# New Trident Molecule with Phosphoric Acid Functionality for Trivalent Rare Earth Extraction

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## ABSTRACT

*Tripodal extraction reagent with three phosphoric acid groups, together with the corresponding monopodal molecule has been prepared to investigate some metals extraction behavior, in particular, trivalent rare earth elements (REEs). The tripodal reagent exhibited extremely high selectivity for metals with high valency such as Zr(IV), In(III), Lu(III), and Fe(III). Tripodal reagent also exhibited exceptionally high extraction ability compared with the corresponding monopodal one in the extraction of trivalent REEs. The result for the stoichiometry of tripodal reagent to heavy REEs showed the inflection point between Er (2:1 for a ligand with ion) and Tm (1:1). The extraction reactions were determined for all rare earths with both reagents. The extraction equilibrium constants ($K_{ex}$), the separation factors (β), half pH values ($pH_{1/2}$), difference of half pH values ($\Delta pH_{1/2}$) for extraction of REEs with both reagents are estimated.*

***Keywords***: *tripodal compound; solvent extraction; rare earth metals*

## ABSTRAK

*Reagen ekstraksi tripodal dengan tiga gugus fungsi asam fosfat, bersama dengan molekul monopodalnya telah dibuat untuk menginvestigasi sifat ekstraksi beberapa logam, terutama, elemen tanah jarang bervalensi tiga. Reagen tripodal memiliki selektivitas yang sangat tinggi untuk logam dengan valensi tinggi seperti Zr(IV), In(III), Lu(III) dan Fe(III). Reagen tripodal juga menunjukkan kemampuan ekstraksi yang tinggi dibandingkan dengan reagen monopodal dalam ekstraksi elemen tanah jarang bervalensi tiga. Hasil penelitian terkait stoikiometri reagen tripodal terhadap logam tanah jarang menunjukkan titik belok antara Er (2:1 untuk sebuah ligan dengan ion) dan Tm (1:1). Reaksi-reaksi pada proses ekstraksi ditentukan untuk semua elemen tanah jarang dengan kedua reagen. Konstanta kesetimbangan ekstraksi ($K_{ex}$), factor pemisahan (β), nilai pH paro ($pH_{1/2}$), perbedaan nilai pH paro ($\Delta pH_{1/2}$) untuk elemen tanah jaranguntuk kedua reagen telah diestimasi.*

***Kata Kunci***: *senyawa tripodal; ekstraksi pelarut; logam tanah jarang*

## INTRODUCTION

A series of rare earth elements (REEs) are essential and have been employed as advanced materials such as electronic, magnetic, luminescence devices due to their specific physical properties [1]. They are typical critical metals due to their similar chemical properties and their ionic sizes, although their abundance in the earth's crust is sufficient for their demand, consequently, mutual separation of REEs has been required.

Solvent extraction is one of the most versatile techniques and has been used for separation of metal ions [2-3]. There are many factors to determine extraction efficiency [4] and the selection of optimal extraction reagent is the most important one among them. Organophosphorus acid type extraction reagents are well known to be most effective for extraction of REEs. Peppard et al. reported REEs extraction with newly prepared organophosphorus acid reagents [5-6]. Yuan et al. also prepared many organophosphonic acid type reagents to investigate REEs extraction and correlate between structure and extraction ability [7-9]. The organophosphorus acid reagents with bulky substituents for REEs by our groups were also reported [10-11]. The highly effective extraction reagent is required for the mutual separation of REEs.

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Calixarenes are macrocyclic compounds and provide three-dimensionally arranged coordination site for guest molecules or ions [12-14]. Their derivatives can exhibit structural effects such as size-fitting effect, converging effect of functional groups, complementary effect, and allosteric effect, based on specific cyclic structures [15-16]. Rohovec et al. prepared phosphonic acid type derivatives of calixarenes for REEs extraction [17-18]. Other derivatives were also prepared to investigate REEs extraction by our group [19-23]. All derivatives exhibited remarkably higher extraction ability for REEs than the corresponding monomeric ones due to such specific structural effects and also exhibited a higher ability than carboxylic acid derivatives [24] due to the presence of phosphonic acid functionality. The mutual separation of REEs has still been difficult even using calix[4]arene type reagents probably due to the slightly larger coordination site.

