Structural Effect of Phosphoric Esters Having Bulky Substituents on the Extraction of Rare Earth Elements

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Phosphoric esters having bis(4-ethylcyclohexyl) (D4ECHPA) and bis(4-cyclohexylcyclohexyl) (D4DCHPA) groups as the alkyl substituents were synthesized in order to investigate their selectivity in the extraction of rare earth elements from acidic nitrate media, together with the apparent molecular weights of the extractants in toluene, the acid dissociation constants and the aqueous distribution coefficients of the extractants. These extractants were found to exist as dimeric species in toluene. The acid dissociation constants of the extractants are nearly the same as that of bis(2-ethylhexyl) hydrogenphosphate (D2EHPA), which is a typical commercial acidic phosphorus extractant. The aqueous distribution coefficients of the extractants become greater in the order D4ECHPA>D2EHPA>D4DCHPA. From the concentration dependencies of the hydrogen ion and extractant on the distribution ratio of rare earth elements, it was concluded that the rare earth elements (M^{3+}) were extracted with D4ECHPA and D4DCHPA (HR) as $M(HR_2)_3$ in the organic phase; also, the extraction equilibrium constants (K_{ex}) were evaluated. The extraction equilibrium constants of rare earth elements become greater in the order D4DCHPA>D4ECHPA>D2EHPA. It was very noticeable that the separation factor between Ho^{III} and Gd^{III}, β(Ho/Gd), and β(Yb/Y) with D4ECHPA, and β(Ce/La), β(Pr/La), and β(Ho/Gd) with D4DCHPA are significantly greater than those with D2EHPA. The structural effects of the extractant on the selectivity of rare earth elements are discussed in terms of the molecular modelling. Furthermore, we found that the loading capacity of Nd^{III} with these extractants is excellent compared with that of D2EHPA, due to preventing gelation of the organic phase.

Extractants for the commercial-scale separation of rare earth elements should satisfy at least the following three requirements: (1) high loading capacity without any gel formation at high loading, (2) ease of stripping, in addition to, (3) high selectivity among adjacent rare earth elements. The majority of commercial separation and refining of rare earth elements has been carried out by means of solvent extraction with bisalkyl hydrogenphosphates, especially bis(2-ethylhexyl) hydrogenphosphate (henceforth, abbreviated as D2EHPA), and many fundamental studies on the extraction of rare earth elements have been conducted[1—10]. Although these extractants provide fairly good separation factors between adjacent rare earth elements, the extracted metal complexes are apt to polymerize to give rise to a gel that is insoluble in organic diluents at approximately 50% saturation, which greatly limits the effective use of the extractants. One approach to the design of extractant molecules without gel formation at high loading may be to introduce bulky substituents, which may impede the mutual approach of metal complexes for polymerization. Recently, Ishida et al.[11—13] reported on the structural effect of phosphoric esters having bulky alkyl groups on the equilibrium extraction of rare earth elements. They synthesized ten kinds of bisalkyl hydrogenphosphates containing alicyclic and/or aliphatic alkyl groups, and measured the extraction of rare earth elements. It was found that the position of the bulky substituents in the bisalkyl hydrogenphosphates is closely related to the extractability and selectivity of the rare earth elements.

In the present study, bis(4-ethylcyclohexyl) hydrogenphosphate (abbreviated as D4ECHPA henceforth, and expressed as HR for monomeric species, and H_2R_2 for dimeric species) and bis(4-cyclohexylcyclohexyl) hydrogenphosphate (henceforth abbreviated as D4DCHPA), as shown in Fig. 1 were synthesized in order to investigate the extraction behavior for rare earth elements from acidic aqueous nitrate media, together with the apparent molecular weight of the extractant in toluene by means of vapor phase osmometry and the acid dissociation constants of the extractants by potentiometric titration. The structural effect of these extractants on the extractability and selectivity of rare earth elements are discussed from the view point of molecular modelling with molecular mechanics and semi-empirical molecular orbital methods. Furthermore, the loading capacities of Nd^{III} with these extractants were carried out in order to compare them with that of D2EHPA from the view point mentioned above.

Experimental

Synthesis of Extractants. Bis(4-ethylcyclohexyl) Hydrogenphosphate (D4ECHPA). Scheme 1. 4-Ethylcyclohexanol was mixed together with phosphorus trichloride in dehydrated benzene using triethylamine as a catalyst. The mixture was refluxed for 12 h under a nitrogen atmosphere. The mixture was then washed sequentially with water, 0.5 mol dm^{-3} sulfuric acid several times by turns and finally with water to obtain a neutral pH. The water phase was discharged and the organic phase was evaporated to remove benzene and a byproduct (4-ethylcyclohexyl chloride), and to obtain the intermediate product {bis(4-ethylcyclohexyl) phospho-

