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Solvent Extraction of Trivalent Yttrium, Holmium, and Erbium by Novel Types of Acidic Organophosphonates

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New types of acidic organophosphonates, HR with different hydrophobic groups, were synthesized in order to investigate their extraction behavior for heavy rare earth elements (Y^{3+}, Ho^{3+}, and Er^{3+}) from aqueous acidic chloride media. Their physicochemical properties, such as aggregation in an organic diluent and the acid dissociation constants (K_a) in the aqueous phase, were also examined. These rare earth elements were supposed to be extracted according to the stoichiometric relation,

$$M^{3+} + 3(HR)_2 \rightleftharpoons MR_3{\cdot}3HR + 3H^+.$$

This idea and the extraction equilibrium constants (K_{ex}) for each metal ion were evaluated. Both the extraction equilibrium constants and the separation factors (β) between these metal ions were found to be greater than those of commercial extractants. The correlation between the extractability of heavy rare earth elements, the selectivity among these elements and the chemical structures of these extractants are discussed from a qualitative perspective.

The solvent extraction of rare earth elements has been investigated extensively from the late 1950s[1] in relation to application to isolations from nuclear wastes and actinide.[2,3] As is well known, it is very difficult to separate rare earth elements mutually, due to their similar chemical properties. Acidic organophosphorus extractants are most suitable for separating them efficiently from both extractive and separative points of view. However, even with acidic organophosphorus extractants, a large number of steps when using mixer-settler equipment are necessary to obtain highly purified rare earth elements.[4] The development of more efficient extractants will play an important role in decreasing the required number of steps.

Yuan et al. synthesized a series of acidic organophosphorus extractants in order to investigate their structure–extractability relationship, that is, their steric effects on the extraction behaviors of rare earth elements. For each extractant, the substituent constants, which provide important structural information concerning the molecular design of new extractants, were estimated.[5—7]

In this paper we report on the syntheses and physicochemical properties of five kinds of new organophosphorus extractants, as well as their extraction behavior for three kinds of heavy rare earth elements in order to investigate the steric effect and the effect of ethereal oxygen on their selectivity and extractability. We selected yttrium(III), holmium(III), and erbium(III) as the target metal ions, since the mutual separation of these elements is the most difficult among pairs of adjacent elements of rare earths.

In solvent extraction, the extracting reagents should exhibit excellent extraction behavior for metal ions: high selectivity and high loading capacity, as well as easiness of stripping under moderate conditions. For this reason, stripping tests were carried out with various mineral acids in order to determine the strongest extractant among the present ones.

Experimental

Synthesis of Extractants. All of the extractants were synthesized from the corresponding alcohols and the corresponding phosphonic dichlorides according to the following reaction:[8]

$$R_1OH + R_2P(O)Cl_2 \rightleftharpoons R_1O(R_2)P(O)OH.$$

The structures of the extractants used in present work are shown in Fig. 1.

Ethyl [*p*-(1,1,3,3-Tetramethylbutyl)phenoxy]acetate (1a):[9] Under a nitrogen atmosphere 300 cm^3 of distilled tetrahydrofuran was added to 11.63 g (oil, 60 %, 290.7 mmol) of sodium hydride; then 50.00 g (95%, 230.2 mmol) of *p*-(1,1,3,3-tetramethylbutyl)phenol was added to this solution and stirred. To this solution was added dropwise 120 cm^3 of tetrahydrofuran containing 25.00 g (85.5 mmol) of ethyl bromoacetate. The solution was refluxed at 66 °C for 2 h. After cooling, 50 cm^3 of ethanol was carefully added dropwise to deactivate any excess sodium hydride in the ice bath. The organic solvent was removed and 150 cm^3 of ethyl acetate was added. The organic phase was washed with 150 cm^3 of 1 mol dm^{-3} hydrochloric acid three times, and then with 150 cm^3 of a saturated aqueous solution of sodium chloride once. After drying with anhydrous magnesium sulfate, the solution was filtrated, and the filtrate was dried in vacuo. The excess ethyl bromoacetate was removed with a glass-tube oven in vacuo (Chart 1). The crude product was purified by column chromatography (silica gel, chloroform : hexane = 1 : 1 v/v); light-yellow oil, yield 89%; TLC (SiO_2, chloroform : hexane = 1 : 1 v/v,

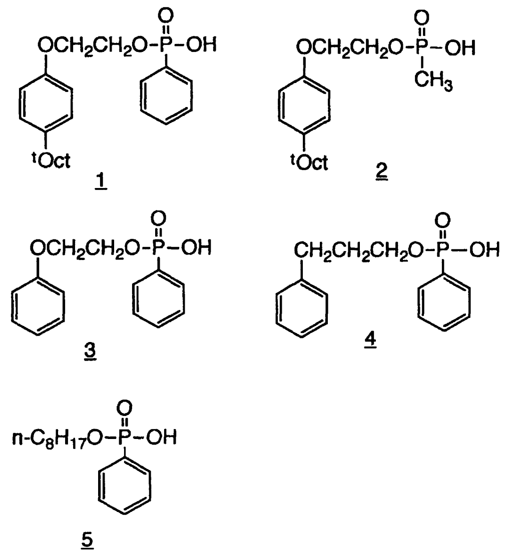

Fig. 1. Structures of the extractants.

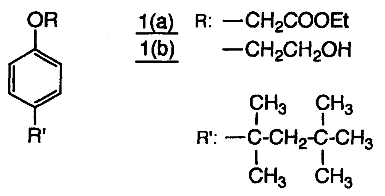

Chart 1.