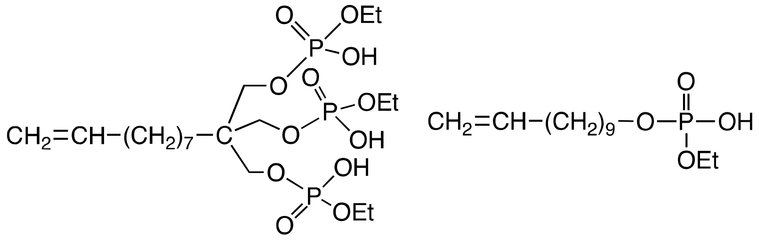
Alkyltrimethylols are non-macrocyclic tripodal compounds. They also provide three-dimensionally arranged coordination site for guest molecules or ions [25-26]. They were employed as extraction reagents and ion-selective electrodes [25-33], and we named as “trident” molecules [29]. Their coordination site can be narrower than that of calix[4]arene derivative when functional groups are introduced close to the carbon atom as a junction to tripodal branched groups.

In the present paper, phosphoric acid type of trident molecule has been prepared to verify the potential of a tripodal framework for REEs extractive separation, together with extraction ability of other metal ions. The chemical structure of the extraction reagent employed in the present study is shown in Fig. 1.

## EXPERIMENTAL SECTION

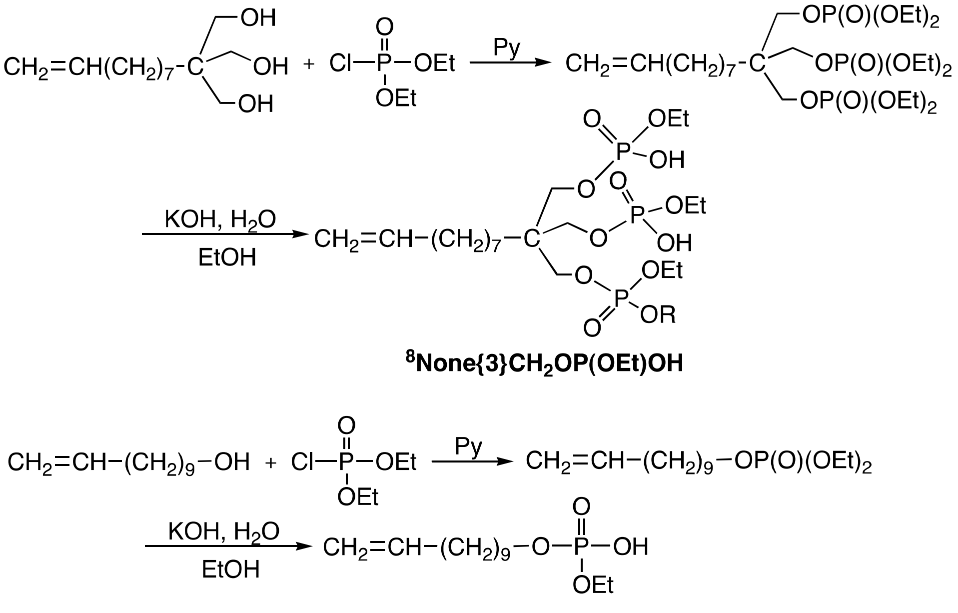
### Materials

Trident molecule, 1,1,1-tris(hydroxymethyl)-9-decene was synthesized in similar manners to the previously reported procedures [25,34-35].



**$^{8}$None{3}CH$_2$OP(OEt)OH** **$^{8}$None{1}CH$_2$OP(OEt)OH**

**Fig 1.** Chemical structures of the compounds employed in the present work



**$^{8}$None{3}CH$_2$OP(OEt)OH**

**$^{8}$None{1}CH$_2$OP(OEt)OH**

**Fig 2.** Synthetic scheme of the extraction reagent employed in the present study

## Procedure

### *Synthesis of extraction reagent*

The synthetic route of the extraction reagent employed in the present study is shown in Fig. 2.

