyl)phenol

Under a nitrogen atmosphere, to 40 cm³ of distilled water was added potassium hydroxide (85%, 8.01 g, 121 mmol). To this solution was added the mixture of 1,4-dioxane and methanol (1 : 1 v/v, total volume was 30 cm³) containing p-(1,1,3,3-tetramethylbutyl)phenol (97%, 20.00 g, 96.9 mmol); then formaldehyde aqueous solution (37 vol%, 24.63 g, 30.4 mmol) was added dropwise. The solution was stirred at room temperature (ca. 20°C) for two weeks. To the solution was added concentrated hydrochloric acid in order to adjust the pH to around 1 - 2. The final compound was extracted twice with chloroform; this organic solution was washed twice with 1 mol dm⁻³ hydrochloric acid and once with brine. After drying with anhydrous magnesium sulfate, the solution was dried in vacuo. The residue was recrystallized from hexane and dichloromethane; white needle, yield 56%; TLC (SiO₂, chloroform : ethyl acetate : hexane=1 : 3 : 2 v/v/v, R_f=0.48); mp. 70°C, IR (KBr) ν_{O-H} 3300(br) cm⁻¹; ¹H NMR (60 MHz, CDCl₃, TMS, 30°C) δ 0.71 (9H, s, C(CH₃)₃), 1.30 (6H, s, C(CH₃)₂), 1.67 (2H, s, C-CH₂-C), 2.61 (2H, s, CH₂OH), 4.77 (2H, s, ArCH₂), 7.02 (2H, s, ArH), 7.87 (1H, s, ArOH). Found: C, 72.35; H, 9.66%. Calcd for C₁₆H₂₆O₃: C, 72.15; H, 9.83%.

2,6-Bis[5-(1,1,3,3-tetramethylbutyl)salicyl]-4-(1,1,3,3-tetramethylbutyl)phenol (1₃)

Under a nitrogen atmosphere, to 90 cm³ of dry benzene p-(1,1,3,3-tetramethylbutyl)phenol (62.03 g, 300 mmol) and was added p-toluenesulfonic acid (0.10 g, 0.58 mmol). As soon as the solution was refluxed, to this solution was added dropwise 100 cm³ of dry benzene containing 2,6-bis(hydroxymethyl)-4-(1,1,3,3-tetramethylbutyl)phenol (10.00 g, 37.5 mmol). The solution was refluxed for 16 h while removing water by a Dean-Stark trap. After removing the solvent in vacuo, the excess p-(1,1,3,3-tetramethylbutyl)phenol was removed by steam distillation. The residue was extracted twice with benzene. The organic solution was washed twice with 1 mol dm⁻³ hydrochloric acid and once with brine. After drying with anhydrous magnesium sulfate, the solution was dried in vacuo. The residue was re-crystallized from hexane and dichloromethane; white powder, yield 63%; TLC (SiO₂, acetone : hexane=1 : 5 v/ v, R_f=0.22); mp. 160°C, IR (KBr) 830(br) cm⁻¹ 1,2,4-trisubstituted benzene; ¹H NMR (400 MHz, CDCl₃, TMS, 30°C) δ 0.67 (9H, s, C(CH₃)₃), 0.68 (18H, s, C(CH₃)₃×2), 1.30 (6H, s, C(CH₃)₂), 1.31 (12H, s, C(CH₃)₂×2), 1.66 (2H, s, C-CH₂-C), 1.69 (4H, s, C-CH₂-C×2), 3.89 (4H, s, ArCH₂Ar), 6.72 (2H, d, O-ArH), 7.03 (2H, d, outside C-ArH), 7.13 (2H, s, center ArH),

7.25 (2H, m, inside ArH), 7.97 (1H, s, ArOH), 8.74 (2H, s, ArOH×2). Found: C, 82.16; H, 10.51%. Calcd for C₄₄H₆₇O₃: C, 82.07; H, 10.48%.