R_f=0.35); IR (neat) ν_{O-H} 3200(br) cm^{-1}, $\nu_{C=O}$ 1770, 1740 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$, TMS, 30 °C) δ=0.70 (9H, s, $C(CH_3)_3$), 1.30 (9H, s and t, $C(CH_3)_2$ and $COOCH_2\underline{CH_3}$), 1.69 (2H, s, $C-CH_2-C$), 4.27 (2H, q, $COO\underline{CH_2}CH_3$), 4.58 (2H, s, OCH_2COO), 6.80 (2H, d, C–O–ArH), 7.25 (2H, d, C–C–ArH). Found: C, 73.64; H, 9.88%. Calcd for ($C_{18}H_{28}O_3$): C, 73.94, H, 9.64%.

2-[*p*-(1,1,3,3-Tetramethylbutyl)phenoxy]ethanol (1b): To 3.97 g (104.7 mmol) of aluminum lithium hydride was added 100 cm^3 of distilled tetrahydrofuran. The solution was stirred; to this solution was added dropwise 120 cm^3 of tetrahydrofuran containing 25.00 g (85.5 mmol) of **1a**. This solution was refluxed at 66 °C for 20 h under a nitrogen atmosphere; 100 cm^3 of an aqueous methanol mixture (5 : 95 v/v%) was then carefully added dropwise to deactivate any excess of aluminum lithium hydride in the ice bath. The solution was concentrated in vacuo. To the residue was added 400 cm^3 of a sulfuric acid solution (20 vol%) and 400 cm^3 of chloroform; the solution was then stirred for 4 h. The organic layer was separated and washed with distilled water until the pH of the water became equal to 4—5, and was then dried with anhydrous magnesium sulfate. After the solution was filtrated, the filtrate was dried in vacuo; colorless viscous liquid, yield 99%; TLC (SiO_2, chloroform : ethyl acetate : hexane=1 : 3 : 2 v/v/v, R_f=0.58); IR (neat) ν_{O-H} 3400(br) cm^{-1}, no peak $\nu_{C=O}$ 1770, 1740 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$, TMS, 30 °C) δ=0.64 (9H, s, $C(CH_3)_3$), 1.25 (6H, s, $C(CH_3)_2$), 1.55 (2H, s, $C-CH_2-C$), 2.10 (1H, s, OH), 3.91 (4H, m, OCH_2CH_2OH), 6.76 (2H, d, C–O–ArH), 7.19 (2H, d, C–C–ArH). Found: C, 76.57; H, 10.46%. Calcd for ($C_{16}H_{26}O_2$): C, 76.45, H, 10.42%.

2-[*p*-(1,1,3,3-Tetramethylbutyl)phenoxy]ethyl Hydrogenphenylphosphonate (1): To 60 cm^3 of pyridine was added 15.28 g (78.4 mmol) of phenylphosphonic dichloride in a salt ice bath (−7±3 °C). A solution of 16.26 g (64.9 mmol) of **1b** in 30 cm^3 of pyridine was added dropwise to this solution while keeping it cool. This mixture was stirred in an ice bath for 3 h, and then poured into 300 cm^3 of ice water. Concentrated hydrochloric acid was added to the solution until the pH of the aqueous solution became equal to 1 to hydrolyze phosphonochloridic acid as a product. To the solution was added 500 cm^3 of benzene in order to extract the organic portion. Two phases were stirred for 10 min. The organic layer was separated, washed twice with 300 cm^3 of 1 mol dm^{-3} hydrochloric acid, then with 300 cm^3 of a saturated aqueous sodium chloride solution once and dried with anhydrous magnesium sulfate. The solution was filtrated and the filtrate was dried in vacuo; yellow viscous liquid, yield 88%; TLC (SiO_2 chloroform : methanol=10 : 1 v/v, R_f=0.03); IR (neat) ν_{P-OH} 2600(br), 2300(br) cm^{-1}, $\nu_{P=O}$ 1660(br) cm^{-1}; ^{1}H NMR (60 MHz, DMSO-d_6, TMS, 30 °C) δ=0.68 (9H, s, $C(CH_3)_3$), 1.27 (6H, s, $C(CH_3)_2$), 1.66 (2H, s, $C-CH_2-C$), 4.10 (4H, m, OCH_2CH_2O), 6.76 (2H, d, C–O–ArH), 7.20 (2H, d, C–C–ArH), 7.56 (5H, m, P–ArH). Found: C, 68.62; H, 8.15%. Calcd for $C_{22}H_{31}O_4P\cdot 1/5C_6H_6$: C, 68.63, H, 7.99%.

2-[*p*-(1,1,3,3-Tetramethylbutyl)phenoxy]ethyl Hydrogenmethylphosphonate (2): To 60 cm^3 of pyridine was added 12.00 g (90.3 mmol) of methylphosphonic dichloride in the salt ice bath (−7±3 °C). A solution of 18.86 g (75.2 mmol) of **1b** in 30 cm^3 of pyridine was slowly added dropwise to this solution while keeping it cool. This mixture was stirred in the bath for 2 h. The other procedures were similar to the manner for preparing **1**. The crude product was purified by column chromatography (silica gel, chloroform : methanol=10 : 1 v/v and ethyl acetate : hexane=1 : 1 v/v); light yellow viscous liquid, yield 33%; TLC (SiO_2, chloroform : methanol=10 : 1 v/v, R_f=0.08); IR (neat) ν_{O-H} 2600(br), 2300(br) cm^{-1}, $\nu_{P=O}$ 1700(br) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 30 °C) δ=0.71 (9H, s, $C(CH_3)_3$), 1.33 (6H, s, $C(CH_3)_2$), 1.53 (3H, d, $P-CH_3$), 1.69 (2H, s, $C-CH_2-C$), 4.13 (2H, t, $O\underline{CH_2}CH_2O-P$), 4.33 (2H, m, $OCH_2\underline{CH_2}O-P$), 6.81 (2H, d, C–O–ArH), 7.24 (2H, d, C–C–ArH), 9.77 (1H, s(br), P–OH). Found: C, 62.27; H, 8.89%. Calcd for $C_{17}H_{29}O_4P$: C, 62.18, H, 8.90%.