**1,1,1-Tris(diethyl phosphoryloxymethyl)-9-decene ($^8$None{3}$CH_2OP(O)(OEt)_2$).** Under a nitrogen stream, 1,1,1-tris(hydroxymethyl)-9-decene 3.80 g (16.5 mmol) in 250 $cm^3$ toluene and triethylamine 10.1 g (99.5 mmol, 6.0eq) were mixed. Diethyl chlorophosphate 17.4 g (101 mmol, 6.1 eq) was added dropwise for 15 min to the mixture at room temperature (25±4 °C) and the mixture was shaken for 45 h. The precipitated triethylamine hydrochloride salt was removed by filtration and solvent and free triethylamine were removed by evaporation. Toluene (100 $cm^3$) was added to the residue. The organic solution was washed twice with 1 M (M = mol $dm^{-3}$) hydrochloric acid (100 $cm^3$) and four times with distilled water (100 $cm^3$), then dried over anhydrous magnesium sulfate. After the filtration, the filtrate was evaporated and dried *in vacuo* to obtain the desired compound; 9.91 g (94.1%), brown viscous liquid, TLC ($SiO_2$, chloroform:methanol = 9:1, $R_f$ = 0.50), $^1$H-NMR (300 MHz, $\delta$, $CDCl_3$, TMS, 25 °C), 1.34 (30H, m, $CH_2(CH_2)_6C$)+3($OCH_2CH_3)_2$), 2.04 (2H, m, $CH_2(CH_2)_6C$), 3.97 (6H, s, $CCH_2OP$), 4.11 (12H, m, 3($OCH_2CH_3)_2$), 4.95 (2H, m, $CH_2CH$), 5.81 (1H, m, $CH_2CH$).

**1,1,1-Tris(ethyl hydrogen phosphoryloxymeth-yl)-9-decene ($^8$None{3}$CH_2OP(O)(OEt)OH$).** 1,1, 1-Tris(diethyl phosphoryloxymethyl)-9-decene 2.00 g (3.13 mmol) in 130 $cm^3$ ethanol and potassium hydroxide 3.66 g (65.2 mmol, 21 eq) in 25 $cm^3$ water were mixed and the mixture was refluxed for 48 h. After evaporation, chloroform (100 $cm^3$) was added to the residue, and the organic solution was washed once each with 5 M and 1 M hydrochloric acid (100 $cm^3$) followed by three times with distilled water (100 $cm^3$), then was dried over anhydrous magnesium sulfate. After the filtration, the filtrate was evaporated and dried *in vacuo* to obtain the desired compound; 9.91 g (94.1%), brown viscous liquid, TLC ($SiO_2$, chloroform:methanol = 9:1, $R_f$ = 0.50), $^1$H-NMR (300 MHz, $\delta$, $CDCl_3$, TMS, 25 °C), 0.529 g (30.5%); FT-IR (neat) $\nu_{P(O)OH}$ 2622, 2270, 1650 $cm^{-1}$; $^1$H-NMR (300 MHz, $\delta$, $CDCl_3$, TMS, 25 °C), 1.25 (21H, m, $CH_2(CH_2)_6C$)+3($OCH_2CH_3$)), 1.95 (2H, m, $CH_2(CH_2)_6C$), 3.91 (6H, s, $CCH_2OP$), 4.03 (6H, m, 3($OCH_2CH_3$)), 4.88 (2H, m, $CH_2CH$), 5.72 (1H, m, $CH_2CH$), 9.64 (3H, s(br), POH); Found: H, 7.61; C, 40.93%, Calcd for $C_{19}H_{41}O_{12}P_3$: H, 7.40; C, 41.16%.

**Diethyl 10-undecenylphosphate ($^8$None{1}$CH_2O P(O)(OEt)_2$).** Under the nitrogen stream, 10-undecen-1-ol 2.00 g (11.7 mmol) in 30 $cm^3$ toluene and triethylamine 7.31 g (70.5 mmol, 6.0 eq) were mixed. Diethyl chlorophosphate 6.09 g (35.3 mmol, 3.0 eq) was added dropwise for 15 min to the mixture at room temperature (15±3°C) and the mixture was shaken for 20 h. The rest procedure was similar to that of $^8$None{3}$CH_2OP(O)(OEt)_2$ to obtain the desired compound; 5.92 g (over 100%), yellow liquid, TLC ($SiO_2$, chloroform:methanol = 9:1, $R_f$ = 0.62), $^1$H-NMR (300 MHz, $\delta$, $CDCl_3$, TMS, 25 °C), 1.28-1.44 (30H, m, $CH_2(CH_2)_7CH_2O$)+($OCH_2CH_3)_2$), 2.05 (2H, m, $CH_2(CH_2)_6C$), 4.12 (6H, m, $CCH_2OP$+($OCH_2CH_3)_2$), 4.95 (2H, m, $CH_2CH$), 5.82 (1H, m, $CH_2CH$).