Ethyl 2,6-bis[2-ethoxycarbonylmethoxy-5-(1,1,3,3-tetramethylbutyl)]benzyl-4-(1,1,3,3-tetramethylbutyl)phenoxyacetate (2₃)[12]

Under a nitrogen atmosphere, to 50 cm³ of dry tetrahydrofuran was added 1₃ (7.00 g, 10.8 mmol); to the solution was then added sodium hydride (oily, 60%, 1.56 g, 39.1 mmol) and stirred to reflux for 2 h. After cooling the solution at room temperature, to the solution was added dropwise ethyl bromoacetate (7.54 g, 45.1 mmol). The solution was refluxed for 35 h. After cooling, to the solution ethanol was carefully added dropwise in order to deactivate any excess sodium hydride in the ice bath. After the organic solvent was removed in vacuo, ethyl acetate was added. The organic layer was washed twice with 1 mol dm⁻³ hydrochloric acid and then once with brine. After drying with anhydrous magnesium sulfate, the solution was dried in vacuo. The excess ethyl bromoacetate was removed by a vacuum pump. The crude product was purified by column chromatography (SiO₂, acetone : hexane=1 : 5 v/v); yellow viscous liquid, yield 97%; TLC (SiO₂, acetone : hexane=1 : 5 v/v, R_f=0.35); IR (KBr) disappeared peak ν_{O-H} 3200(br) cm⁻¹, $\nu_{C=O}$ 1750(br) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS, 30°C) δ 0.57 (9H, s, C(CH₃)₃), 0.69 (18H, s, C(CH₃)₃×2), 1.13 (6H, s, C(CH₃)₂), 1.23 (12H, s, C(CH₃)₂×2), 1.25 (9H, t+t, CH₂CH₃×3), 1.49 (2H, s, C-CH₂-C), 1.65 (4H, s, C-CH₂-C×2), 4.10 (4H, s, ArCH₂Ar), 4.23 (6H, q+q, CH₂CH₃×3), 4.42 (2H, s, OCH₂COO), 4.55 (4H, s, OCH₂COO×2), 6.66 (2H, d, O-ArH), 6.84 (2H, s, center ArH), 7.11 (4H, m, outside and inside ArH). Found: C, 74.91; H, 9.41%. Calcd for C₅₆H₈₅O₉: C, 74.55; H, 9.50%.

2,6-Bis[2-carboxymethoxy-5-(1,1,3,3-tetramethylbutyl)benzyl]-4-(1,1,3,3-tetramethylbutyl)phenoxyacetic acid (3₃)[12]

To 300 cm³ of tetrahydrofuran was added 2₃ (12.56 g, 13.9 mmol), tetramethyl ammonium hydroxide aqueous solution (25%, 148.69 g, 417.5 mmol), and 90 cm³ of water. The following procedures were similar to the method used to prepare 3₆. The resulting crude product was purified by column chromatography (SiO₂, chloroform); pale yellow viscous oil, yield 68%, TLC (SiO₂, chloroform : methanol=5 : 1 v/v, R_f=0.00 - 0.10, tailing); IR (neat) ν_{O-H} 3160(br) cm⁻¹, $\nu_{C=O}$ 1740(br) cm⁻¹; ¹H NMR (270 MHz, CDCl₃, TMS, 30°C) δ 0.56 (9H, s, C(CH₃)₃), 0.70 (18H, s, C(CH₃)₃×2), 1.17 (6H, s, C(CH₃)₂), 1.29 (12H, s, C(CH₃)₂×2), 1.50 (2H, s, C-CH₂-C), 1.67 (4H, s, C-CH₂-C×2), 4.04 (4H, s, ArCH₂Ar), 4.47 (2H, s, OCH₂COO), 4.53 (4H, s, OCH₂COO×2), 6.66 (2H, d, C-ArH), 6.88 (2H, s, center ArH), 7.15 (4H, m, outside and inside O-ArH), 8.33 (3H, s(br), OH). Found: C, 72.80; H, 8.66%. Calcd for C₅₀H₇₂O₉: C, 73.50; H, 8.88%.

Measurement of aggregation of the extractants

The procedure was a similar manner to the previous paper.[14]

Distribution equilibria of rare earth metal ions

An organic solution was prepared by diluting each extractant into an analytical grade of toluene or chloroform to desired concentrations. The following three kinds of aqueous solutions, each of which contained three different kinds of rare earth ions, were prepared by dissolving the analytical grade of rare earth chlorides into 0.1 mol dm^{-3} aqueous nitric acid or sodium nitrate or glycine solutions: the first one contained La, Pr, and Nd, the second Sm, Eu, and Gd, and the third Ho, Er, and Y. The concentration of each rare earth metal ion was 1×10^{-4} mol dm^{-3}. The initial pH was adjusted by mixing the following stock solutions at an arbitrary volume ratio, *i.e.* 0.1 mol dm^{-3} nitric acid–0.1 mol dm^{-3} glycine. Equal volumes of both phases were mixed and shaken vigorously at 30°C for more than 7 h, which was long enough to reach equilibrium. After phase separation, the concentrations of the rare earth metal ions in the aqueous phase before and after equilibration were measured by ICP-AES (Seiko SPS 1200VR and Shimadzu ICPS-1000 III). The amount of extracted metal ions was calculated from the differences between the metal concentrations in the aqueous phase before and after equilibration.