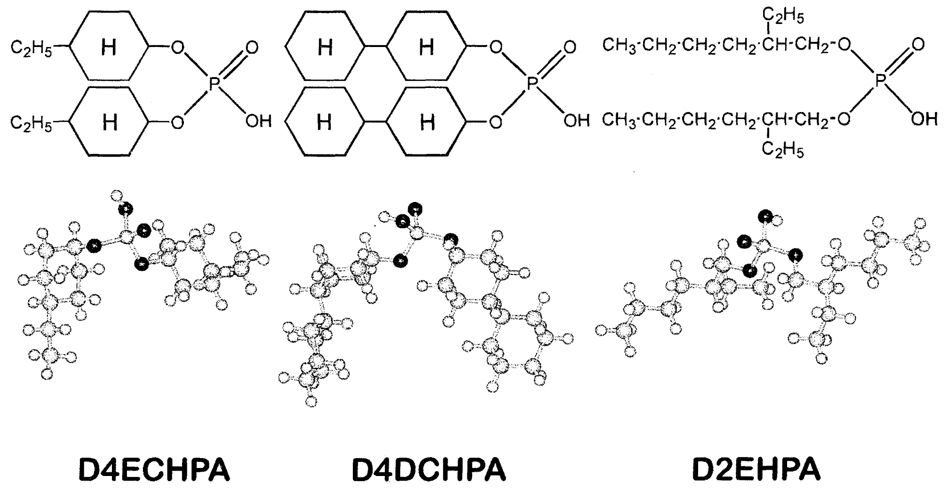
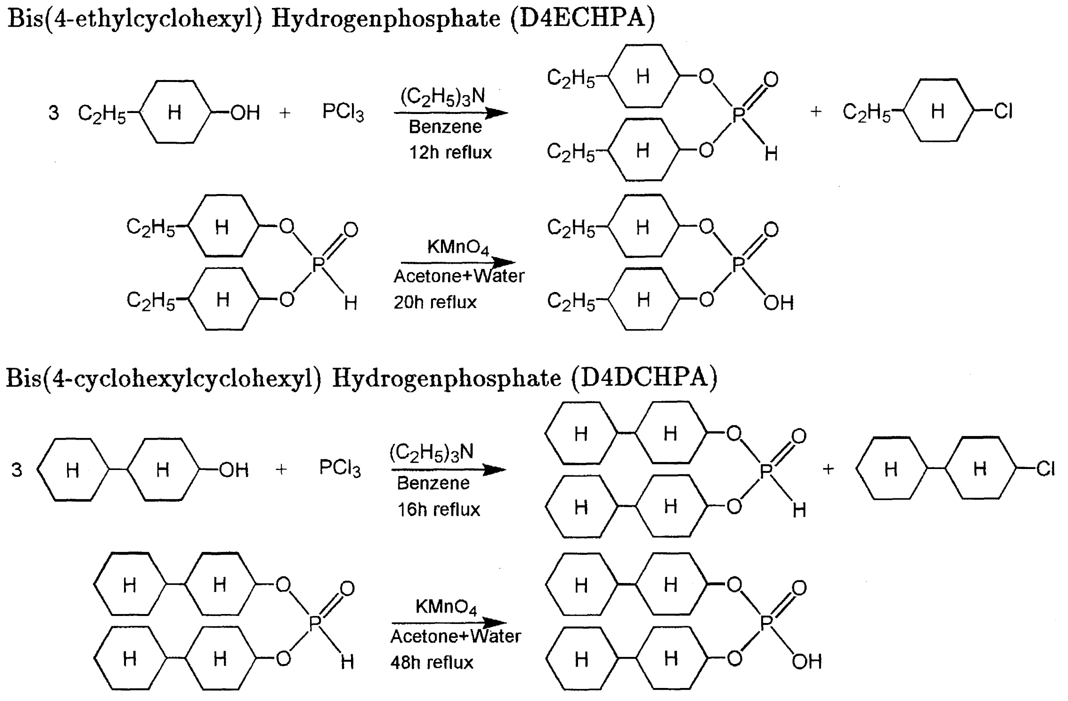


Fig. 1. Chemical structures of D4ECHPA, D4DCHPA, and D2EHPA.



Scheme 1. Synthetic route of D4ECHPA and D4DCHPA.

nate}. The intermediate product was refluxed for 20 h in a mixture of acetone and water with potassium permanganate as an oxidant. After ethanol was added to the solution, the solution was filtered and evaporated. Benzene was added to the residue, and the solution was washed sequentially with water, a mixture of 0.5 mol dm^{-3} sulfuric acid and hydrogen peroxide several times and finally with water to become neutral pH. The water phase was discarded and the organic phase was evaporated in order to remove benzene and to obtain the final product (D4ECHPA). The final product was recrystallized from ethyl acetate. Product identification was carried out by infrared and ^{1}H NMR spectroscopies. The elemental analysis of the product was obtained as follows: Found: C, 60.43; H, 9.80%. Calcd for $C_{16}H_{31}O_4P$: C, 60.36; H, 9.81%.

Bis(4-cyclohexylcyclohexyl) Hydrogenphosphate (D4DCHPA). Scheme 1. The synthetic procedures and identificantions of D4DCHPA were almost the same as that of D4ECHPA. The elemental analysis of the product was obtained as follows: Found: C, 67.48; H, 10.18%. Calcd for $C_{24}H_{43}O_4P$: C, 67.57; H, 10.16%.

Materials. The D2EHPA used for a comparison was delivered from Daihachi Chemical Industry Co., Ltd. (Lot No. K20801). The purity of D2EHPA was found to be above 98% by means of neutralization titration. An organic solution was prepared by dissolving the extractants in reagent grade toluene to the required concentration gravimetrically. The aqueous solutions were prepared by dissolving oxides of the corresponding rare earth elements in aqueous mixtures of 1 mol dm^{-3} nitric acid and 1 mol dm^{-3} solution nitrate. The purity of the oxides of the rare earth elements was greater than 99.99%.

Apparent Molecular Weights of Extractants. The apparent molecular weights of the extractants in toluene were measured at 313 K with a Hitachi model 117 vapor-phase osmometer, using benzil as a standard material.