The crude compound still includes the reactant, diethyl chlorophosphate, although $^1$H-NMR spectra suggested the desired compound successfully obtained. Further purification was not carried out in this step because diethyl chlorophosphate can be hydrolyzed and converted to water-soluble diethyl hydrogen phosphate in the next step, which is easily removed from the desired compound.

**Ethyl hydrogen 10-undecenylphosphate** (**$^8$None {1}$CH_2OP(O)(OEt)OH$**). Diethyl 10-undecenylphosphate 5.92 g (19.3 mmol) in 40 $cm^3$ ethanol and potassium hydroxide 6.47 g (115 mmol, 6.0 eq) in 25 $cm^3$ water was mixed and refluxed for 20 h. The rest of the procedure was similar to that of $^8$None{3}$CH_2OP(O)(OEt)OH$ to obtain the desired compound; 2.23 g (41.5%), brown viscous liquid, TLC ($SiO_2$, chloroform:methanol = 9:1, $R_f$ = 0.00), FT-IR (neat); $^1$H-NMR (300 MHz, $\delta$, $CDCl_3$, TMS, 25 °C), 1.34 (17H, m, $CH_2(CH_2)_7CH_2O$)+$OCH_2CH_3$), 2.05 (2H, m, $CH_2(CH_2)_6C$), 4.05 (4H, m, $CCH_2OP$+$OCH_2CH_3$), 4.95 (2H, m, $CH_2CH$), 5.82 (1H, m, $CH_2CH$), 8.43 (1H, s, POH).

### *Extraction study*

The metal extractions were carried out in a similar manner to that described previously [23]. For trivalent rare earth metals, the organic solution was prepared by diluting the tripodal or monopodal type extraction reagent into analytical grade chloroform to yield 5 mM or 15 mM concentrations so as to equal to the amount of phosphoric acid functional groups. Three aqueous solutions, each containing four rare earth ions, were prepared by dissolving analytical grade rare earth nitrates in 5 M, 1 M, 0.1 M, and 0.01 M hydrochloric acid to yield each metal ion concentration of 0.1 mM. The first solution contained La, Ce, Pr, and Nd, the second was Sm, Eu, Gd, and Dy, and the third was Ho, Er, Y, and Lu. The acid concentrations were adjusted and estimated by mixing the above four stock solutions. Equal volumes (3 $cm^3$:3 $cm^3$) of the organic and aqueous phases were mixed and shaken vigorously at 303 K for more than 1 h. The metal concentrations of the aqueous solutions before and after shaking were measured by ICP-AES (Shimadzu ICPS-8100). The amount of the extracted metal ion was calculated from the difference between the metal concentration in the aqueous phase before and after shaking. For other metals, the procedures using respective metal salts were similarly carried out. Grouping of metals are Al(III), Ga(III) and In(III); Fe(III), Zn(II), and Ca(II); Zr(IV), Mo(VI), W(VI), and V(V).

Time course dependency was carried out by changing the shaking time of both phases. Loading test was also carried out by changing metal concentrations.

## RESULTS AND DISCUSSION

### Extraction of Metal Ions

The effects of shaking time on percentage extraction of three REEs $^8$None{3}CH$_2$OP(O)(OEt)OH are shown in Fig. 3. The extraction rate for three ions was significantly faster and reached equilibrium within 10 min even at 130 rpm because the extraction reagent possesses three phosphoric acid groups and easily adsorbs on the interface of both phases. The extraction described below was carried out by shaking time more than 1 h.

The effects of pH on percentage extraction of some metal ions with $^8$None{3}CH$_2$OP(O)(OEt)OH are shown in Figs. 4(a)–(c). This tripodal type extraction reagent exhibited ion-exchangeable property and extremely higher extraction ability into a series of trivalent REEs, aluminum group metals, Fe(III), Zr(IV), and Mo(VI). While it exhibited a moderate ability to W(VI) and hardly extracted Zn(II), Ca(II), and V(V), neither nor Cu(II), Co(II), and Ni(II) although their results are not shown in the figure. In particular, it exhibited extremely high extraction of metals with high valency such as Zr(IV), In(III), Lu(III), and Fe(III). It means that $^8$None{3}CH$_2$ OP(O)(OEt)OH would contribute to the separation of Lu over other rare earths, that of In over Ga, Al and Zn, removal of Fe from other base metals. The framework of the tripodal alkylmethylol provides coordination site with a certain size, which is generally narrow.