Stripping test

An organic solution was prepared by dissolving each extractant into analytical grade chloroform. The aqueous solution was prepared by using the above-mentioned stock solutions. In the present experiment, only three kinds of light rare earth elements, La, Pr , and Nd, were selected for stripping tests, since they were the most extractable metals with the present extractants as mentioned later. The initial pH of the aqueous phase was adjusted so that 100% of the metal ions could be extracted into the organic phase; 50 cm^3 of chloroform solutions containing each extractant were equilibrated with equal volumes of aqueous solutions containing rare earths. Ten cubic centimeters of separated organic solutions were equilibrated with equal volumes of hydrochloric acid solutions for at least 15 h in order to strip the loaded metal ions. The concentrations of the metal ions in the initial aqueous solutions, the raffinates, and the stripped solutions were measured in order to calculate the stripped percentage of metal ions, similarly to those in the case of extractions.

Results and Discussion

Solubility and aggregation of the extractants in organic diluents

The solubility in toluene of the new reagents synthesized in the present work was much higher than those of the corresponding derivatives of *t*-butyl-

calixarenes; especially, 37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexakis(1,1,3,3-tetramethylbutyl)calix[6]arene was dissolved in toluene to a concentration as high as more than 0.1 mol dm^{-3}, whereas the corresponding derivatives of *t*-butylcalixarene were dissolved as low as only 1.3×10^{-3} mol m^{-3}.

As is well known, some acidic extractants dimerize in non-polar organic diluents as follows:[15]

$$2HR \rightleftharpoons (HR)_2 \quad : K_d. \tag{1}$$
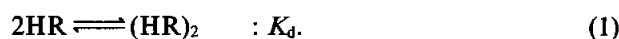
The total concentration (C_T) and the summation of the concentration of the monomeric and dimeric species in the organic solution (C^*), which can be measured experimentally, are expressed as follows:[16]

$$C_T = [HR] + 2[(HR)_2] \tag{2}$$

and

$$C^* = [HR] + [(HR)_2]. \tag{3}$$

From Eqs. (2) and (3), the dimerization constant (K_d) and the average aggregation number (m) are expressed as follows:

$$K_d = [(HR)_2]/[HR]^2 = (C_T - C^*)/(2C^* - C_T)^2 \tag{4}$$

and

$$m = C_T/C^*. \tag{5}$$

The relation between the average aggregation numbers, m, and the total concentrations, C_T, of 3_6 and 3_4 in both toluene and chloroform, as well as those of 3_1 in chloroform are shown in Fig. 2. This figure suggests that the majority of 3_4 exists as the dimeric species in toluene under the present experimental conditions, while 3_6 in toluene or chloroform and 3_4 in chloroform exists as mixtures of the monomeric and dimeric species. The majority of 3_1 exists as the monomeric species in chloroform. The values of $[(HR)_2]$ were plotted against that of $[HR]^2$ according to Eq. (4) in order to evaluate the dimerization constants, K_d, for each extractant, as shown in Fig. 3. The evaluated values of K_d are listed in Table 1 (the aggregation for 3_3 was not able to be measured because of slight amount of impurities).

Distribution equilibria of rare earth metal ions

The effect of the pH on the distribution ratio in the extraction from aqueous mixtures of 0.1 mol dm^{-3} nitric acid–glycine with 3_6, 3_4, 3_1 and 3_3 is shown in Figs. 4(a) – (e), respectively. The all plots lie on a straight line with a slope of 3, indicating that three protons are released from the extractants according to cation-exchange mechanism by a trivalent rare earth ion.