2-(Phenoxy)ethyl Hydrogenphenylphosphonate (3): To 12 cm^3 of pyridine was added 5.15 g (26.1 mmol) of phenylphosphonic dichloride in a salt ice bath (−7±3 °C). A solution of 3.00 g (21.7 mmol) of 2-phenoxyethanol in 6 cm^3 of pyridine was slowly added dropwise to this solution while keeping it cool. This mixture was stirred in the bath for 2 h. All other procedures were similar to those used for preparing **2**. The crude product was purified by column chromatography (silica gel, chloroform); brown viscous liquid, yield 65%; TLC (SiO_2, chloroform : methanol=10 : 1 v/v, R_f=0.02); IR (neat) ν_{P-OH} 2600(br), 2280(br) cm^{-1}, $\nu_{P=O}$ 1750(br) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$, TMS, 30 °C) δ=4.09 (2H, m, $O\underline{CH_2}CH_2O-P$), 4.29 (2H, m, $OCH_2\underline{CH_2}O-P$), 6.63 (2H, d, O–ArH(*o*-position)), 6.93 (1H, t, O–ArH(*p*-position)), 7.24 (2H, t, O–ArH(*m*-position)), 7.40 (2H, t, P–ArH(*m*-position)), 7.51 (1H, t, P–ArH(*p*-position)), 7.83 (2H, m, P–ArH(*o*-position)), 8.94 (1H, s, P–OH). Found: C, 59.71; H, 5.38%. Calcd for $C_{14}H_{15}O_4P\cdot 0.03CHCl_3$: C, 59.79, H, 5.38%.

3-Phenylpropyl Hydrogenphenylphosphonate (4): To 13 cm^3 of pyridine was added 6.87 g (35.2 mmol) of phenylphosphonic dichloride in a salt ice bath (−7±3 °C). A solution of 4.00 g (29.4 mmol) of 3-phenyl-1-propanol in 8 cm^3 of pyridine was slowly added dropwise to this solution while keeping it cool. This mixture was then stirred in the bath for 2 h. All other procedures were similar to those used for preparing **3**; deep-brown viscous liquid, yield 47%; TLC (SiO_2, chloroform, $R_f=0.01$); IR (neat) ν_{P-OH} 2600(br), 2300(br) cm^{-1}, $\nu_{P=O}$ 1680(br) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$, TMS, 30 °C) $\delta=1.93$ (2H, m, $CH_2\underline{CH_2}CH_2OP$), 2.60 (2H, t, $\underline{CH_2}CH_2CH_2OP$), 3.96 (2H, m, $CH_2CH_2\underline{CH_2}OP$), 7.23 (2H, d, C–ArH(*o*-position)), 7.25 (3H, m, C–ArH), 7.38 (2H, t, P–ArH(*m*-position)), 7.48 (1H, m, P–ArH(*p*-position)), 7.81 (2H, m, P–ArH(*o*-position)), 9.23 (1H, s(br), P–OH). Found: C, 64.04; H, 6.13%. Calcd for $C_{15}H_{17}O_3P\cdot0.05CHCl_3$: C, 64.05, H, 6.09%.

Octyl Hydrogenphenylphosphonate (5): To 18 cm^3 of pyridine was added 7.08 g (29.5 mmol) of phenylphosphonic dichloride in a salt ice bath (−7±3 °C). A solution of 3.69 g (35.2 mmol) of 1-octanol in 8 cm^3 of pyridine was slowly added dropwise to this solution while keeping it cool. This mixture was then stirred in the bath for 2 h. All other procedures were similar to those used for preparing **3**; yellow liquid, yield 52%; TLC (SiO_2, chloroform : methanol = 10 : 1 v/v, $R_f=0.07$); IR (neat) ν_{P-OH} 2620(br), 2280(br) cm^{-1}, $\nu_{P=O}$ 1680(br) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$, TMS, 30 °C) $\delta=0.88$ (3H, t, CH_3), 1.11 (10H, m, $CH_3(\underline{CH_2})_5$), 1.62 (2H, m, $(CH_2)_5\underline{CH_2}CH_2$), 4.00 (2H, m, CH_2OP), 7.40 (3H, m, P–ArH(*m*-, *p*-position)), 7.81 (2H, m, P–ArH(*o*-position)), 12.00 (1H, s(br), P–OH). Found: C, 62.11; H, 8.47%. Calcd for $C_{14}H_{23}O_3P$: C, 62.21, H, 8.58%.

Measurement of Aggregation of the Extractants. The sample solutions were prepared by diluting each extractant with toluene to the desired concentrations. Analytical-grade toluene (from Dojindo) was used without further purification. A complex of copper(II) with *E*-5-nonyl-2-hydroxy benzophenon oxime was washed three times with ethanol and used as a referential sample. The mean molecular weight of each extractant in toluene was measured by means of vapor-phase osmometry using a Corona model 117 osmometer.