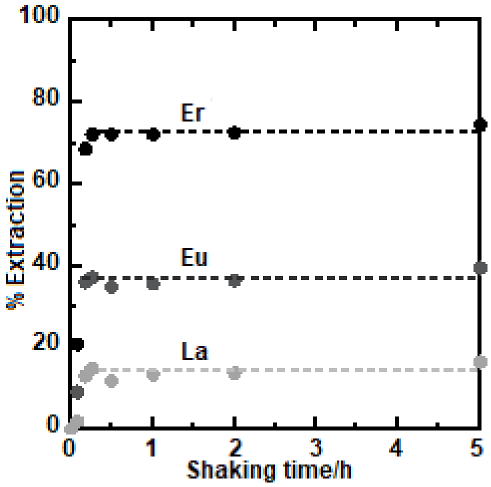


**Fig 3.** Effects of shaking time on percentage extraction of three REEs with $^8$None{3}CH$_2$OP(O)(OEt)OH. [$^8$None{3}CH$_2$OP(O)(OEt)OH] = 5 mM, [REE$^{3+}$] = 0.1 mM each in 1 M HCl, volume ratio = 1:1 (aq:org), 303 K

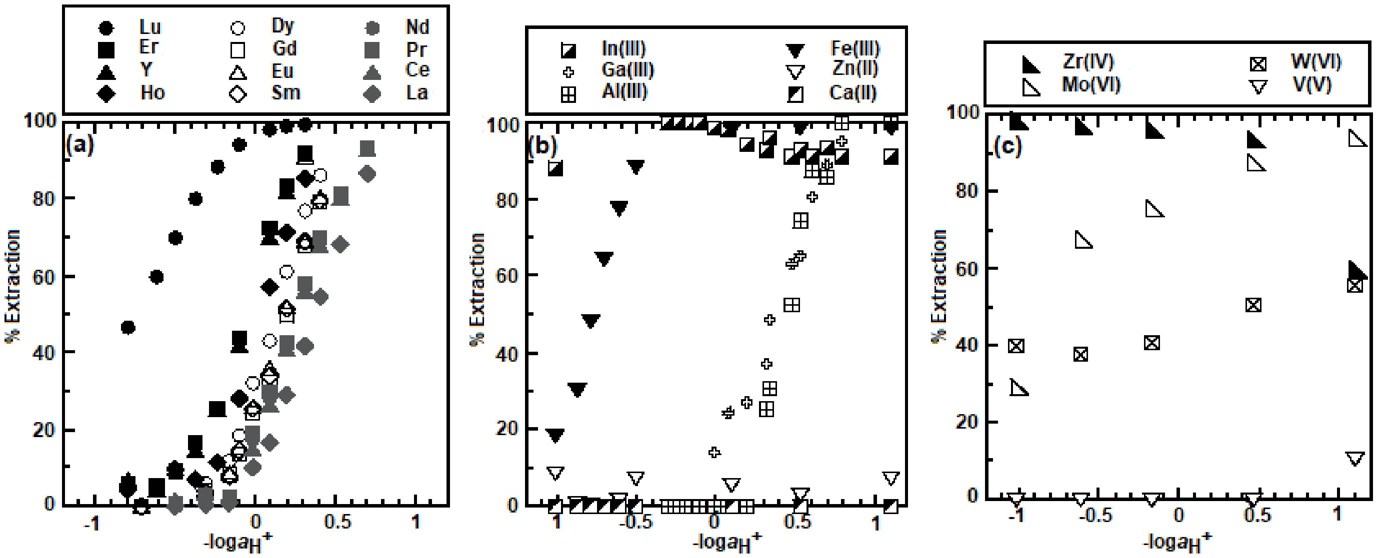


**Fig 4.** Effects of pH on percentage extraction of some metal ions with $^8$None{3}CH$_2$OP(O)(OEt)OH. (a) REEs, (b) aluminum group metals, divalent and trivalent metals, (c) tetravalent and pentavalent metals, [$^8$None{3}CH$_2$OP(O)(OEt)OH] = 5 mM, [metal ion] = 0.1 mM each, [HCl] = 5 M, 1 M, 0.1 M, volume ratio = 1:1 (aq:org), 303 K