Figures 4(a) and (b) show that the extractions take place in a similar pH region as 3_6, suggesting that there appears not to be dependency concerning the extraction
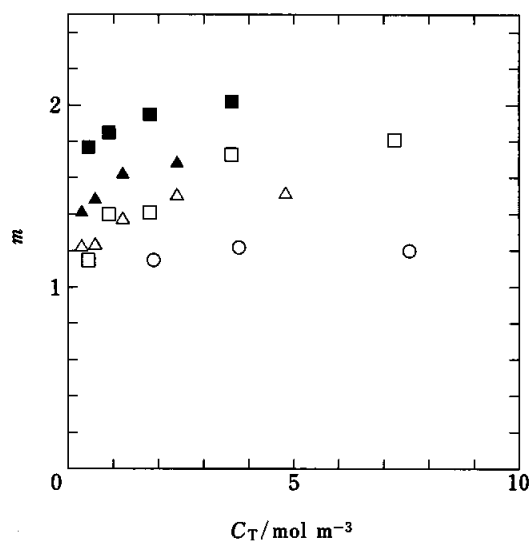
Fig. 2   Relation between the average aggregation numbers and total concentrations of the extractants. ▲, 3_6 in toluene; △, 3_6 in chloroform; ■, 3_4 in toluene; □, 3_4 in chloroform; ○, 3_1 in chloroform.
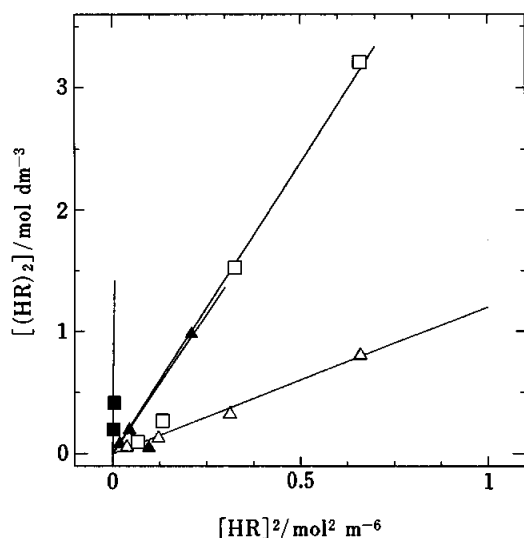

Fig. 3   Relation between concentration of dimeric and monomeric species. ▲, 3_6 in toluene; △, 3_6 in chloroform; ■, 3_4 in toluene; □, 3_4 in chloroform.

Table 1   Dimerization constants for the extractants

Extractant	Diluent	$K_d/\mathrm{dm^3\ mol^{-1}}$
3_6	toluene	4.54×10^{-3}
3_6	chloroform	1.21×10^{-3}
3_4	toluene	7.00×10^{-2}
3_4	chloroform	4.78×10^{-3}
3_1	chloroform	1.03×10^{-4}

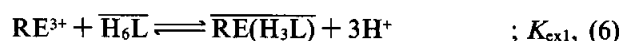on the diluent whether it is toluene or chloroform.

From a comparison between Figs. 4(b) and (c), the pH at which the extraction takes place is shifted to a higher pH in the latter, suggesting that the extractant, 3_6, has a higher extractability than 3_4. This difference in the extractability between the two extractants may be attributable to the total number of the functional groups in the extractants. That is, since, under the present extraction condition, the concentration of the extractant was the same (5 mM) in the both cases, the total number of functional carboxyl groups in 3_6 and 3_4 was six (30 mM) and four (20 mM), respectively. Similarly, the extractant, 3_3, has a slightly higher extractability than 3_4 based on a comparison between Figs. 4(c) and (d). Under the present extraction condition, since the concentration of 3_4 and 3_3 was also the same, the total number of the functional groups was four (20 mM) and three (15 mM), respectively. In spite of the greater total number of functional groups for 3_4 than for 3_3, the extractability of 3_4 was lower than that of 3_3, which is considered to be due to the structural difference in the extracted complexes; because the extractant, 3_3, is linear and an acyclic compound, while 3_4 is a cyclic one, the former is more flexible than 3_4. In complexation with a rare earth metal ion, it is considered that the cyclic extractant gives rise to more a distored complex than does the acyclic one, suggesting that the strain due to the structure of the extractant in complexation causes a contraction of the extractability.

As a result, the order of extractability for rare earths among these extractants is as follows:
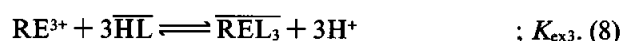
$$3_6 > 3_3 > 3_4 > 3_1.$$

The effect of the extractant concentration on the distribution ratio is shown in Figs. 5(a) and (b) for three types of extractants. In Fig. 5(a), it is plotted against the concentration of the monomeric species of 3_6 and 3_1, while in Fig. 5(b) it is against that of the dimeric species of 3_4 calculated from Eq. (2) using the value of the dimerization constants evaluated earlier (the dimerization constant of 3_3 could not be measured by a vapor-phase osmometer due to the presence of a slight amount of impurity). The plots for 3_6 and 3_4 lie on straight lines with a slope of 1, while those for 3_1 lie on straight lines with a slope of 3.