Distribution Equilibria. An organic solution was prepared by dissolving each extractant into an analytical-grade toluene. The aqueous solution was prepared by dissolving each rare earth chloride into the following three kinds of stock solutions (containing 1×10^{-4} mol dm^{-3} of each rare earths): 2 mol dm^{-3} HCl, 0.1 mol dm^{-3} HCl–1.9 mol dm^{-3} KCl, 0.01 mol dm^{-3} HCl–1.99 mol dm^{-3} KCl. The initial pH of the aqueous phase was adjusted by mixing them arbitrarily. (The values of the pH were calculated based on the hydrogen-ion concentration determined by neutralization titration and the literature values for the activity coefficient of the hydrogen ion.$^{10)}$ The equilibrium pH was postulated to be the same as the initial pH, since the pH was sufficiently low to ignore any change before or after extraction.) In the case of experiments concerning the effect of the dimeric concentration on the distribution ratio, the initial pHs for each extractant were adjusted (**1**: 0.34, **2**: 1.22, **3**: 0.20, **4**: 0.66, **5**: 0.66); 5 cm^3 of toluene solutions containing each extractant were shaken with equal volumes of aqueous solutions containing rare earth elements ($\mu=2$, HCl/KCl; 30 °C) for at least 2 h, which was sufficiently long to reach equilibrium. After phase separation, the equilibrium concentrations of the rare earth elements in the aqueous phase were measured by ICP/AES (Seiko SPS1200VR).

Stripping Test. An organic solution was prepared by dissolving extractant **3** into analytical-grade toluene. The aqueous solution was prepared using the above-mentioned three stock solutions. The initial pH of the aqueous phase was adjusted to 1.1, so that 100% of the metal ions could be extracted into the organic phase; 5 cm^3 of toluene solutions containing each extractant were equilibrated with equal volumes of aqueous solutions containing rare earth elements, and equilibrated for at least 2 h in order to strip the loaded metal ions. The concentrations of the metal ions in the initial aqueous phase, raffinate and stripping solution were measured in order to calculate the stripped percentage of metal ions, similarly to those in the cases of extraction.

Acid Dissociation Constants of the Extractants. The apparent acid dissociation constants ($K_{a,app}$) were determined by the titration of 50 cm^3 of 75% 1,4-dioxane aqueous solutions containing 10^{-2} mol dm^{-3} of extractants, except for **3** with tetramethylammonium hydroxide aqueous solution (75% 1,4-dioxane) at 30 °C using Automatic titrator AT 117 (Kyoto electronics). The concentration of the tetramethylammonium hydroxide was determined by titration with 0.1 mol dm^{-3} hydrochloric acid. For a comparison, p$K_{a,app}$s of bis(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexyl hydrogen(2-ethylhexyl)phosphonate (PC-88A) were also determined by a similar method. In the case of extractant **3**, a solution containing 5×10^{-3} mol dm^{-3} of the reagent of 50 cm^3 of a 90% methanol aqueous mixture was used.$^{\#}$ The ratio of 1,4-dioxane to water for extractant **5** was varied at 60, 67.5, and 75 vol% (1,4-dioxane) in order to measure the p$K_{a,app}$s at the corresponding vol% of 1,4-dioxane. For the extractants, except for **3**, only the value of p$K_{a,app}$ at 75% 1,4-dioxane was measured in the same way as that for extractant **5**; their pK_as were then estimated.

Results and Discussion

Aggregation of the Extractants. Acidic organophosphorus compounds are well known to dimerize in nonpolar solvents, such as toluene.$^{11)}$ This dimerization of organophosphorus compounds in toluene can be expressed by

$$2\mathrm{HR} \rightleftharpoons (\mathrm{HR})_2 \quad : K_d. \tag{1}$$

Their total concentration ($\mathbf{C}_{\mathbf{HR}}$) and the sum of the monomer and dimer concentrations in toluene (C^*), which is obtained experimentally,$^{12)}$ are expressed as follows:

$$\mathbf{C}_{\mathbf{HR}} = \mathrm{C}_{\mathrm{HR}} + 2\mathrm{C}_{(\mathrm{HR})_2} \tag{2}$$

and

$$C^* = C_{\mathrm{HR}} + 2C_{(\mathrm{HR})_2}. \tag{3}$$

From Eqs. 2 and 3, the dimerization constant (K_d) is obtained from

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#The solubility of extractant **3** in 1,4-dioxane-water solution was very low.

$$K_{\mathrm{d}} = C_{(\mathrm{HR})_2}/C_{\mathrm{HR}}{}^2 = (\boldsymbol{C}_{\mathbf{HR}} - C^*)/(2C^* - \boldsymbol{C}_{\mathbf{HR}})^2. \quad (4)$$

The average aggregation number of the extractant is defined as

$$m = \boldsymbol{C}_{\mathbf{HR}}/C^*. \quad (5)$$

The relations between the reagent concentration and the average aggregation numbers of the compounds are listed in Table 1. The average aggregation numbers for most of the present extractants are greater than 2. These results suggest that all of the extractants, except for **1**, exist not only as monomeric and dimeric species, but also as trimeric species. The trimerization of the reagents should thus be considered to be

$$(\mathrm{HR})_2 + \mathrm{HR} \rightleftharpoons (\mathrm{HR})_3 \quad : K_{\mathrm{t}}, \quad (6)$$

where K_{t} is the trimerization constant, and is expressed by

$$K_{\mathrm{t}} = C_{(\mathrm{HR})_3}/(C_{(\mathrm{HR})_2} \cdot C_{\mathrm{HR}}) = C_{(\mathrm{HR})_3}/(K_{\mathrm{d}} C_{\mathrm{HR}}{}^3). \quad (7)$$