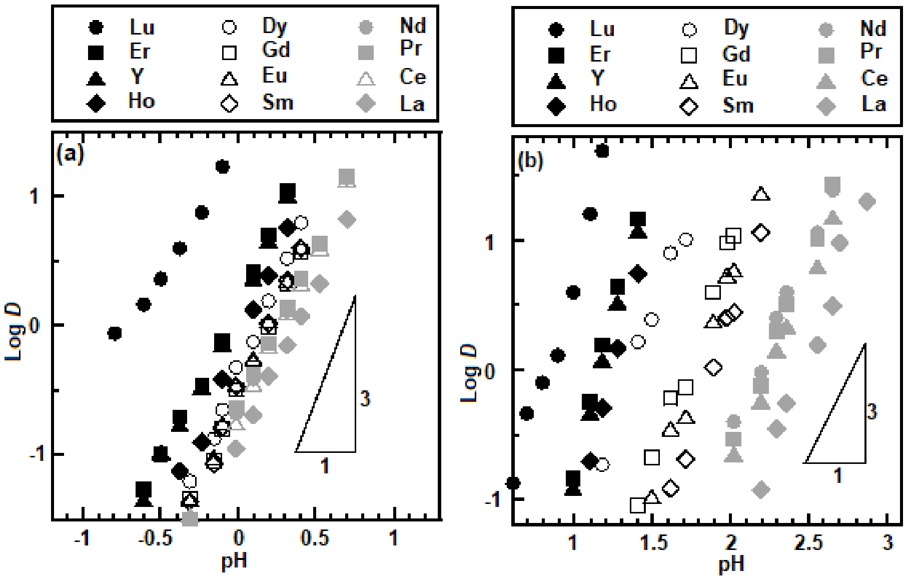


**Fig 5.** Effects of pH on distribution ratio of REEs with (a) $^{8}$None{3}CH$_2$OP(O)(OEt)OH and (b) $^{8}$None{1}CH$_2$OP(O)(OEt)OH. [$^{8}$None{3}CH$_2$OP(O)(OEt)OH] = 5 mM, [$^{8}$None{1}CH$_2$OP(O)(OEt)OH] = 15 mM, [REE$^{3+}$] = 0.1 mM each, [HCl] = 5 M, 1 M, 0.1 M, 0.01 M, volume ratio = 1:1 (aq:org), 303 K

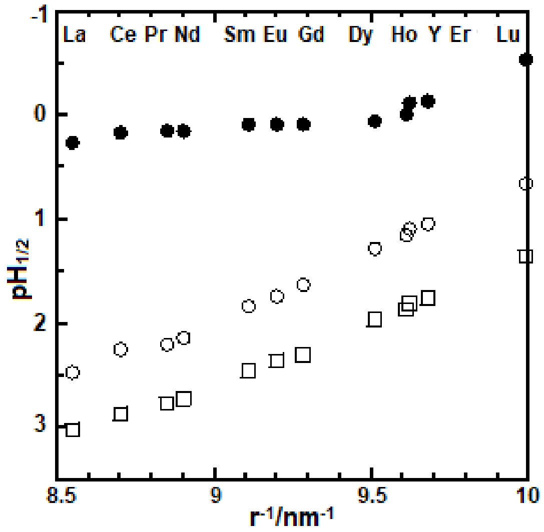


**Fig 6.** Relationship between a reciprocal number of ionic radii of REEs and half pH values of extraction of REEs with (●) $^{8}$None{3}CH$_2$OP(O)(OEt)OH and (○) $^{8}$None{1}CH$_2$OP(O)(OEt)OH together with (□) commercial phosphoric acid type extraction reagent, D2EHPA

However, the mutual separation of REEs except Lu seemed to be difficult from Fig. 4(a). Next, effects of pH on the distribution ratio of REEs with $^{8}$None{3}CH$_2$ OP(O)(OEt)OH and $^{8}$None{1}CH$_2$OP(O)(OEt)OH is shown in Figs. 5(a) and (b). All plots in both figures lie on the straight lines with a slope of 3. This result indicates that three protons are released from both the extraction reagents by ion-exchange with a trivalent ion. The extraction sequence of REEs with both reagents is usual and followed from heavy to light REEs. However, trident type reagent exhibited less separation efficiency for REEs except for Lu. The relationship between a reciprocal number of ionic radii of REEs and half pH values of extraction of REEs with both reagents, together with the commercial phosphoric acid type extraction reagent, D2EHPA (bis(2-ethylhexyl) hydrogen phosphate) is shown in Fig. 6. For the expression of high extraction ability, the values of y-axis are upside down. It was found that plots for the trident molecule are extremely higher than those for the others, and it has extremely higher extraction ability than the others because the amount of phosphoric acid functionality of three reagents are adjusted to be same. On the contrary, the slope of the plots for the trident molecule are gentler than those of the others. The slope expresses the separation efficiency. The trident molecule has just poorer separation efficiency to REEs compared with the others. The monomeric derivative, $^{8}$None{1}CH$_2$OP(O)(OEt)OH exhibited comparable efficiency. Therefore, the present trident molecule exhibited the negative structural effect for REEs separation. The optimized molecular design is required, such as depressing the extraction efficiency by changing from phosphoric acid to phosphonic acid or phosphinic acid and introducing more bulky substituents.