Acid Dissociation Constants of Extractants. The determination of the acid dissociation constants (pK_a) of the extractants was carried out at 303 K by potentiometric titration, as described by Preston.[14)] The samples (0.01 mol) dissolved in a mixture of 20 ml of 2-propanol and 20 ml of 0.2 mol dm^{-3} aqueous sodium nitrate were titrated potentiometrically by 0.1 mol dm^{-3} aqueous sodium hydroxide.

Aqueous Distribution of Extractants. The aqueous distribution of the extractants between toluene and the aqueous nitrate media was measured at 303 K by a previously reported method.[15)] The pH of the aqueous phases was adjusted to 3.2 and 1.0, respectively. The concentration of phosphor in the aqueous phase was measured using a Shimadzu model ICP-1000III inductively coupled plasma atomic emission spectrometer to determine the concentration of phosphor atom of the extractants.

Extraction Equilibria. The measurement of the extraction equilibria of rare earth elements was carried out batchwise by the conventional method.[16)] The two phases were shaken for 24 h in a water bath incubator maintained at 303 K to attain equilibrium. The concentration of the rare earth element was measured using an inductively coupled plasma atomic emission spectrometer. The amount of rare earth elements extracted was calculated from the difference of the concentration in the aqueous phase before and after equilibration. The experimental conditions were as follows: initial concentration of rare earth elements = 5×10^{-4} mol dm^{-3}, initial concentration of the extractant = 3×10^{-3}—0.1 mol dm^{-3}, and initial pH of aqueous phase = 0.5—6.5.

Loading Test of a Rare Earth Element. In order to examine the loading capacity of the extractants for the rare earth elements, loading tests were carried out for Nd$^{\mathrm{III}}$ as a rare earth element. The experimental procedures were the same that mentioned above. The loaded organic phase was first separated from the aqueous phase, and then a fresh aqueous solution was added for further extraction. The extraction was repeated until the Nd$^{\mathrm{III}}$ concentration in the aqueous phase did not change before and after extraction. The experimental conditions were as follows: initial concentration of Nd$^{\mathrm{III}}$ = 5×10^{-3} mol dm^{-3}, initial concentration of extractant = 5×10^{-2} mol dm^{-3}, and initial pH of aqueous phase = 3.0.

Molecular Modelling Computation. Molecular modelling computations for the extractants and their rare earth complexes were carried out using the molecular modelling software HyperChem™ Release 4 (Hypercube, Inc., Canada). A molecular mechanics program, MOMEC,[17)] was used to obtain the optimal structures and heat of formation. The convergence criterion for the MOMEC computation was set at an RMS gradient of 0.001. Semi-empirical PM3 type of molecular orbital calculations of the extractant molecules were carried out using MOPAC93.[18)] A precise mode was used which set the convergence criteria for GNORM = 0.01 and SCFRT = 0.00001. The characteristics of D4ECHPA, D4DCHPA, and D2EHPA, i.e., the molecular weight and net charge of the hydrogen of the PO(OH) group are listed in Table 1.

Results And Discussion

Dimerization of Extractants. D4ECHPA and D4DCHPA are considered to exist as dimeric species in a nonpolar diluent, such as toluene and kerosene, similarly to D2EHPA.[1,2,4,5,9,8,11—13,16,19)]

The dimerization of the extractant in the organic phase is expressed as

$$2\overline{\mathrm{HR}} \overset{K_\mathrm{d}}{\rightleftarrows} \overline{\mathrm{H_2R_2}}. \tag{1}$$

From the above equation, the dimerization constant (K_d) and the number-averaged aggregation number (m) are given by

$$K_\mathrm{d} = [\overline{\mathrm{H_2R_2}}]/[\overline{\mathrm{HR}}]^2 = (C_{\overline{\mathrm{HR}}} - C^*)/(2C^* - C_{\overline{\mathrm{HR}}})^2 \tag{2}$$

and

$$m = C_{\overline{\mathrm{HR}}}/C^*, \tag{3}$$

where $C_{\overline{\mathrm{HR}}}$ (=2[$\overline{\mathrm{H_2R_2}}$]+[$\overline{\mathrm{HR}}$]) and C^* (=[$\overline{\mathrm{H_2R_2}}$]+[$\overline{\mathrm{HR}}$]) are the analytical concentration of the extractant and the total concentration of the monomeric and dimeric species in toluene measured experimentally, respectively.

Figure 2 shows a plot of $C_{\overline{\mathrm{HR}}}$ against C^* according to Eq. 3. From the linear relationship, the number-averaged aggregation number of D4ECHPA and D4DCHPA (m) was found to be equal to 2.0 and 1.9, respectively, under the present experimental conditions. From the relationship between $C_{\overline{\mathrm{HR}}}-C^*$ and $(2C^*-C_{\overline{\mathrm{HR}}})^2$ shown in Fig. 2, the dimerization constant (K_d) for D4DCHPA was evaluated to be $(1.54\pm0.06)\times10^4$ dm^3 mol^{-1}. However the dimerization constant of D4ECHPA cannot be obtained, because the difference between $2C^*$ and $C_{\overline{\mathrm{HR}}}$ is negligibly small. It can be concluded that more than 95% of D4DCHPA exists as

Table 1. Characteristics and Equilibrium Constants of D4ECHPA, D4DCHPA, and D2EHPA