Their total concentration ($\boldsymbol{C}_{\mathbf{HR}}$) and the sum of the monomer, dimer, and trimer concentrations in toluene (C^*) are expressed as

$$\begin{aligned} \boldsymbol{C}_{\mathbf{HR}} &= C_{\mathrm{HR}} + 2C_{(\mathrm{HR})_2} + 3C_{(\mathrm{HR})_3} \\ &= C_{\mathrm{HR}} + 2K_{\mathrm{d}} C_{\mathrm{HR}}{}^2 + 3K_{\mathrm{d}} K_{\mathrm{t}} C_{\mathrm{HR}}{}^3 \end{aligned} \quad (8)$$

and

$$\begin{aligned} C^* &= C_{\mathrm{HR}} + C_{(\mathrm{HR})_2} + C_{(\mathrm{HR})_3} \\ &= C_{\mathrm{HR}} + K_{\mathrm{d}} C_{\mathrm{HR}}{}^2 + K_{\mathrm{d}} K_{\mathrm{t}} C_{\mathrm{HR}}{}^3. \end{aligned} \quad (9)$$

Table 1. Relation between the Concentrations and Apparent Mean Aggregation Number (m) of Each Extractant

Extractant	Concn/mol m^{-3}	m[—]
1	0.512	1.73
	1.28	1.78
	2.56	1.85
	5.12	1.88
2	0.609	1.63
	1.52	1.96
	3.05	2.09
	6.09	2.24
3	0.719	2.42
	1.80	2.50
	3.59	2.52
	7.18	2.64
4	0.724	2.04
	1.81	2.20
	3.62	2.32
	7.24	2.39
5	0.740	1.65
	1.85	2.08
	3.70	2.14
	7.40	2.18
	14.8	2.20

Eq. 8 is substituted into Eq. 9, giving

$$\begin{aligned} 3C^* &= 3C_{\mathrm{HR}} + 3K_{\mathrm{d}} C_{\mathrm{HR}}{}^2 + \boldsymbol{C}_{\mathbf{HR}} - C_{\mathrm{HR}} - 2K_{\mathrm{d}} C_{\mathrm{HR}}{}^2 \\ &= \boldsymbol{C}_{\mathbf{HR}} + 2C_{\mathrm{HR}} + K_{\mathrm{d}} C_{\mathrm{HR}}{}^2. \end{aligned} \quad (10)$$

From Eq. 10, the following equation is obtained:

$$C_{\mathrm{HR}} = [-1 + \{1 + K_{\mathrm{d}}(3C^* - \boldsymbol{C}_{\mathbf{HR}})\}^{1/2}]/K_{\mathrm{d}}. \quad (11)$$

The dimerization constant (K_{d}) and the trimerization constant (K_{t}) were evaluated by numerically solving Eqs. 8 and 11 by the Simplex method, combined with the Newton–Raphson method. The evaluated values of K_{d} and K_{t} for each extractant are listed in Table 2.

As a result, it was found that in the present extraction study extractant **1** exists as a mixture of monomeric and dimeric species,while the other extractants are a mixture of monomeric,dimeric, and trimeric species in toluene. It is predicted that the trimer bonds cyclicly due to hydrogen bondings, whereas the dimer bonds towards each other due to them.

Distribution Equilibria. The effect of the pH on the distribution ratio (D) in the extraction of Y^{3+}, Ho^{3+}, and Er^{3+} with extractant **1** is shown in Fig. 2 as a typical result. All of the plots lie on straight lines with a slope of 3. The selectivity for metal ions appears to be in the order $\mathrm{Er}^{3+} > \mathrm{Y}^{3+} > \mathrm{Ho}^{3+}$. This result is consistent with those observed for other organophosphorus acids,[13,14] the same results were also obtained for the figures of other extractants.

The effect of the concentration of extractant **2** on D is shown in Fig. 3 as a typical result. (Inherently although $\log(D \cdot [\mathrm{H}^+]^3)$ should be taken as an axis, the term $[\mathrm{H}^+]^3$ is omitted because the initial pH is equal to the equilibria pH, and considered only when the equilibrium constants are evaluated.) Even though all of the extractants, except for **1**, exist as mixtures of monomeric, dimeric, and trimeric species in toluene, it is plotted against the concentration of dimeric species, $(\overline{\mathrm{HR}})_2$. All of the plots lie on straight lines with a slope of 3. The same results were also obtained for the figures of the other extractants.

From these results, the extraction equilibria for extractant **1** is represented as

$$\mathrm{M}^{3+} + 3(\overline{\mathrm{HR}})_2 \rightleftharpoons \overline{\mathrm{MR}_3 \cdot 3\mathrm{HR}} + 3\mathrm{H}^+ \quad : \ K_{\mathrm{ex}}, \quad (12)$$

where M, $(\overline{\mathrm{HR}})_2$ denotes the rare earth element and dimeric extractant, respectively. The superscript $(\overline{})$

Table 2. Dimerization Constants (K_{d}) and Trimerization Constants (K_{t}) for the Extractants

Extractant	K_{d}/m^{3}mol^{-1}	K_{t}/m^{3}mol^{-1}
1	24.2	—
2	6.79	2.11
3	156	28.0
4	191	8.16
5	6.20	1.81

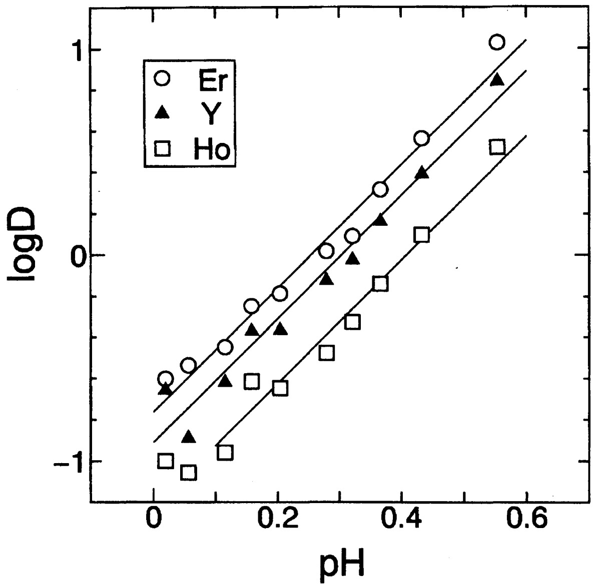

Fig. 2. Effect of the equilibrium pH on the distribution ratio. $[M^{3+}]=0.1\ \mathrm{mol\,m^{-3}}$, $[HR]_t=20\ \mathrm{mol\,m^{-3}}$, $I=$ 2.303 K, Extractant **1**.

