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Masahiro Goto[a]; Satoshi Matsumoto[a]; Kazuya Uezu[a]; Fumiyuki Nakashio[b]; Kazuharu Yoshizuka[c]; Katsutoshi Inoue[c]
[a] DEPARTMENT OF CHEMICAL SCIENCE & TECHNOLOGY, GRADUATE SCHOOL OF ENGINEERING, KYUSHU UNIVERSITY, HAKOZAKI, FUKUOKA, JAPAN [b] Kumamoto Institute of Technology, Kumamoto, Japan [c] DEPARTMENT OF APPLIED CHEMISTRY, FACULTY OF SCIENCE & ENGINEERING, SAGA UNIVERSITY, SAGA, JAPAN

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Development and Computational Modeling of Novel Bifunctional Organophosphorus Extractants for Lanthanoid Separation

MASAHIRO GOTO,* SATOSHI MATSUMOTO, KAZUYA UEZU, and FUMIYUKI NAKASHIO†

DEPARTMENT OF CHEMICAL SCIENCE & TECHNOLOGY
GRADUATE SCHOOL OF ENGINEERING
KYUSHU UNIVERSITY
HAKOZAKI, FUKUOKA 812-8581, JAPAN

KAZUHARU YOSHIZUKA and KATSUTOSHI INOUE

DEPARTMENT OF APPLIED CHEMISTRY
FACULTY OF SCIENCE & ENGINEERING
SAGA UNIVERSITY
HONJYO 1, SAGA 840-8502, JAPAN

ABSTRACT

Novel organophosphorus extractants, which have two functional groups in the molecular structure, have been developed for the separation of lanthanoids using the liquid–liquid extraction technique. The separation efficiency and extractability of the novel extractants were investigated for nine lanthanoids. These bifunctional extractants have an extremely high extractability to all the lanthanoids compared to those of commercially available organophosphorus extractants. Two isomers having an identical chemical formulation show significantly different behaviors in lanthanoid extraction. This means that the extraction and separation abilities are quite sensitive to the structure of the spacer connecting the two functional groups. We also discuss the experimental results with a computational modeling by means of molecular mechanics and semiempirical molecular orbital methods. The novel molecular mechanics (MM) calculation program MOMEC enables us to analyze the stable conformation of a series of lanthanoid complexes. The calculation suggests that the structural effect of the spacer is one of the decisive factors for enhancing selectivity and extractability in lanthanoid extraction.

* To whom correspondence should be addressed.
† Present address: Kumamoto Institute of Technology, Kumamoto 860-0082, Japan.

INTRODUCTION

Lanthanoids are important elements for producing advanced materials such as supersemiconductors, ultramagnets, and laser crystals. However, their chemical and physical similarities make the mutual separation of adjacent elements among lanthanoids quite difficult.

Conventional solvent extraction is well-known as a promising technique for the separation of lanthanoids on an industrial scale owing to the advantage for large-scale operation. In the liquid–liquid extraction of actinoids and lanthanoids, acidic organophosphorus extractants are considered to be one of the best candidates from both extractive and separative points of view (1, 2). Even with organophosphorus extractants, many stages in a series of mixer–settlers are required for separating all the lanthanoids because there is some poor selectivity among the lanthanoid series. The extractant is crucially influential in the liquid–liquid extraction operation. Thus, a new extractant to enhance both the separation efficiency and extractability is desirable to simplify the solvent extraction process. A number of studies have been carried out on the selective extraction of lanthanoids. In most reports, however, conventional and commercially available extractants, such as D2EHPA (bis-2-ethylhexyl hydrogen phosphate) and PC-88A (bis-2-ethylhexyl hydrogen phosphonate), or newly synthesized bis-alkyl hydrogen phosphate have been used in liquid–liquid extraction. In the late 1950s, Peppard et al. reported the extraction of actinides from nuclear wastes using some newly developed organophosphorus extractants (3). Later, Yuan synthesized a series of acidic organophosphorus extractants in order to investigate the structure–extractability relationship (4), and the structure of the hydrophobic group in the extractants was found to have a predominant effect to the selectivity of lanthanoids. However, the development of novel organophosphorus extractants has not been performed except for the idea of changing the hydrophobic moieties in the organophosphorus extractants (5).

In the present study we have synthesized novel organophosphorus extractants which have two functional phosphoric groups in the molecular structure for effectively separating lanthanoids based on the new concept to introducing a spacer to connect the bifunctional groups. Using newly synthesized extractants, we have investigated the extraction behavior of nine lanthanoids for comparison with those of conventional monoacidic organophosphorus extractants. Furthermore, the structural effects of the extractants on the extraction behavior of lanthanoids are discussed with computational modeling by means of molecular mechanics and semiempirical molecular orbital methods.

EXPERIMENTAL

Extractants

Three new extractants with two phosphoric acid groups, tri(ethylene glycol) *o,o′*-di-(4-*tert*-octylphenyl phosphoric acid) (abbreviated EG3PA), 1,2-di(2-

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hydroxyethoxy)benzene *o*,*o′*-di(4-*tert*-octylphenyl phosphoric acid)(abbreviated *o*-type), and 1,4-di(2-hydroxyethoxy)benzene *o*,*o′*-di(4-*tert*-octylphenyl phosphoric acid) (abbreviated *p*-type), have been synthesized as follows.