A notable result is a high selectivity for Lu over other REEs, although the trident molecule exhibited poor efficiency. The results of loading tests of heavy REEs and Zr(IV) on $^{8}$None{3}CH$_2$OP(O)(OEt)OH are

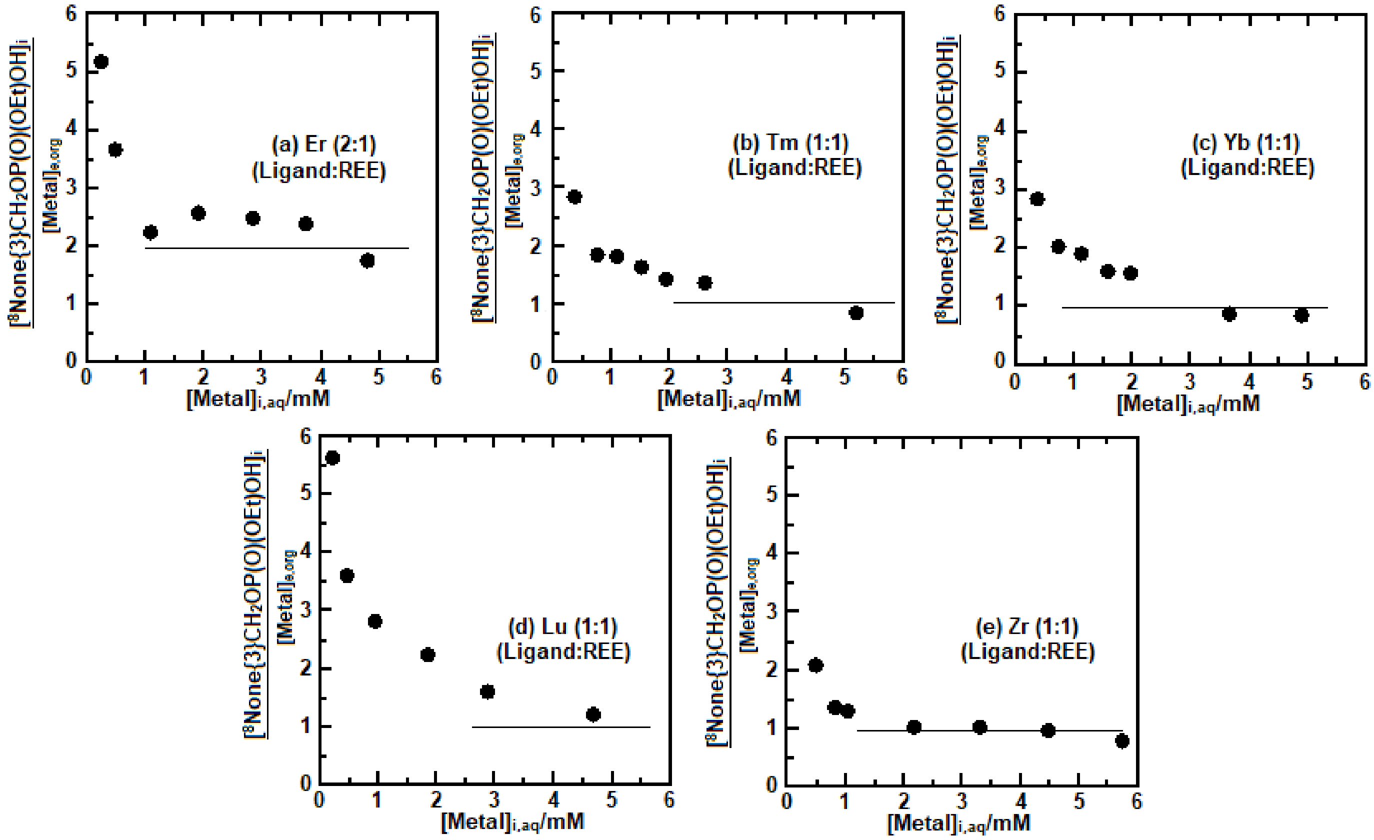


**Fig 7.** Loading test of REEs and Zr(IV) on $^{8}$None{3}CH$_2$OP(O)(OEt)OH. (a) Er, (b) Tm, (c) Yb, (d) Lu, (e) Zr, [$^{8}$None{3}CH$_2$OP(O)(OEt)OH] = 5 mM, [HCl] = 0.1 M, volume ratio = 1:1 (aq:org), 303 K