On the basis of these results, the stoichiometric relations for the extraction of a trivalent rare earth ion are represented for 3_6, 3_4 and 3_1 as follows:

$$\mathrm{RE^{3+} + \overline{H_6L} \rightleftharpoons \overline{RE(H_3L)} + 3H^+} \qquad ; K_{ex1}, \ (6)$$

$$\mathrm{RE^{3+} + \overline{(H_4L)_2} \rightleftharpoons \overline{RE(H_2L)(H_3L)} + 3H^+} \qquad ; K_{ex2}, \ (7)$$

and

$$\mathrm{RE^{3+} + 3\overline{HL} \rightleftharpoons \overline{REL_3} + 3H^+} \qquad ; K_{ex3}. \ (8)$$

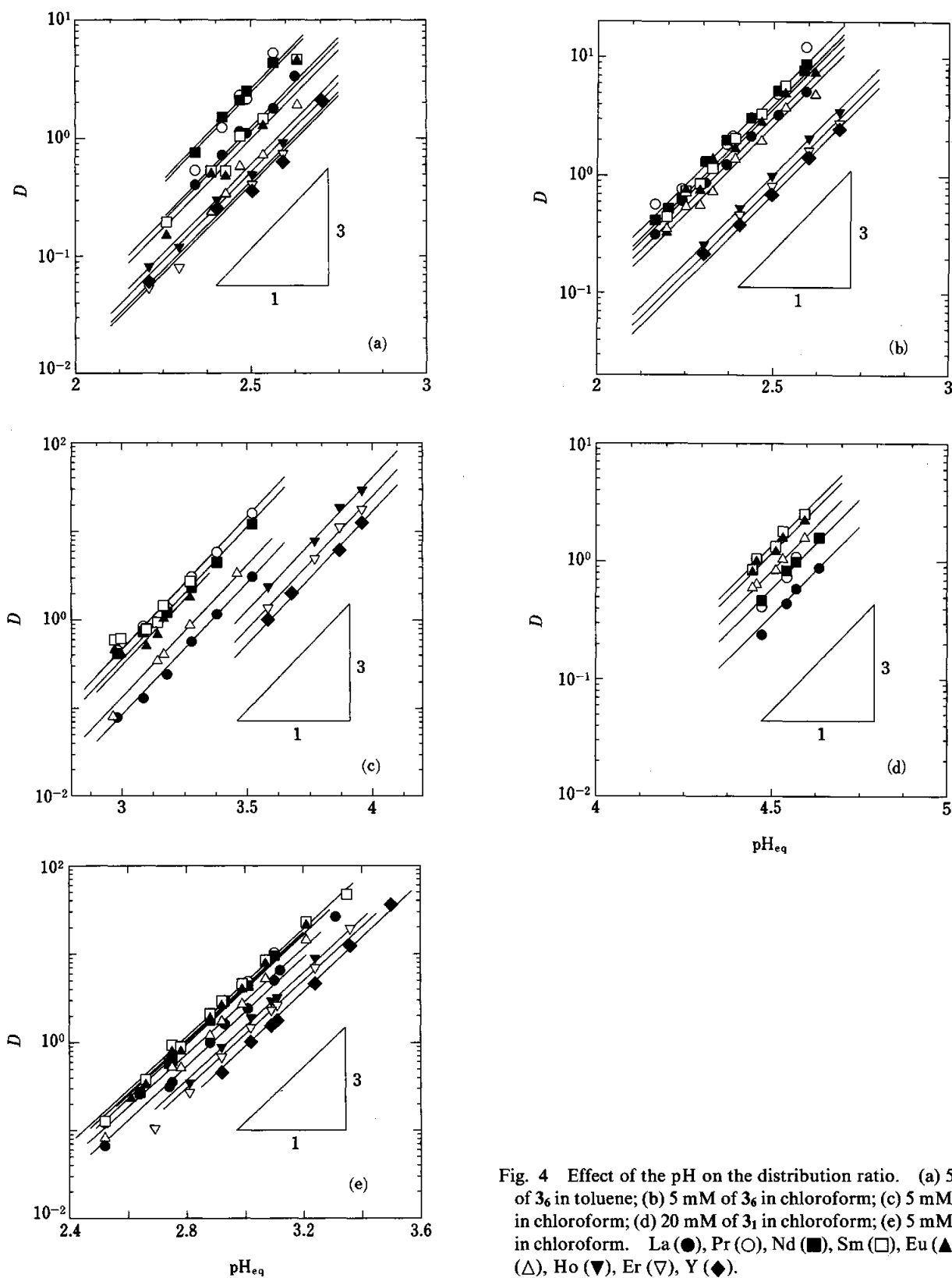where RE, H_6L, H_4L, and HL denote the rare earth