(I) EG3PA

There are two steps for synthesizing EG3PA. In the first step, *p*-tertiary octylphenoxy dichlorophosphine oxide was prepared by refluxing 150 cm^3 phosphorus oxychloride (1.64 mol), 51.5 g (0.25 mol) tertiaryoctylphenol, and 0.1 g (0.7 mmol) anhydrous aluminum chloride for 4 hours. The product was purified by reduced distillation, and the fraction at 379–380 K under 3 mmHg was collected with 48% yield. In the second step, 9.0 g (28 mmol) *p*-tertiary-octylphenoxy dichlorophosphine oxide was added to a mixture of 150 cm^3 dry toluene and 10 cm^3 pyridine placed in an iced bath. A solution of 1.9 g (13 mmol) triethylene glycol in 50 cm^3 dry toluene and pyridine was slowly added dropwise to the above solution at 273 K. This mixture was stirred in an iced bath for 24 hours, and then poured into 100 cm^3 of iced water. A concentrated hydrochloric acid was added to the solution until the pH in the aqueous solution reached between 1 and 2. Then the product was extracted with 100 cm^3 toluene. The toluene phase was washed twice with 100 cm^3 of 1 M hydrochloric acid, and dried with anhydrous magnesium sulfate. After the organic phase was evaporated, the final product was obtained. The crude product was finally purified by column chromatography (silica gel, solvent: dichloromethane). The final product assayed as follows: light yellow liquid, yield 37.0%; IR (neat) ν_{OH} 2628 cm^{-1}, $\nu_{P\text{-}O}$ and δ_{OH} 2288 cm^{-1}, $\nu_{P\text{-}OR}$ 1684 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$, TMS, 303 K) $\delta = 0.70$ (18H, s, —C—*CH*$_3$), $\delta = 1.33$ (12H, s, Ar—C—*CH*$_3$), $\delta = 1.77$ (4H, s, —C—*CH*$_2$—C), $\delta = 3.69$ (8H, d, —O—*CH*$_2$—*CH*$_2$—O—P—), $\delta = 4.22$ (4H, m, —O—*CH*$_2$—*CH*$_2$—O—), $\delta = 7.12$ (4H, d, P—ArH (*m*-position)), $\delta = 7.27$ (4H, d, P—ArH (*o*-position)), $\delta = 10.08$ (2H, bs, P—OH). The elemental consti tu ents of the final product were as follows: C, 59.54%; H, 8.04%. By calculation, $C_{34}H_{56}O_{10}P_2$ gives: C, 59.46%; H, 8.22%.

(II) o-Type

Before synthesizing the final product, the compartment of the spacer [diol compound: 1,2-bis(2-hydroxyethoxy)benzene] was prepared as follows: Under nitrogen atmosphere, 7.0 g (64 mmol) catechol and 50 g (16 mmol) Cs_2CO_3 were mixed for a while in 150 cm^3 dry DMF at room temperature. A solution of 24 g (0.14 mol) of bromoethyl acetate in 100 cm^3 of dry DMF was slowly added dropwise to the above solution at 273 K, and the mixture was stirred for 48 hours. The product was extracted with diethyl ether and was obtained after evaporation. The product was dissolved in 50 cm^3 THF and added dropwise to the THF solution which included 6.0 g (0.13 mol) $LiAlH_4$ placed

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in an ice bath. The THF solution was refluxed for 24 hours. The final product of the spacer was extracted with chloroform and purified by recrystallization with a mixture of chloroform and hexane. A white crystal was obtained with 40% yield (mp 355–357 K). The subsequent steps are similar to the procedures reported in synthesizing EG3PA. The final product assayed as follows: light yellow liquid, yield 62%; IR (neat) ν_{OH} 2620 cm^{-1}, $\nu_{P\text{-}O}$ and δ_{OH} 2280 cm^{-1}, $\nu_{P\text{-}OR}$ 1681 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$, TMS, 303 K) $\delta = 0.68$ (18H, s, —C—*CH_3*), $\delta = 1.19$ (12H, s, Ar—C—*CH_3*), $\delta = 1.68$ (4H, s, —C—*CH_2*—C), $\delta = 4.13$ (4H, m, O—*CH_2*—CH_2—O—P—), $\delta = 4.45$ (4H, m, —O—CH_2—*CH_2*—O—P—), $\delta = 6.87$ (4H, m, O—ArH—O), $\delta = 7.09$ (4H, d, P—ArH (*m*-position)), $\delta = 7.23$ (4H, d, P—ArH (*o*-position)), $\delta = 10.10$ (2H, bs, P—OH). The elemental constituents of the final product were as follows: C, 62.44%; H, 7.55%. By calculation, $C_{38}H_{56}O_{10}P_2$ gives: C, 62.13%; H, 7.68%.