Extractant	D4ECHPA	D4DCHPA	D2EHPA
Molecular weight/g mol^{-1}	318.39	426.58	322.43
Acid dissociation comstant$^{a)}$ /mol dm^{-3}	$(1.07\pm0.13)\times10^{-3}$	$(1.41\pm0.19)\times10^{-3}$	1.38×10^{-3} $^{d)}$
(pK_a)	(2.97±0.12)	(2.85±0.13)	(3.01)
Apparent aqueous distribution coefficient$^{b)}$ $K_\mathrm{D}/K_\mathrm{d}^{1/2}$/mol$^{0.5}dm^{-1.5}$	$(6.97\pm0.08)\times10^{-3}$	$(1.36\pm0.05)\times10^{-4}$	$(3.38\pm0.04)\times10^{-3}$
Acid dissociation constant$^{b)}$ /mol dm^{-3}	$(3.14\pm0.22)\times10^{-3}$	$(3.26\pm0.31)\times10^{-3}$	$(2.60\pm0.19)\times10^{-3}$
(pK_a)	(2.50±0.07)	(2.49±0.10)	(2.59±0.07)
Net charge of hydrogen in PO(OH)$^{c)}$	0.237	0.235	0.241

a) Obtained value in 50% 2-propanol–50% aqueous sodium nitrate. b) Obtained value in aqueous nitrate media. c) Calculated by using PM3 type of semi-empirical molecular orbital method.[18)] d) Ref. 20.

dimeric species, and that D4ECHPA was completely dimerized in toluene under the present experimental conditions.

Acid Dissociation Constants of Extractants. The acid dissociation constants and pK_a values of the extractants in 50% 2-propanol–50% aqueous nitrate media are listed in Table 1. The acid dissociation constants of the extractants (pK_a) are nearly the same as that of D2EHPA (described in previous paper[20]). This result can be explained by the good agreement of the net charge of the hydrogen in the PO(OH) of each extractant.

Aqueous Distribution of Extractants. Since the extractant exists as both the nonionic and anionic species in the aqueous phase, the aqueous distribution equilibrium of the extractant is expressed by Eq. 1 and the following equations:

$$\overline{HR} \overset{K_D}{\rightleftharpoons} HR \tag{4}$$

and

$$HR \overset{K_a}{\rightleftharpoons} R^- + H^+. \tag{5}$$

Combined with Eqs. 1, 4, and 5, the total concentration of the extractant in the aqueous phase (C_{HR}) can be expressed by

$$C_{HR} = 0.5^{1/2}(K_D/K_d{}^{1/2})(1+K_a/a_H)C_{\overline{HR}}{}^{1/2}. \tag{6}$$

Figure 3 shows the relation between the total concentration of the extractant in the aqueous phase (C_{HR}) and the square root of the analytical concentration in the organic phase ($C_{\overline{HR}}{}^{0.5}$) at pH=3.2 and 1.0, respectively. From the linear relationships at both pH regions, the apparent aqueous distribution coefficient ($K_D/K_d{}^{1/2}$) and acid dissociation constant (K_a) of the extractants were obtained, as listed in Table 1. The aqueous distribution coefficients of the extractants become greater in the order to D4ECHPA>D2EHPA>D4DCHPA. As already described above, the acid dissociation constants of the extractants are nearly the same as that of D2EHPA. However, the pK_a values obtained in aqueous nitrate media were 0.5 pH unit smaller than those in 50% 2-propanol–50% aqueous nitrate media.

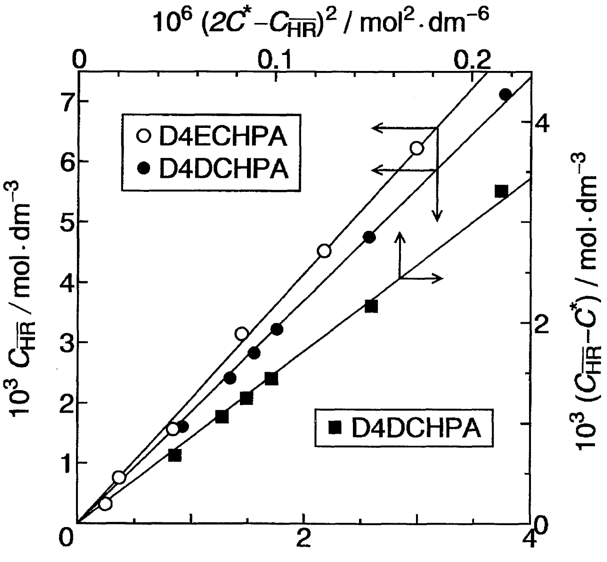


Fig. 2. Dimerizations of D4ECHPA and D4DCHPA.

Extraction Equilibria. Figures 4(a) and 4(b) show the effects of the pH on the distribution ratios of rare earth elements (D) in the cases of D4ECHPA and D4DCHPA, respectively. The plots lie on a straight line with a slope of 3 for all of the rare earth elements, as observed in the extraction of trivalent rare earth elements with other acidic organophosphorus extractants, such as D2EHPA. This suggests that the extraction of rare earth elements with these extractants has an inverse third order dependency on the hydrogen ion activity based on the cation-exchange extraction reaction.

Figures 5(a) and 5(b) show the effects of the concentration of the dimeric species of the extractant in the organic phase ($[\overline{H_2R_2}]$) on the distribution ratio of rare earth elements (D) in the cases of D4ECHPA and D4DCHPA, respectively. The concentration of the dimeric species of D4DCHPA was calculated using the dimerization constant (K_d) while that of D4ECHPA was half the analytical concentration of the extractant ($C_{\overline{HR}}$). The plots lie on a straight line with a slope of 3 for all rare earth elements in both cases of the extractants. This suggests that the extraction reactions of rare earth elements show a third dependency on $[\overline{H_2R_2}]$. We considered that these extractants form a complex of 1 : 3 rare earth element: dimeric extractant, as does D2EHPA.