Fig. 4 Effect of the pH on the distribution ratio. (a) 5 mM of 3_6 in toluene; (b) 5 mM of 3_6 in chloroform; (c) 5 mM of 3_4 in chloroform; (d) 20 mM of 3_1 in chloroform; (e) 5 mM of 3_3 in chloroform. La (●), Pr (○), Nd (■), Sm (□), Eu (▲), Gd (△), Ho (▼), Er (▽), Y (◆).

elements, extractant 3_6, 3_4 and 3_1, respectively. The overline $(\overline{})$ denotes the species present in the organic phase. For extraction with 3_4, the 1 : 2 complex of the metal ion and the extractant was confirmed by Job's method[17] (on the basis of the order of the acid

dissociation in 3_4, a major component of the complex is not $RE(HL)(H_4L)$, but $RE(H_2L)(H_3L)$).

The extraction equilibrium constants are defined as

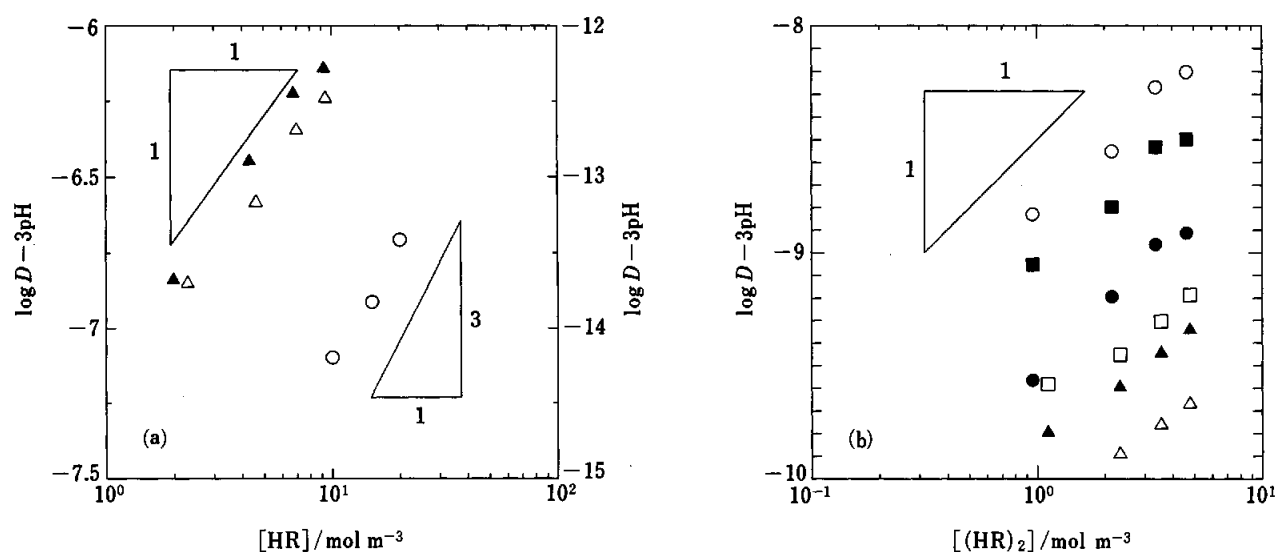$$K_{ex1} = [\overline{RE(H_3L)}][H^+]^3/([RE^{3+}][\overline{H_6L}]), \tag{9}$$

Fig. 5 Effect of the concentration of the extractants on the distribution ratio. (a) ▲, La with 3_6 in toluene (left ordinate); △, Sm with 3_6 in chloroform (left ordinate); ○, Nd with 3_1 in chloroform (right ordinate). (b) La (●), Pr (○), Nd (■), Sm (□), Eu (▲), Gd (△) with 3_4 in chloroform.

Table 2 Extraction equilibrium constants for the extractants

	$K_{ex1}{}^a$	$K_{ex1}{}^a$	$K_{ex2}{}^a$	$K_{ex3}{}^a$
Extractant: 3_6 Diluent: Toluene	3_6 Chloroform	3_4 Chloroform	3_1 Chloroform
La	7.97×10⁻⁶	1.98×10⁻⁵	3.37×10⁻⁸	1.38×10⁻⁹
Pr	1.55×10⁻⁵	2.97×10⁻⁵	1.86×10⁻⁷	2.32×10⁻⁹
Nd	1.67×10⁻⁵	2.97×10⁻⁵	1.43×10⁻⁷	2.32×10⁻⁹
Sm	7.21×10⁻⁶	2.50×10⁻⁵	1.88×10⁻⁷	5.36×10⁻⁹
Eu	6.21×10⁻⁶	2.32×10⁻⁵	1.22×10⁻⁷	4.62×10⁻⁹
Gd	3.79×10⁻⁶	1.68×10⁻⁵	5.34×10⁻⁸	3.27×10⁻⁹
Ho	3.28×10⁻⁶	6.46×10⁻⁶	1.63×10⁻⁸	
Er	2.76×10⁻⁶	5.30×10⁻⁶	9.98×10⁻⁹	
Y	2.56×10⁻⁶	4.46×10⁻⁶	6.72×10⁻⁹	