(III) p-Type

The spacer of the *p*-type [diol compound: 1,4-bis(2-hydroxyethoxy)benzene] was prepared by the same method described above. The subsequent steps are similar to the procedures reported in synthesizing EG3PA. The final product assayed as follows: light yellow liquid, yield 68%; IR (neat) ν_{OH} 2620 cm^{-1}, $\nu_{P\text{-}O}$ and δ_{OH} 2280 cm^{-1}, $\nu_{P\text{-}OR}$ 1680 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$, TMS, 303 K) $\delta = 0.68$ (18H, s, —C—*CH_3*), $\delta = 1.35$ (12H, s, Ar-C—*CH_3*), $\delta = 1.68$ (4H, s, —C—*CH_2*—C), $\delta = 4.00$ (4H, m, —O—*CH_2*—CH_2—O—P—), $\delta = 4.38$ (4H, m, —O—CH_2*CH_2*—O—P—), $\delta = 6.79$ (4H, m, O—ArH—O), $\delta = 7.10$ (4H, d, P—ArH (*m*-position)), $\delta = 7.26$ (4H, d, P—ArH (*o*-position)), $\delta = 10.33$ (2H, bs, P—OH). The elemental constituents of the final product were as follows: C, 61.78%; H, 7.55%. By calculation, $C_{38}H_{56}O_{10}P_2$ gives: C, 62.13%; H, 7.68%. Moreover, a monofunctional extractant that has a structure similar to the right/left part of the bifunctional extractants (abbreviated MPA) was prepared to compare the extraction behavior (6). Figure 1 shows the structures and abbreviations of extractants employed in this study. Since the *o*- and *p*-types have an identical chemical formulation, these extractants have an isomeric relationship.

Solvent Extraction

An organic solution was prepared by weighting each extractant into analytical-grade toluene. An aqueous solution was prepared by dissolving each lanthanoid chloride into a hydrochloride solution (0.1–2 M). The aqueous solution always contained three kinds of metals, i.e., La, Pr, Nd, or Sm, Gd, Dy, or Ho, Y, Er. Equal volumes (5 mL) of aqueous and organic solutions were shaken with a mechanical shaker at 303 K for at least 5 hours which was a suf-

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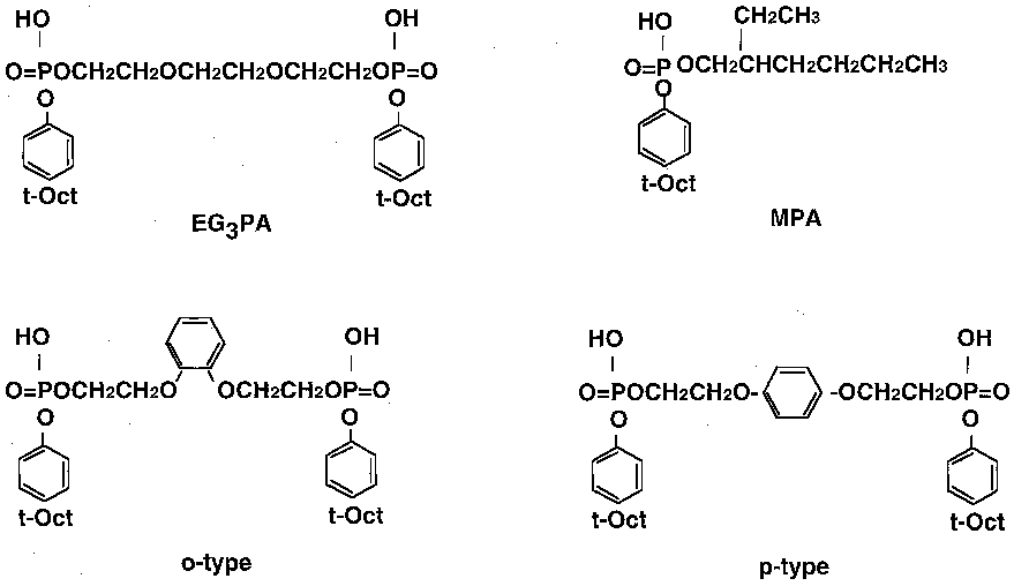

FIG. 12131 Molecular structures and abbreviations of novel extractants developed in this

ficiently long time to reach equilibrium. After phase separation the initial and equilibrium concentrations of the metals in the aqueous phase were measured by an ICP emission spectrophotometer (Seiko SPS1200VR). The initial concentration of each metal ion in the material source and that of the extractant were 0.1 and 10 mM, except when investigating the concentration dependency of extractants on lanthanoid extraction. Extraction species of the complex between a metal ion and each extractant were determined based on both slope analysis and Job's method. Measurements of aggregation number and acid dissociation constants were also conducted for all the extractants using a vapor-phase osmometer (Corona 117) and an automatic titrator (Kyoto electronic AT-117).