From the results described above, it can be considered that all rare earth elements are extracted with these extractants according to the following extraction reaction:

$$M^{3+} + 3\overline{H_2R_2} \overset{K_{ex}}{\rightleftharpoons} \overline{M(HR_2)_3} + 3H^+. \tag{7}$$

The extraction equilibrium constant (K_{ex}) is expressed by

$$K_{ex} = \frac{[\overline{M(HR_2)_3}]a_H{}^3}{[M^{3+}][\overline{H_2R_2}]^3} = D\frac{a_H{}^3}{[\overline{H_2R_2}]^3}. \tag{8}$$

Equation 8 can be rearranged as

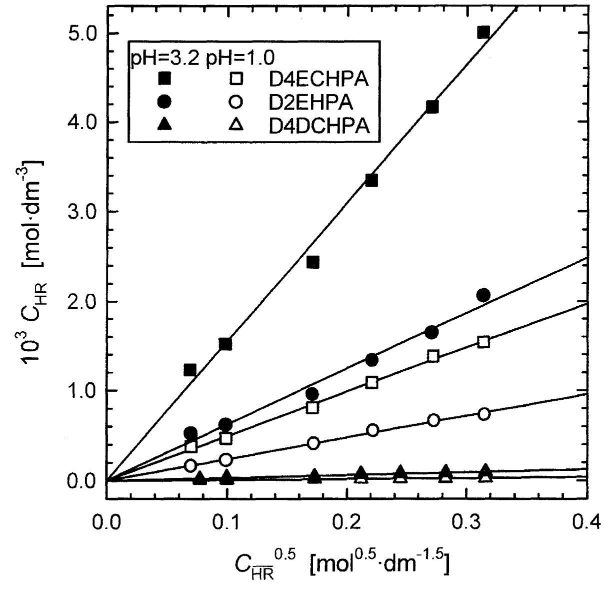


Fig. 3. Aqueous distributions of D4ECHPA, D4DCHPA, and D2EHPA.

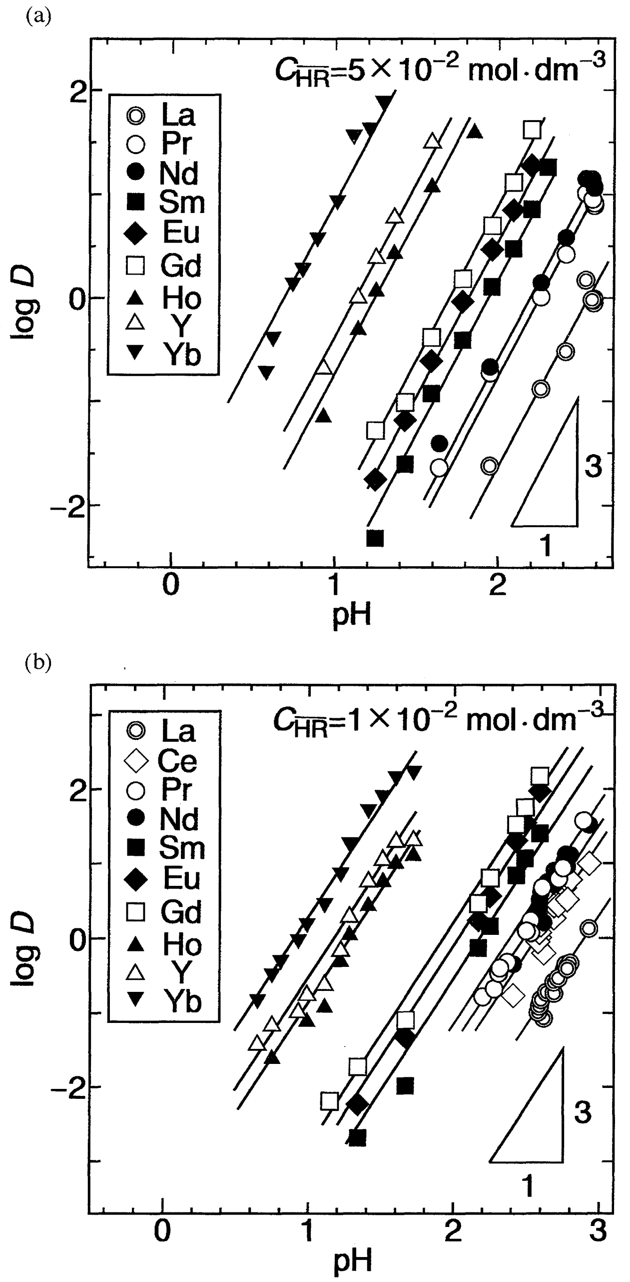


Fig. 4. Effect of pH on distribution ratios of rare earth elements, D, in the cases of (a) D4ECHPA and (b) D4DCHPA.

$$\log D = 3\mathrm{pH} + 3\log[\overline{\mathrm{H_2R_2}}] + \log K_{\mathrm{ex}}. \tag{9}$$

Equation 9 is satisfactory for all of the experimental results shown in Figs. 4 and 5, as expected. From all of the experimental results, the extraction equilibrium constants of rare earth elements with D4ECHPA and D4DCHPA (K_{ex}) were obtained.