a. K_{ex1}, K_{ex2} and K_{ex3} were evaluated from Eqs. (12), (13) and (14), respectively.

$$K_{ex2} = \overline{[RE(H_2L)(H_3L)]}[H^+]^3/([RE^{3+}]\overline{[(H_4L)_2]}), \quad (10)$$

and

$$K_{ex3} = \overline{[REL_3]}[H^+]^3/([RE^{3+}]\overline{[HL]}^3). \quad (11)$$

The logarithms of the Eqs. (9), (10) and (11) and the definition of distribution ratio give

$$\log K_{ex1} = \log D - 3pH - \log\overline{[H_6L]}, \quad (12)$$

$$\log K_{ex2} = \log D - 3pH - \log\overline{[(H_4L)_2]}, \quad (13)$$

and

$$\log K_{ex3} = \log D - 3pH - 3\log\overline{[HL]}. \quad (14)$$

The separation factor (β) is defined as

Table 3 Separation factors for the extractants

	β (1/β)			
Extractant: 3_6 Diluent: Toluene	3_6 Chloroform	3_4 Chloroform	3_1 Chloroform
La				
	1.94	1.50	5.53	1.68
Pr				
	1.08	1.00	0.769(1.30)	1.00
Nd				
	0.433(2.31)	0.841(1.19)	1.31	2.31
Sm				
	0.861(1.16)	0.929(1.08)	0.652(1.53)	0.862(1.16)
Eu				
	0.610(1.64)	0.726(1.38)	0.437(2.29)	0.708(1.41)
Gd				
	0.865(1.16)	0.382(2.61)	0.305(3.28)	
Ho				
	0.841(1.19)	0.820(1.22)	0.612(1.66)	
Er				
	0.928(1.08)	0.842(1.19)	0.673(1.49)	
Y				

$$\beta = K_{ex}(RE')/K_{ex}(RE), \quad (15)$$

where RE' denotes the adjacent and rare earth element with a higher atomic number. The extraction equilibrium constants and the separation factors are listed in Tables 2 and 3, respectively (yttrium was placed next to erbium for convenience). The separation efficiencies by all of the present extractants were inferior to those of di(2-ethylhexyl)hydrogenphosphate (D2EHPA) or 2-ethylhexyl hydrogen(2-ethylhexyl)phosphonate (PC-88A), one of the most effective, commercial acidic organophosphorus extractants for rare earth metal ions.
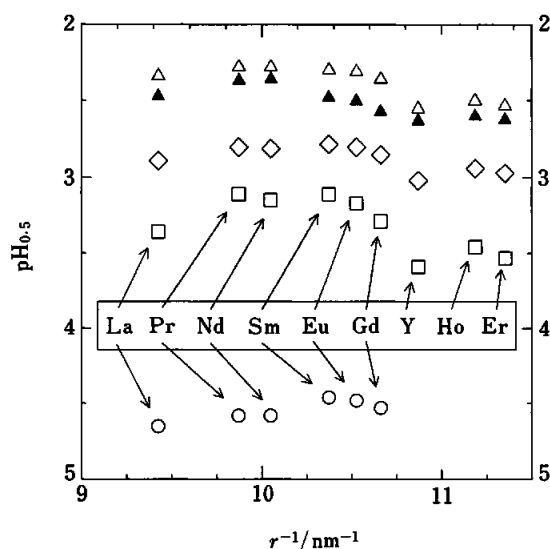
Fig. 6   Relation between $pH_{0.5}$ and reciprocal of ionic radius of each rare earth element. ▲, 3_6 in toluene; △, 3_6 in chloroform; □, 3_4 in chloroform; ○, 3_1 in chloroform; ◇, 3_3 in chloroform.

However, 3_6 and 3_4 have higher extractabilities and separation efficiencies than does 3_1, which are attributed to the chelate effects of multi-functional groups and the rigid skeletons of calixarenes, respectively.