Molecular Modeling

The molecular mechanics (MM) calculation of the lanthanoid complexes was performed with the strain minimization program MOMEC97 (7). In the molecular mechanics framework, the structure of a molecule is modified in order to minimize its total strain energy (U_{total}), consisting of bond length deformation (E_{b}), valence angle deformation (E_{θ}), torsion angle deformation (E_{ϕ}), and nonbonded interaction (E_{nb}), as expressed by Eq. (1). The functions used in the present study are expressed in Eqs. (2)–(8), where k_{r}, k_{θ}, and k_{ϕ} are the respective force constants for bond length, valence angle, and torsion angle deformations; r_0, θ_0, and ϕ_0 are the respective strain-free values; r_{vdW}

represents the van der Waals radius; *a*, *b*, and *c* are the variables calculated by Eqs. (6)–(8); "m" is the periodicity; and ε denotes the hardness parameter which means the work necessary to separate the pair of atoms to infinity. The other terms may be included to account for out-of-plane deformation, electrostatic interactions, and hydrogen bonding, however, these were not included here in order to simplify the model.

$$U_{\text{total}} = \sum(E_{\text{b}} + E_{\theta} + E_{\phi} + E_{\text{nb}}) \tag{1}$$

$$E_{\text{b}} = \tfrac{1}{2}\, k_{\text{r}}(r_{ij} - r_0)^2 \tag{2}$$

$$E_{\theta} = \tfrac{1}{2}\, k_{\theta}\, (\theta_{ij} - \theta_0)^2 \tag{3}$$

$$E_{\phi} = \tfrac{1}{2}\, k_{\phi}\, [1 + \cos\{\text{m}(\phi_{ijk} + \phi_0)\}] \tag{4}$$

$$E_{\text{nb}} = ae^{-br_{ij}} - cr_{ij}^{-6} \tag{5}$$

$$a = 2014(\varepsilon_i\, \varepsilon_j)^{1/2} \tag{6}$$

$$b = 12.50/(r_{\text{vdWi}} + r_{\text{vdWj}}) \tag{7}$$

$$c = \{2.55(\varepsilon_i\, \varepsilon_j)^{1/2}\, (r_{\text{vdWi}} + r_{\text{vdWj}})^6\}/144 \tag{8}$$

No symmetry restrictions were imposed on the local coordination sphere, and nonbonded interactions involving the metal center were neglected. This approach has also been performed by others in earlier force field calculations for transition metal complexes (8, 9), and lanthanoid complexes (10–12).

Input coordinates were obtained from the graphics package HyperChem Release 4 (Hypercube, Inc., Canada). Calculation was conducted using the strain-free bond lengths, strain-free angles, and the force constant for each type of bond for lanthanoid complexes in a previous paper (12) to obtain the global minimum structures. The optimized structures were calculated under the convergence criteria for RMS = 0.001.

For comparison of the structures of the extractants calculated by MOMEC97, PM3 type of semiempirical molecular orbital calculations (SMO) of the extractants was carried out using MOPAC93 (13) (the convergence criteria for GNORM = 0.01 and SCFCRT = 0.00001).

RESULTS AND DISCUSSION

Aggregation and Acid Dissociation Behavior of the Novel Extractants

Organophosphorus extractants such as D2EHPA and PC-88A are well-known to dimerize in a nonpolar organic solvent (14–20). We first investigated the aggregation behavior of the synthesized extractants in the diluent toluene. On the basis of vapor-phase osmometric measurement, it was found

that EG3PA and the *o*-type mainly exist as dimeric species, while the main species of the *p*-type is a trimer in toluene. The difference in the aggregation mode of these extractants in toluene clearly affects the extraction behavior of the three extractants. In the measurement of acid dissociation constants for the three extractants, no significant difference was observed, and the values of pK_{a1} and pK_{a2} in their bifunctional extractants were obtained to be around 1.6 and 2.1, respectively.

Extraction Equilibrium of Lanthanoids

Figure 2 shows a typical pH dependence on the distribution ratio ($D = [\text{Metal}]_{org}/[\text{Metal}]_{aq}$) in lanthanoid extraction using the *p*-type or *o*-type. All the plots lie on straight lines with a slope of 3. This result means that the complex formation proceeds through a proton-exchange mechanism. The extraction behavior of EG3PA showed a similar tendency to that of the *o*-type. The selectivity for the metal ions is in the order light (Nd) > middle (Gd) > heavy (Ho) lanthanoid series; this order is consistent with that of conventional organophosphorus extractants (21). However, it is surprising that the extractant isomers with an identical chemical formulation show significantly different extraction behaviors. The *p*-type exhibited an extremely high selectivity compared to that of the *o*-type. Since molecular modeling by PM3-SMO indicates that the two extractants possess a similar electric density on the phosphoric acid part in the extractants, the quite different extraction behavior is considered to be caused by a steric effect of the spacer. Further, the concentration dependency of each extractant on lanthanoid extraction was investigated, and a slope of 2 was obtained for the dimer (EG3PA and *o*-type) and trimer (*p*-type).