Figure 6 shows the relation between the extraction equilibrium constant evaluated and the order of the atomic number of rare earth elements in the cases of D4ECHPA and D4DCHPA, together with the literature data of extraction with D2EHPA in toluene from perchlorate media.[1] The extraction equilibrium constants tend to increase along with increasing atomic number of the rare earth elements for each extractant. This phenomenon is related to the lanthanoid contraction and stabilized energy of repulsion between f-electrons, which have been observed in many extraction systems for rare earth elements.[1,11—13,21,22] The extraction equilibrium constants of rare earth elements become greater in the order D4DCHPA>D4ECHPA>D2EHPA. Since the extraction equilibrium constants of D4ECHPA and D4DCHPA have almost similar tendencies, it can be considered that the

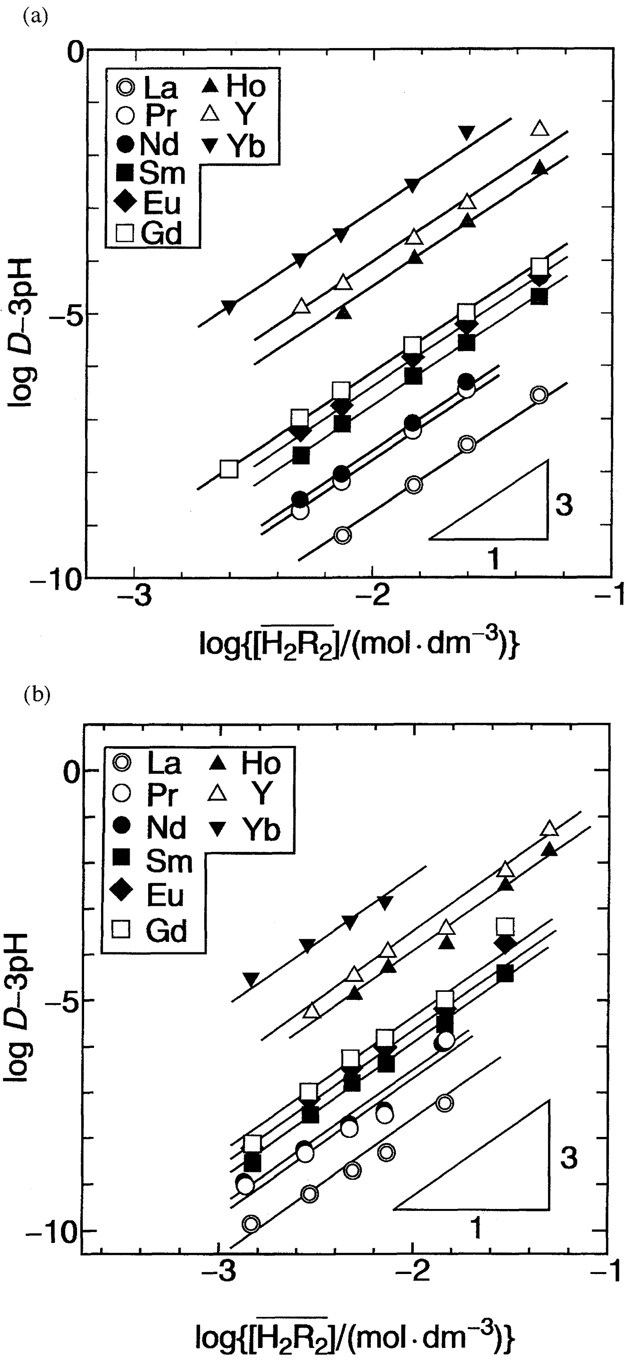


Fig. 5. Effect of concentration of dimeric species of extractant in organic phase, [$\overline{\mathrm{H_2R_2}}$], on the distribution ratio of rare earth elements, D, in the case of (a) D4ECHPA and (b) D4DCHPA.

extractabilities depend on the structures of the cyclohexyl groups adjacent to the PO(OH) group.

In this extraction system, the extraction equilibrium relation (expressed by Eq. 7) can be elucidated by using Eqs. 1, 4, and 5 and the following elementary steps:

$$M^{3+} + 3R^- \overset{K_1}{\rightleftarrows} MR_3 \tag{10}$$

$$MR_3 \overset{K_D'}{\rightleftarrows} \overline{MR_3} \tag{11}$$

$$\overline{MR_3} + 3/2\overline{H_2R_2} \overset{K_{sol}}{\rightleftarrows} \overline{M(HR_2)_3} \tag{12}$$

The extraction equilibrium constant (K_{ex}) can be expressed as

$$K_{ex} = (K_D K_a / K_d^{1/2})^3 K_1 K_D' K_{sol}. \tag{13}$$

Since the acid dissociation and dimerization constants of the extractants are the same as each other, and the distribution coefficients become greater in the order D4ECHPA>D2EHPA>D4DCHPA, it could be considered that the tendency of extractability is influenced by the steric hindrance of alkyl substances adjacent to the PO(OH) group related to K_1 and K_{sol} as well as the hydrophobicity of the rare earth complex related to K_D'.

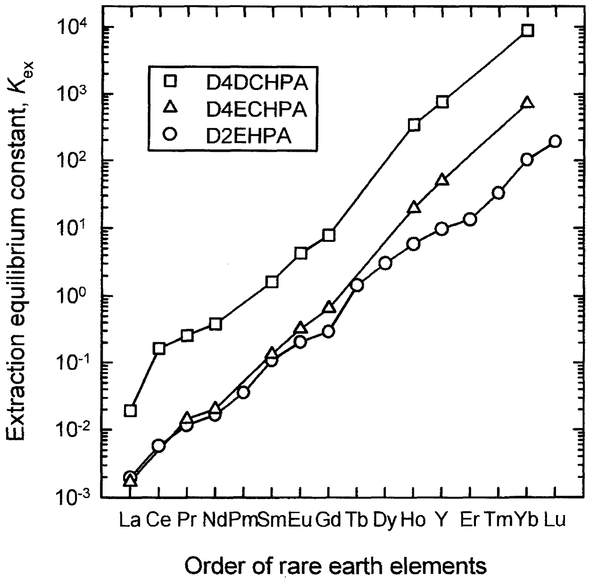


Fig. 6. Relation between the extraction equilibrium constant, K_{ex}, and order of atomic number of rare earth elements.