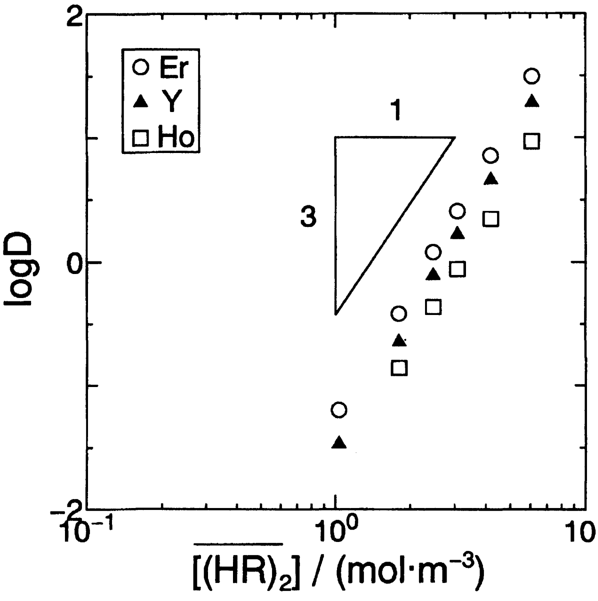

Fig. 3. Effect of the concentration for dimeric species on the distribution ratio. $[M^{3+}]=0.1\ \mathrm{mol\,m^{-3}}$, $I=$ 2.303 K, Extractant **2**.

denotes the organic phase. The extraction equilibrium constant (K_{ex}) is defined as

$$K_{ex} = [\overline{MR_3\cdot 3HR}][H^+]^3/([M^{3+}][(\overline{HR})_2]^3). \qquad (13)$$

The logarithm of the Eq. 13 gives

$$\log K_{ex} = \log D - 3\mathrm{pH} - 3\log[(\overline{HR})_2], \qquad (14)$$

where the distribution ratio (D) is defined as

$$D = [\overline{MR_3\cdot 3HR}]/[M^{3+}]. \qquad (15)$$

Even though all of the extractants, except for **1**, exist as a mixture of monomeric, dimeric, and trimeric species, it is supposed that only dimeric species participate in extraction reactions analogous to Eq. 12. The equilibrium constants (K_{ex}) were evaluated on the basis of Eq. 12 by plotting figures as similar to those in Fig. 3. These values are listed in Table 3, along with separation factors (β). The corresponding values for D2EHPA and PC-88A[15] are also listed. $[(\overline{HR})_2]$ were calculated using trimerization and dimerization constants evaluated earlier according to Eqs. 11 and 8 (Table 2) and neglecting their partition into aqueous phase.

The effects of the pH on the % extraction of each metal are shown in Fig. 4 (a)—(c). The solid lines represent the calculated values for extractants **1**—**5**, while the broken lines represent those for D2EHPA; PC-88A is given for a comparison. From these figures, the order of extarctability for these extractants is

(**3**) > **1** > **4** > **5** > **2** > D2EHPA > PC-88A.

Obviously, all of the extractants have higher a extractability than do commercial extractants, such as D2EHPA and PC-88A.

The extractability of extractant **1** is much greater than that of extractant **2**. The difference between extractants **1** and **2** regarding extractability is only due to the substituent adjacent to the phosphorus atom, that is, whether it is a phenyl group or a methyl group. Compared with the methyl group, the phenyl group adjacent to the phosphorus atom enhances the extractability. Despite its larger steric hindrance, this phenomenon can be attributed to its own electron-resonance. The phosphonate anions, resulting from proton dissociation are stabilized by the electron-resonance effect by the phenyl group, so that the dissociation of the proton of phenylphosphonic acid takes place at a lower pH than that of methylphosphonic acid.

From Figs. 4 (a)—(c), it is shown that extractant **3** has a much greater extractability than does extractant **4**. The difference between extractants **3** and **4** regarding extractability is due to only the presence or absence of an ethereal oxygen in the ester group of phosphonic acid. The existence of an ethereal oxygen enhances the extraction ability of the extractant. This result may suggest that the ethereal oxygen provides a chelating effect by forming coordinate bonding with the metal ion. Peppard et al. reported that the ethereal oxygen in bis(2-hexoxyethyl)phosphoric acid may have some coordination ability with trivalent lanthanide and actinide ions, such as Tm^{3+}, Y^{3+}, and Sc^{3+}.[16]

The extraction ability of extractant **3** is greater than that of **1**. The difference between extractants **1** and **3** regarding extraction ability is due only to the presence or the absence of the 1,1,3,3-tetramethylbutyl group in the ester group; i.e. the 1,1,3,3-tetramethylbutyl group depresses the extractability. If the hypothesis that the

Table 3. Values of Equilibrium Constants (K_{ex}) and Separation Factors (β) for Each Extractant