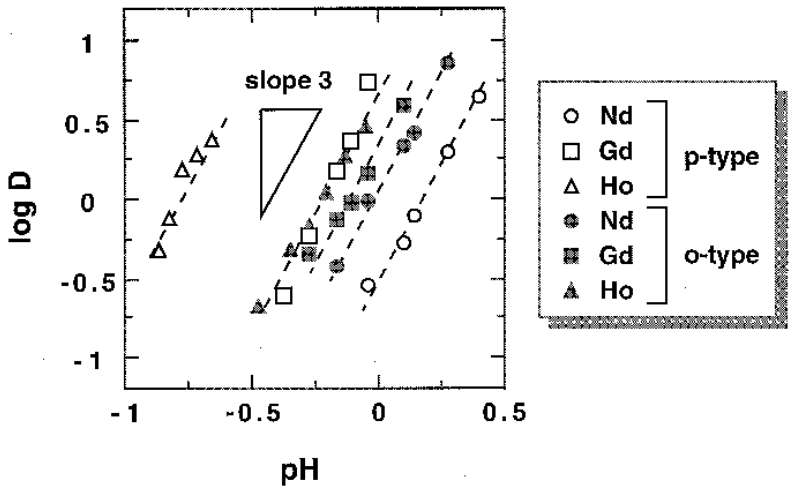

FIG. 2 pH dependence on lanthanoid extraction with novel bifunctional extractants.

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Based on the slope analysis and the Job's method (data not shown), we found that the extraction equilibrium of lanthanoids for each extractant could be expressed as follows.

For EG3PA or the *o*-type:

$$Ln^{3+} + 2(H_2R)_2 = LnRHR(H_2R)_2 + 3H^+ \qquad (K_{ex,\,Ln}) \qquad (9)$$

For the *p*-type:

$$Ln^{3+} + 2(H_2R)_3 = Ln(HR)_3(H_2R)_3 + 3H^+ \qquad (K_{ex,\,Ln}) \qquad (10)$$

where Ln and H_2R denote the lanthanoid elements and the bifunctional organophosphorus extractants, respectively.

All the extraction equilibrium constants ($K_{ex,\,Ln}$) were evaluated on the basis of Eqs. (9) and (10) by plotting data similar to those in Fig. 2, and they are summarized in Table 1. Evidently the structure of the spacer connecting the bifunctional moieties in the extractant has a crucial effect on extractability and selectivity for lanthanoid extraction.

Extractability and Selectivity of Lanthanoids

Figure 3 shows a comparison of extractability of Y(III) with three different bifunctional extractants along with that for the monoacidic extractants. The data of D2EHPA were calculated using the $K_{ex,\,Ln}$ value in toluene reported previously (22). Since the concentration of monoacidic extractants was adjusted to twice that of the bifunctional extractants in order to make the number of functional groups equal, all the bifunctional extractants obviously have a higher extractability than do the monofunctional extractants. The extractability of the *p*-type is much greater than that of the *o*-type although the difference in the two extractants is only the position of oxygen in the spacer. The results indicate that connecting functional groups with a spacer is a useful strategy to control extractability. Furthermore, based on the difference between MPA and D2EHPA, introducing a phenyl group adjacent to the func-

TABLE 1
Extraction Equilibrium Constants ($K_{ex,\,Ln}$) of Lanthanoids for Each Novel Extractant

	$K_{ex,\,Ln}$								
Extractant	La	Pr	Nd	Sm	Gd	Dy	Ho	Y	Er
EG3PA	0.13	0.20	0.24	0.38	0.38	0.48	0.49	0.68	0.77
o-Type	0.03	0.06	0.06	0.13	0.13	0.23	0.31	0.47	0.54
p-Type	0.01	0.02	0.02	0.23	0.54	2.1	13	26	42

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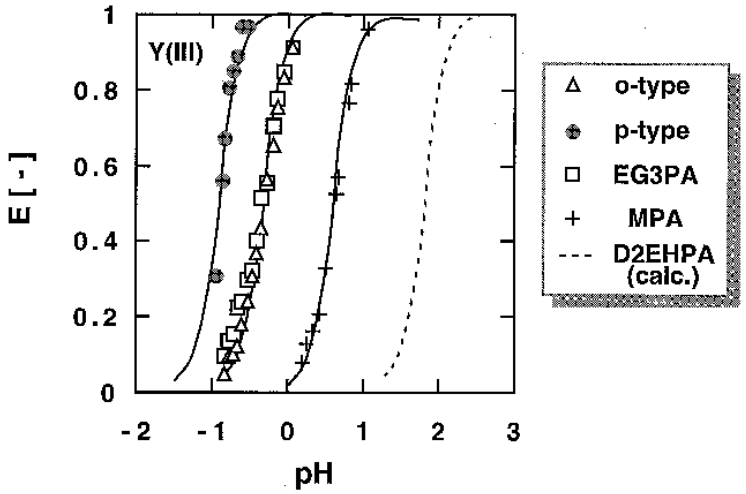

FIG. 3 Extraction behavior of yttrium(III) with bifunctional extractants and monofunctional extractants.

tional phosphonic part appears to be very effective in enhancing the extractability of lanthanoids (2).