The typical separation factors for the adjacent rare earth elements with D4ECHPA, D4DCHPA, and D2EHPA are shown in Table 2. The separation factor ($\beta(M_1/M_2)$) was derived from the ratio of K_{ex} of the heavier metal (M_1) to that of the lighter one (M_2). The selectivities of rare earth elements with D4ECHPA and D4DCHPA increase in the region of heavy rare earth elements compared with that of D2EHPA. Especially, in comparison with each separation factor, it was remarkable that β(Ho/Gd) and β(Yb/Y) with D4ECHPA, and β(Ce/La), β(Pr/La), and β(Ho/Gd) with D4DCHPA are significantly greater than that with D2EHPA.

Loading Test of a Rare Earth Element. A loading test of Nd^{III} in the organic phase was carried out in order to compare the loading capacities of D4ECHPA and D4DCHPA with that of D2EHPA. The maximal loading capacities ($C_t/C_{\overline{HR}}$) with D4ECHPA and D4DCHPA were 40 and 35%, respectively. Furthermore, although gelation of the organic phase was not observed until the maximal loading conditions, when using D2EHPA, a highly viscous gel was formed at 25% loading. This suggests that the steric hindrance of the bulky alicyclic groups of D4ECHPA and D4DCHPA can prevent gelation of the organic phase caused by the formation of a polynuclear complex of rare earth elements, as mentioned later.

Molecular Modelling Computation. Figures 7(a) and 7(b) show the proposed structures of rare earth complexes with D4ECHPA, D4DCHPA, and D2EHPA according to the extraction mechanism mentioned above. The optimized structures of the complexes in vacuo shown in Fig. 7(b) were calculated by the molecular mechanics method, MOMEC. For these calculations, we used the parameters for the ionic radius of Sm^{III} as 0.0958 nm.[23] It was elucidated that the samarium complexes exist in similar globular structures, in which the Sm^{III} ion is fully covered with the extractant

Table 2. Typical Separation Factors for Rare Earth Elements with D4ECHPA, D4DCHPA, and D2EHPA

Extractant	D4ECHPA	D4DCHPA	D2EHPA[a]
Aqueous media Organic diluent	Nitrate Toluene	Nitrate Toluene	Perchlorate Toluene
β(Ce/La)	[b]	8.51±0.81	2.95
β(Pr/Ce)	[b]	1.56±0.18	2.04
β(Pr/La)	6.75±0.71	13.27±0.95	6.03
β(Nd/Pr)	1.48±0.12	1.50±0.12	1.41
β(Sm/Nd)	6.66±0.32	4.25±0.34	6.52
β(Eu/Sm)	2.39±0.12	2.65±0.29	1.89
β(Gd/Eu)	2.05±0.11	1.81±0.21	1.44
β(Ho/Gd)	29.52±2.59	48.83±3.53	20.25
β(Y/Ho)	2.54±0.30	2.22±0.27	1.65
β(Yb/Y)	14.38±1.24	11.57±1.64	10.5

a) Ref. 1. b) Not observed.

molecules. Especially, the bulky cyclohexylcyclohexyl substituents of D4DCHPA covered most tightly over the $\mathrm{Sm^{III}}$ ion. The heats of formation of the $\mathrm{Sm^{III}}$ complexes were calculated as 7080, 4690, and 2310 kJ mol^{-1} for D4DCHPA, D4ECHPA, and D2EHPA, respectively. It was found that the heats of formation of the $\mathrm{Sm^{III}}$ complex with D4ECHPA and D4DCHPA are 3 times and twice greater than that with D2EHPA. This is due to the bulkiness of the 4-ethylcyclohexyl and 4-cyclohexylcyclohexyl substituents of the extractants, compared to the 2-ethylhexyl substituents of D2EHPA. The molecular volumes of these complexes were calculated to be 5.84, 4.80, and 4.44 nm^3 for D4DCHPA, D4ECHPA, and D2EHPA, respectively. It is very interested that the tendency of the molecular volumes of rare earth complexes is approximately in agreement with the tendency of the extractability of these extractants.

Conclusion

Studies concerning the extraction equilibria of rare earth elements with bis(4-ethylcyclohexyl) hydrogenphosphate (D4ECHPA) and bis(4-cyclohexylcylohexyl) hydrogenphosphate (D4DCHPA) were conducted at 303 K from the nitrate media, together with the aggregation states, acid dissociation constants and aqueous distributions of the extractants. The following can be concluded:

(1) The majority of the extractants are dimerized in toluene.

(2) The acid dissociation constants of the extractants are nearly the same as that of D2EHPA.

(3) The aqueous distribution coefficients of the extractants become greater in the order D4ECHPA>D2EHPA>D4DCHPA.