Extractant	K_{ex}			β		
	Er	Y	Ho	Er/Y	Y/Ho	Er/Ho
1	1.73×10^5	1.23×10^5	5.94×10^4	1.4	2.1	2.9
2	1.78×10^4	1.09×10^4	6.40×10^3	1.6	1.7	2.8
3	1.18×10^8	7.95×10^7	4.60×10^7	1.5	1.7	2.6
4	1.03×10^5	6.50×10^5	3.63×10^5	1.6	1.8	2.8
5	4.57×10^5	3.73×10^5	1.90×10^5	1.2	2.0	2.4
D2EHPA	47	35	24	1.3	1.5	2.0
PC-88A	5.9	4.4	2.5	1.4	1.8	2.5

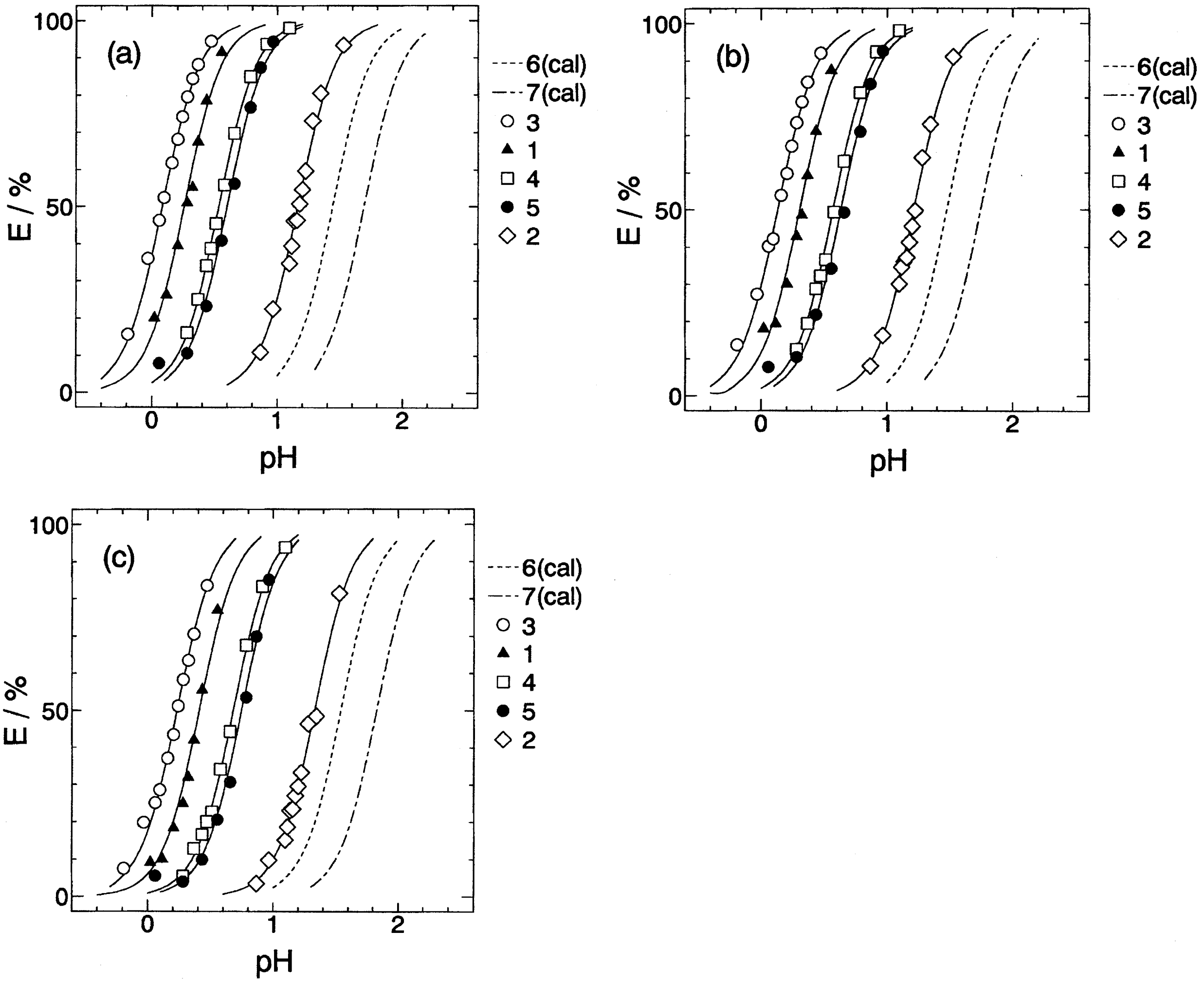

Fig. 4. Effect of the equilibrium pH on extractability: (a)Er, (b) Y, (c) Ho, 6: D2EHPA, 7: PC-88A.

ethereal oxygen forms coordination bonding with metal ions is taken into consideration, it may suggest that the 1,1,3,3-tetramethylbutyl group turns into a steric hindrance when approaching a metal ion.

In order to examine the steric effect due to a phenyl group far from the ion-exchanging and coordinating sites on the extractability, extractant **4** was compared with **5**. These extractants show little difference regarding their extraction behavior. The phenyl group far from the ion-exchanging and coordinating sites appear to not affect the extraction reaction.

The separation factors between Y^{3+} and Ho^{3+} for these new extractants are greater than those for commercial extractants. In general, the higher is the extraction ability of the extractant, the lower is the selectivity. Nevertheless, all of the extractants synthesized in the present work have both high extractability and high selectivity. As result, the following can be concluded:

Concerning the phenylphosphonic acid mono ester, the phenyl group adjacent to the phosphorus atom functions as a group which provides a steric hindrance during the extracton of metals. The steric effect of the phenyl group is large enough to compensate for any loss of selectivity due to an enhancement of extractability itself.

Concerning the methylphosphonic acid mono ester, the methyl group, itself, cannot function as a sterically hindered group. However the effect of the ethereal oxygen atom as the coordinating group is likely to take place due to its weaker extractability compared to that of the corresponding phenyl phosphonic acid mono ester, and to provide high selectivity for methylphosphonic acid with the ethereal oxygen atom.