Since the $K_{ex,\,Ln}$ values of the *p*- and *o*-types have different dimensions, we cannot compare the results directly to evaluate the extractability and selectivity of the two extractants. Thus a pH value at 50% extraction, $pH_{0.5}$, was employed to discuss the extraction behavior of all the bifunctional extractants (Fig. 4). The structure of the spacer in the extractants strongly af-

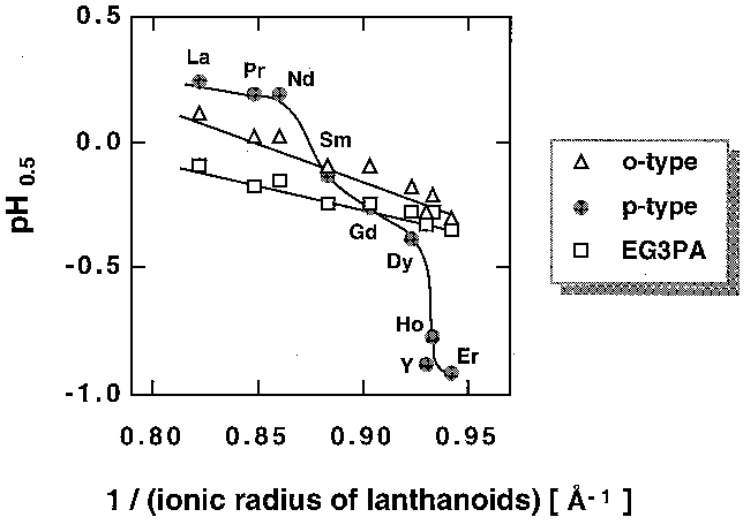

FIG. 4 Half pH value of each bifunctional extractant for all the lanthanoids.

fects not only the extractability but also the selectivity in lanthanoid extractions. A rigid segment appears to be more effective than a flexible one for enhancing selectivity because EG3PA, which has the most flexible spacer, shows the lowest selectivity toward lanthanoids. The *p*-type exhibits a high selectivity, in particular, in the region of the heavy lanthanoid series. The separation factor between Dy and Ho, which is defined by the ratio of $K_{ex,\ Ln}$ values of Dy over Ho, reached around 6; it is threefold that of a monoacidic commercial extractant such as D2EHPA or PC-88A ($K_{ex,\ Dy}/K_{ex,\ Ho} = 2$) (21).

Molecular Modeling

The novel MM calculation program MOMEC, which possesses the force field parameters of lanthanoids, enabled us to analyze the stable conformation of a series of lanthanoid complexes. Figure 5 shows RMS overlays of the lowest energy structures of the extractants calculated by MOMEC and PM3-SMO. The RMS value of residual distances in angstroms is used as a common measure of the similarity of the structures. Since both calculated structures are in substantial agreement, these force field parameters for MOMEC are applicable to the calculation of the lowest energy structures of extractants. The structures of the extractants were found to be quite different from each other; in particular, a phosphoryl group of the *o*-type lies upon another while that of the *p*-type is separated from another. This conformational difference is caused by the different substituent position and the rigidity of the phenolic group in the spacer. On the basis of the most stable extractant structures calculated by computational modeling steric hindrance of the *p*-type is considered to be higher than that of the *o*-type. Meanwhile, from an electrical point of view, we cannot explain why the *p*-type has a higher selectivity for all the lanthanoids, because these three extractants have similar electrical densities on all the functional atoms. This also suggests that enhancement of selectivity is based on the steric effect not on the electrical effect as similar monoacidic organophosphorus extractants with high steric, hindered hydrophobic groups provide high selectivity (2, 23).

In general, lanthanoid complexes with an organic ligand take nona coordination with a tricapped trigonal prismatic (TCTP) geometry (11, 24–30). In a previous paper we calculated lanthanoid complexes with monoacidic organophosphate as a nona coordinate complex with regular or distorted TCTP geometry around the metal center (12). Thus, in the present study we have calculated the nona coordinate lanthanoid complexes with EG3PA, *o*-type, and *p*-type by MOMEC97. Figure 6 exhibits the lowest strain energy structure of the La-*p*-type and La-*o*-type complexes calculated in this study.