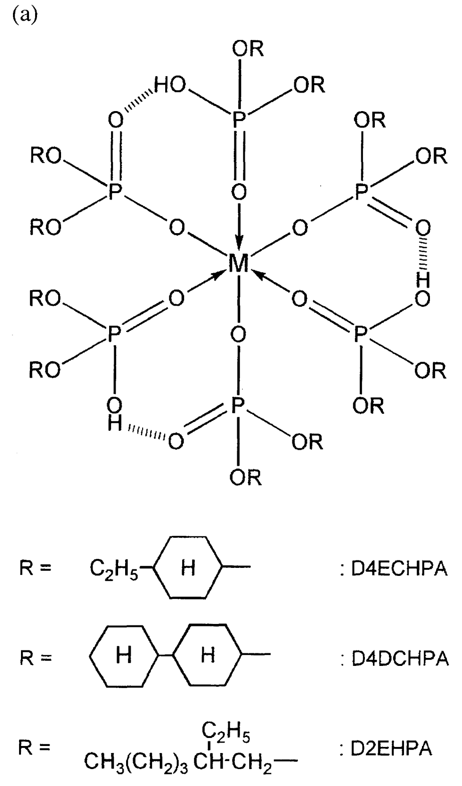
(4) The extracted species of rare earth elements are $\mathrm{M(HR_2)_3}$, and the extraction equilibrium constants for rare earth elements were evaluated.

(5) The extraction equilibrium constants of rare earth elements become greater in the order D4DCHPA>D4ECHPA>D2EHPA.

(6) The separation factors, β(Ho/Gd) and β(Yb/Y), with D4ECHPA, and β(Ce/La), β(Pr/La), and β(Ho/Gd) with D4DCHPA are significantly greater than that with D2EHPA.

(7) The loading capacities of $\mathrm{Nd^{III}}$ with D4ECHPA and D4DCHPA in the organic phase are excellent compared with that of D2EHPA due to the steric hindrance of the bulky alicyclic substituents.

(8) Molecular modelling computations with molecular me-



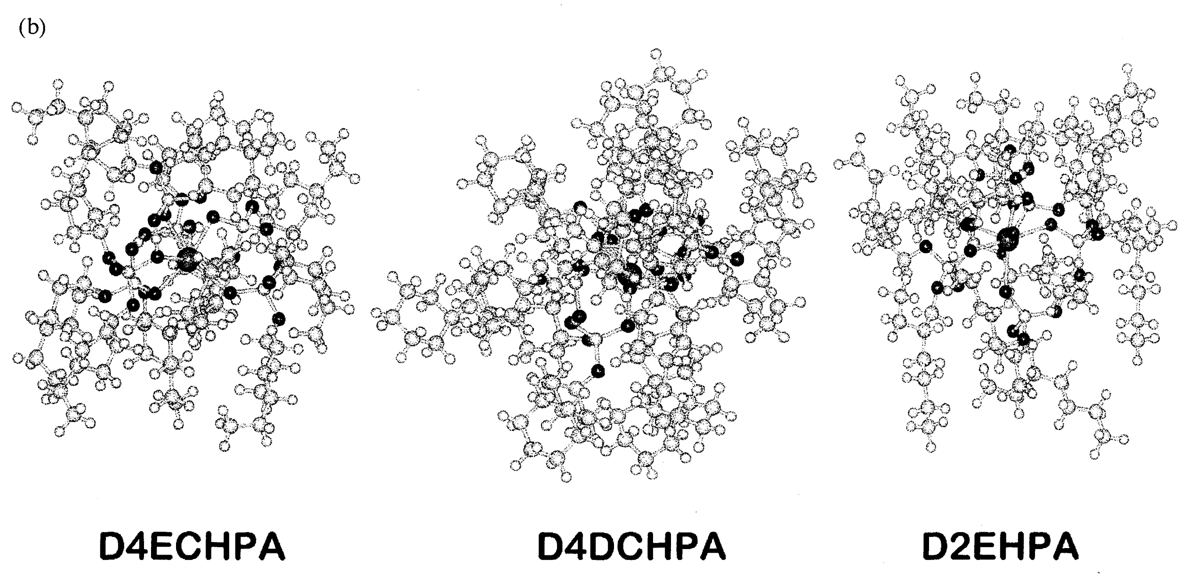


Fig. 7. (a) Proposed structures of rare earth complexes with D4ECHPA, D4DCHPA and D2EHPA. (b) Proposed ball and stick model structures of $\mathrm{Sm^{III}}$ complexes with D4ECHPA, D4DCHPA, and D2EHPA calculated by molecular mechanics method, MOMEC.

chanics and semi-empirical molecular orbital methods were carried out in order to qualitatively elucidate the structural effect of the extractant on complex formation.

Nomenclature

a_H = activity of hydrogen ion [mol dm^{-3}]
C_{HR} = analytical concentration of extractant [mol dm^{-3}]
C^* = total concentration of monomeric and dimeric species of extractant [mol dm^{-3}]
C_t = total concentration of complex of rare earth element in organic phase [mol dm^{-3}]
D = distribution ratio of rare earth element [—]
K_1 = equilibrium constant of Eq. 10 [(dm^3 mol^{-1})^3]
K_D = aqueous distribution coefficient of extractant [—]
K'_D = aqueous distribution coefficient of rare earth complex defined by Eq. 11 [—]
K_a = acid dissociation constant of extractant [mol dm^{-3}]
K_d = dimerization constant of extractant [dm^3 mol^{-1}]
K_{ex} = extraction equilibrium constant [—]
K_{sol} = equilibrium constant of Eq. 12 [(dm^3 mol^{-1})$^{3/2}$]
$\beta(M_1/M_2)$ = separation factor between adjacent rare earth elements derived from ratio of K_{ex} of M_1 to that of M_2 [—]
$[j]$ = concentration of species j (=M^{3+}, HR, H_2R_2, $M(HR_2)_3$) [mol dm^{-3}]
<Superscript>
— = organic phase

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