Figure 6 shows that the relation between $pH_{0.5}$ and the reciprocal of the ionic radius for rare earth elements for each extractant, where $pH_{0.5}$ indicates the pH where 50% of metal ion is extracted into the organic phase under the present condition. The plots appear to lie on convex curves. However, there appears no correlation between the selectivity and the cavity size of the extractant. Both 3_6 and 3_4 have the maximum $pH_{0.5}$ at praseodymium, while it appears to be located at samarium in the case of the monomeric analog. Also, for the trimeric analog, 3_3, it is also located at samarium. Since all of the extractants examined in the present work have the same functional groups, carboxylic groups, the difference in the maximum points is considered to be attributable to their cyclic or acyclic structure.

Stripping test

The relation between the concentration of hydrochloric acid and the stripping fraction percentage of the loaded rare earth metal ions is listed in Table 4. The diluted hydrochloric acid (0.1 mol dm^{-3}) was sufficient to effectively strip the loaded metal ions. We found that the higher is the hydrochloric acid concentration, the lower is the stripped ratio percentage of metal ions, especially in cyclic compounds, which appears to be inconsistent with the cation-exchange extraction mechanism of these extractants. These results might be attributable to another mechanism that is different from the cation-exchange by carboxyl groups, *e.g.* the coordination by carbonyl groups in the high concentration range of hydrochloric acid (ion-pair extraction

Table 4   Relation between concentration of hydrochloric acid and stripping fraction percentage of rare earth metal ions

Extractant	[HCl]/mol dm^{-3}	Stripping, %		
		La	Pr	Nd
3_6	0.01	94	94	98
	0.1	89	83	94
	1	55	53	58
	6	5	0	4
3_4	0.01	100	94	89
	0.1	100	100	100
	1	60	70	73
	6	56	55	56
3_1	0.01	100	100	100
	0.1	100	100	100
	1	97	98	99
	6	90	91	90

with chloride anion).

References

1. C. D. Gutsche, "*Calixarenes*", Royal Society of Chemistry, Cambridge, 1989.
2. J. Vicens and V. Bohmer, "*Calixarenes: A Versatile Class of Macrocyclic Compounds*", Kluwer Academic Publishers, Netherlands, 1992.
3. M. Takeshita and S. Shinkai, *Bull. Chem. Soc. Jpn.*, **68**, 1088 (1995).
4. R. M. Izatt, J. D. Lamb, R. T. Hawkins, P. R. Brown, S. R. Izatt and J. J. Christensen, *J. Am. Chem. Soc.*, **105**, 1782 (1983).
5. S. Shinkai, Y. Shirahama, H. Satoh, O. Manabe, T. Arimura, K. Fujimoto and T. Matsuda, *J. Am. Chem. Soc.*, **108**, 2409 (1986).
6. I. Yoshida, S. Fujii, K. Ueno, S. Shinkai and T. Matsuda, *Chem. Lett.*, **1989**, 1535.
7. Y. Masuda, T. Sawano and E. Sekido, *Anal. Sci.*, **7** (supplement), 31 (1991).
8. T. Nagasaki and S. Shinkai, *Bull. Chem. Soc. Jpn.*, **65**, 471 (1992).
9. R. Ludwig, K. Inoue and T. Yamato, *Solvent Extr. Ion Exch.*, **11**, 311 (1993).
10. C. D. Gutsche, B. Dhawan, K. H. No and R. Muthukrishnan, *J. Am. Chem. Soc.*, **103**, 3782 (1981).
11. F. A. Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. Mckervey, E. Marques, B. L. Ruhl, M. J. S. Weill and E. M. Seward, *J. Am. Chem. Soc.*, **111**, 8681 (1989).
12. S.-K. Chang and I. Cho, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 211.

13. M. J. Pugia, G. Ndip, H. K. Lee, I. W. Yang and R. A. Bartsch, *J. Am. Chem. Soc.*, **58**, 2723 (1986).

14. K. Ohto, K. Inoue, M. Goto, F. Nakashio, T. Nagasaki, S. Shinkai and T. Kago, *Bull. Chem. Soc. Jpn.*, **66**, 2528 (1993).

15. J. R. Ferraro, G. W. Mason and D. F. Peppard, *J. Inorg. Nucl. Chem.*, **22**, 285 (1961).

16. F. Nakashio, K. Kondo, A. Murakami and Y. Akiyoshi, *J. Chem. Eng. Jpn.*, **15**, 274 (1982).

17. T. Nishiyori, M. Goto and F. Nakashio, unpublished data.