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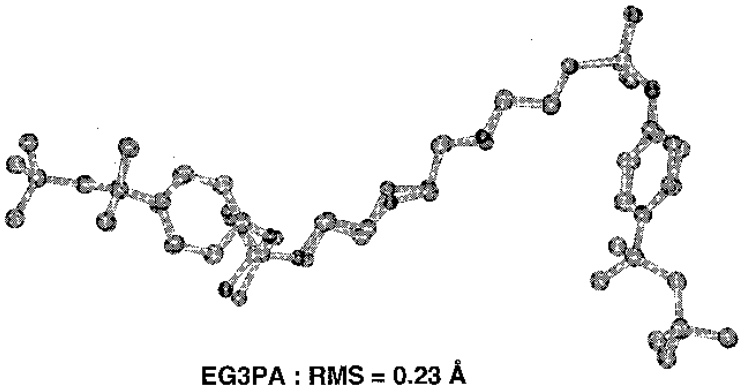
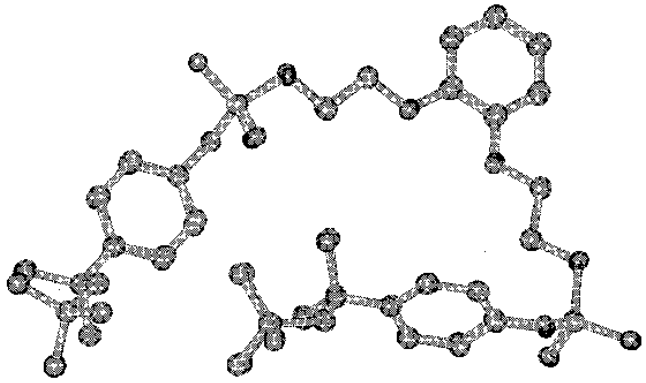
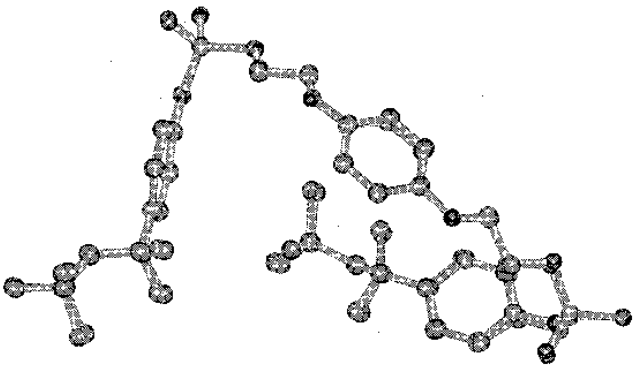


EG3PA : RMS = 0.23 Å



o-type : RMS = 0.22 Å



p-type : RMS = 0.25 Å

FIG. 5 RMS overlay of the computed structures of the extractants by MOMEC and PM3-SMO (hydrogen atoms are not shown).

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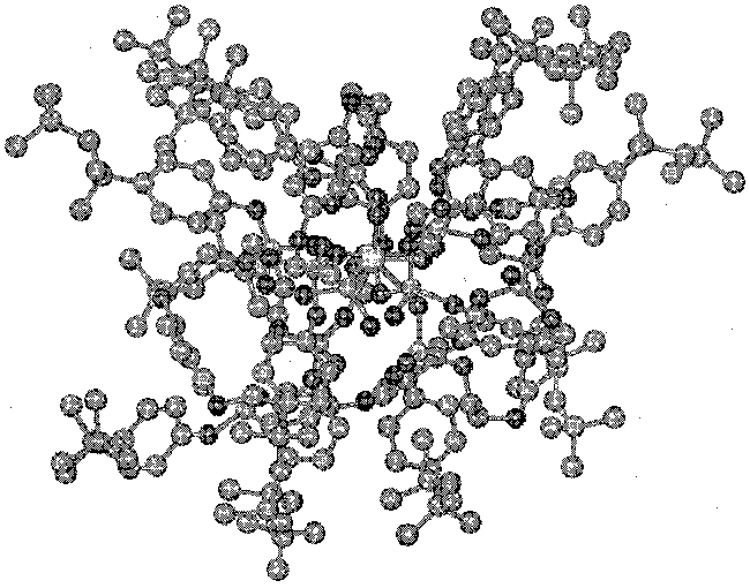
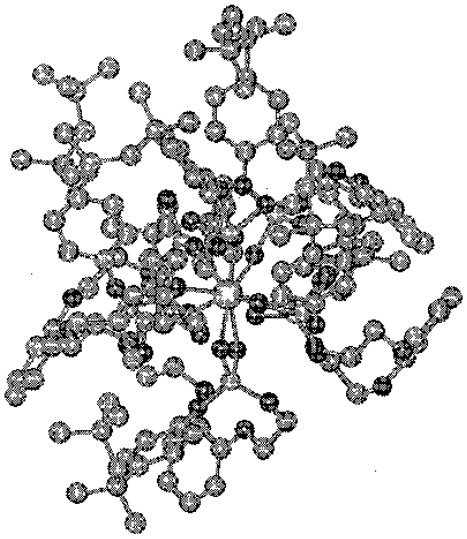


(a) La-p-type complex



(b) La-o-type complex

FIG. 6 The lowest strain energy structures of the La-*p*-type and La-*o*-type complexes calculated by MOMEC97.

Hancock et al. (31, 32) first proposed QSPR theory for estimating the strain energy contribution for the thermodynamics of transition metal complex with polyamines. According to the theory, the relation between the total strain energy and complex formation can be expressed by the following equations.

For EG3PA or the *o*-type:

$$\mathrm{Ln^{3+}} + 2(\mathrm{H_2R})_2 = \mathrm{LnRHR(H_2R)_2} + 3\mathrm{H^+}$$
$$U_{\mathrm{Ln}} \quad 2U_{(\mathrm{H2R})2} \quad U_{\mathrm{Lncom}} \quad 3U_{\mathrm{H}} \tag{11}$$

For the *p*-type:

$$\mathrm{Ln^{3+}} + 2(\mathrm{H_2R})_3 = \mathrm{Ln(HR)_3(H_2R)_3} + 3\mathrm{H^+}$$
$$U_{\mathrm{Ln}} \quad 2U_{(\mathrm{H2R})3} \quad U_{\mathrm{Lncom}} \quad 3U_{\mathrm{H}} \tag{12}$$

where U_i (i = Ln, H_2R, Lncom, or H) is the energy of respective molecule.