Stripping Test. Since extractant **3** has the highest extractability among all of the extractants employed, a stripping test was carried out only for **3**. The relations between acid concentration and % stripping of metal ions are listed in Table 4. These results show that hydrochloric acid and sulfuric acid with concentrations higher than 3 mol dm^{-3} are suitable for stripping rare earth elements. Particularly hydrochloric acid was shown to be effective for stripping, while nitric acid does not appear to be sufficient. For the other extractants, 2 mol dm^{-3} of hydrochloric acid is sufficient for complete stripping.

Acid Dissociation Constants of Extractants. The data concerning $pK_{a,app}$ for each extractant are listed in Table 5. The effect of the volume percentage of 1,4-dioxane on $pK_{a,app}$ of extractant **5** is shown in Fig. 5 as an example. The value of pK_a in pure water was evaluated by extrapolation of the liner relation of $pK_{a,app}$ vs. 1,4-dioxane vol% to the 0 vol% (intercept). The difference between $pK_{a,app}$ at 75 vol% 1,4-dioxane solution and pK_a for **5** is equal to 3.78. Based on the assumption that this difference is also valid for other extractants, their pK_a values were estimated according to

$$pK_a = pK_{a,app} - 3.78. \tag{16}$$

In fact, Ishii et al. reported that the differences between the pK_a's and $pK_{a,app}$'s are quite similar among the extractants.$^{17)}$ They measured the apparent pK_as of four kinds of extractants with different substituents, and discussed relation between the apparent pK_a and the 1,4-dioxane concentration. As a result, they found that those plots lie on straight lines with almost the same slope.

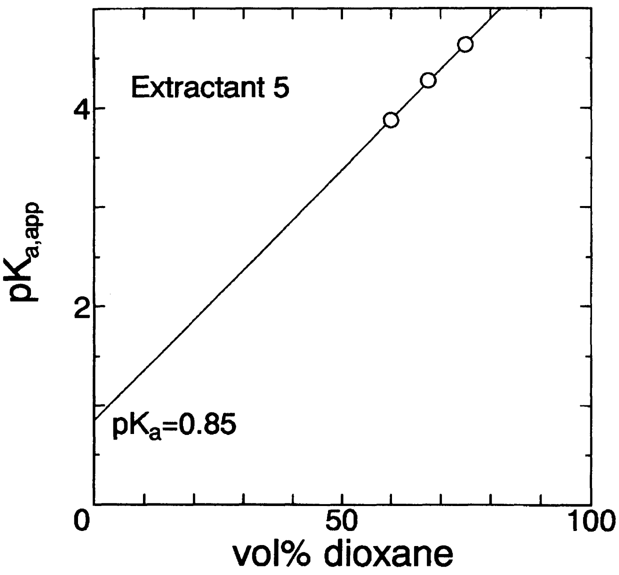

Fig. 5. Effect of the dioxane vol% on the apparent pK_a.

Table 4. Relation between the Acid Concentration and Stripped Percentage of Metal Ions

Acid	Concn	Stripped/%		
	mol dm^{-3}	Er	Y	Ho
HCl	2	93	94	99
	3	100	100	99
	5	100	100	100
HNO_3	2	64	73	81
	3	86	87	90
	5	99	100	98
H_2SO_4	2	81	86	94
	3	98	96	100
	5	100	96	100

Table 5. Apparent pK_a, $pK_{a,app}$ and Actual pK_a for Each Extractant

Extractant	Concn/[mM]$^{a)}$	System	$pK_{a,app}$	pK_a
1	10	75%-dioxane	4.21	0.43
2	10	75%-dioxane	4.94	1.16
3	5	90%-methanol	3.16	
4	10	75%-dioxane	4.52	0.74
5	10	75%-dioxane	4.63	0.85
D2EHPA	10	75%-dioxane	4.76	0.98
PC-88A	10	75%-dioxane	6.04	2.26

a) M=mol dm^{-3}.

The pK_a for each extractant, based on Eq. 16, are listed in Table 5. The values evaluated for D2EHPA and PC-88A closely agree with those obtained by an interfacial tension method (D2EHPA: 1.3, PC-88A: 2.3).$^{18)}$ All of the pK_a for each extractant are somewhat higher than the pH regions where the extraction of rare earth elements takes place. For extractant **3**, pK_a could not be evaluated, because methanol was employed instead of 1, 4-dioxane in this system. However, generally speaking, since the portion of the organic solvent in the sample solution increases, $pK_{a,app}$ also increases; $pK_{a,app}$ of 3.16 in a 90% methanol aqueous solution may be remarkably low.

The order of the extractants' pK_as is according to

(**3**) < **1** < **4** < **5** < D2EHPA < **2** < PC-88A.

This order is opposite to that of the extractability of the extractants, except for the order between D2EHPA and **2**:

(**3**) > **1** > **4** > **5** > **2** > D2EHPA > PC-88A.

This result suggests that the lower is the pK_a of extractant, the higher is its extractability; that is, the extractability depends on pK_a.

Conclusion

New types of acidic organophosphonate were synthesized in order to investigate its aggregation in toluene, distribution equilibria of Ho, Y, and Er and its acid dissociation. The majority of the extractants exist as dimeric species in toluene. All of those employed in the present work were demonstrated to have both high extractability and separation efficiency in the extraction equilibria of heavy rare earth elements. Their pK_a decreased with an increase in extractability. A mutual comparison with each extractant suggested that the enhancement of the extractability and separation efficiency is attributable to a steric effect caused by the phenyl group adjacent to the phosphorus atom and phenoxy oxygen.

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