The increase in the energy of complex formation between La and the corresponding lanthanoid complex is expressed by

$$\Delta U_{\mathrm{Ln}} - \Delta U_{\mathrm{La}} = (U_{\mathrm{Lncom}} - U_{\mathrm{Lacom}}) - (U_{\mathrm{Ln}} - U_{\mathrm{La}}) \tag{13}$$

Figure 7 shows the relation between ($\Delta U_{\mathrm{Ln}} - \Delta U_{\mathrm{La}}$) and the inverse of the ionic radius. As expected, increasing the rigidity of the spacer in bifunctional organophosphorus extractants will lead to increasing selectivity, and this may be predicted qualitatively with the molecular mechanics calculations discussed here. On the basis of the results in Fig. 7, we reach the important conclusion that an extractant which has a high energy difference in complex formation between La and a target lanthanoid ion ($U_{\mathrm{Ln}} - U_{\mathrm{La}}$) will provide high selectivity. Based on the results, we should design novel extractants which give a high energy difference in complex formation by computational modeling before synthesizing them. The physicochemical meanings of these values will be clarified from the viewpoint of thermodynamic aspects in the next work.

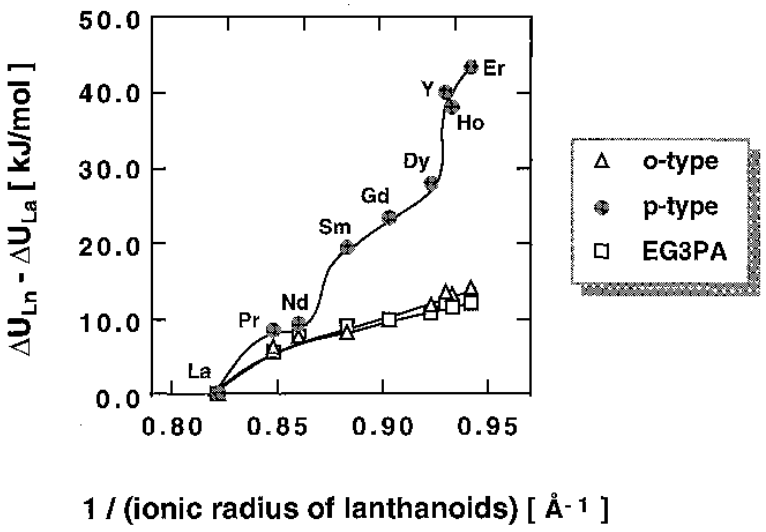


FIG. 7 Plots of ($\Delta U_{\mathrm{Ln}} - \Delta U_{\mathrm{La}}$) for all the lanthanoids.

CONCLUSION

Three novel extractants which have two phosphoric groups in a molecule have been synthesized for the selective extraction of lanthanoid. It is clear that these extractants have a high extractability for lanthanoids compared to ordinary monoacidic extractants. The steric effect of the extractants was a prominent factor for enhancing the extractability and selectivity. In particular, the structure of the spacer connecting the bifunctional groups is important in ensuring the high selectivity of lanthanoids. Molecular modeling also suggests that the steric effect is more important than the electrical effect. These results lead to the conclusion that the new concept to connect some functional moieties with a spacer is a promising strategy for developing a novel extractant for lanthanoid separation.

NOMENCLATURE

a	variable calculated by Eq. (6) (—)
b	variable calculated by Eq. (7) ($Å^{-1}$)
c	variable calculated by Eq. (8) ($Å^{6}$)
E_b	bond length deformation energy ($kJ \cdot mol^{-1}$)
E_{nb}	nonbonded interaction energy ($kJ \cdot mol^{-1}$)
E_ϕ	torsion angle deformation energy ($kJ \cdot mol^{-1}$)
E_θ	valence angle deformation energy ($kJ \cdot mol^{-1}$)
$K_{ex,\,Ln}$	extraction equilibrium constant (—)
k_r	force constant for bond length deformation ($mdyn \cdot Å^{-1}$)
k_ϕ	force constant for torsion angle deformation ($mdyn \cdot rad^{-1}$)
k_θ	force constant for valence angle deformation ($mdyn \cdot rad^{-1}$)
m	periodicity (—)
r_0	strain-free bond length (Å)
r_{vdW}	van der Waals radius (Å)
r_ϕ	strain-free valence angle (rad)
r_θ	strain-free torsion angle (rad)
U_i	strain energy of species i ($kJ \cdot mol^{-1}$)
U_{total}	total strain energy ($kJ \cdot mol^{-1}$)
ΔU_{Ln}	energy difference in complex formation ($kJ \cdot mol^{-1}$)
ε	hardness parameter (—)

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