shown in Figs. 7(a)–(e). Firstly, the results for Er and Lu, which were examined ions for the above-mentioned results, were obtained. Those were different to be 2:1 (Ligand:ion) and 1:1. The results for two REEs between them were added, although they were not investigated. The results for Tm and Yb between Er and Lu were also 1:1, same as Lu. If the separation efficiency is related to the different stoichiometries caused by sizes of ionic radii, it can be improved by the optimized molecular design. The monomeric, $^{8}$None{1}CH$_2$OP(O)(OEt)OH showed same 1:3 stoichiometry for all ions examined. The separation efficiency between Er and Lu were not notable compared with those for other ions.

The stoichiometry for Zr(IV) as a representative of other ions was investigated. The result showed 1:1 stoichiometry probably due to its small size.

## Extraction Mechanism

Based on the quantitative results, the extraction reactions were determined for $^{8}$None{3}CH$_2$OP(O)(OEt)OH and $^{8}$None{1}CH$_2$OP(O)(OEt)OH. The extraction reactions of Lu and other REEs with $^{8}$None{3}CH$_2$OP(O)(OEt)OH are expressed in Eqs. (1) and (2);

$$Lu^{3+} + H_3R \overset{K_{ex1}}{\longleftrightarrow} Lu\cdot R + 3H^{+} \qquad (1)$$

$$REE^{3+} + 2H_3R \overset{K_{ex2}}{\longleftrightarrow} REE\cdot HR\cdot H_2R + 3H^{+} \qquad (2)$$

where H$_3$R represents $^{8}$None{3}CH$_2$OP(O)(OEt)OH molecule.

From the Eqs. (1) and (2), the equations for extraction equilibrium constant, *K*$_{ex}$ were obtained as Eqs.(3) and (4).

$$K_{ex} = \frac{\left[Lu\cdot R\right]\left[H^{+}\right]^{3}}{\left[Lu^{3+}\right]\left[H_3R\right]} \qquad (3)$$

$$K_{ex2} = \frac{\left[REE\cdot HR\cdot H_2R\right]\left[H^{+}\right]^{3}}{\left[REE^{3+}\right]\left[H_3R\right]^{2}} \qquad (4)$$

Distribution ratio is defined as the concentration ratio between organic and aqueous phases, consequently Eqs. (3) and (4) can be rewritten as Eqs. (5) and (6);

$$\log D_{Lu} = 3pH + \log\left[H_3R\right] + \log K_{ex1} \qquad (5$$

$$\log D_{REE} = 3pH + 2\log\left[H_3R\right] + \log K_{ex2} \qquad (6)$$

Using the above data and equations, the extraction equilibrium constants (*K*$_{ex}$) and the separation factor ($\beta$).

**Table 1.** The extraction equilibrium constants (log $K_{ex}$), the separation factors ($\beta$), half pH values ($pH_{1/2}$), difference half pH values ($\Delta pH_{1/2}$) for extraction of REEs with (a)$^{8}$None{3}$CH_2OP(O)(OEt)OH$ and (b) $^{8}$None{1}$CH_2OP(O)(OEt)OH$

(a)

| REE | Stoichiometry (Ligand:REE) | log $K_{ex}$ | $K_{ex}$ | $\beta$ | $pH_{1/2}$ | $\Delta pH_{1/2}$ |
|---|---|---|---|---|---|---|
| La | 2 : 1 | 3.87 | $7.36\times10^{3}$ | 1.86 | 0.25 | 0.09 |
| Ce | 2 : 1 | 4.14 | $1.37\times10^{4}$ | 1.11 | 0.16 | 0.02 |
| Pr | 2 : 1 | 4.18 | $1.48\times10^{4}$ | 1.03 | 0.14 | 0.00 |
| Nd | 2 : 1 | 4.20 | $1.52\times10^{4}$ | 1.42 | 0.14 | 0.05 |
| Sm | 2 : 1 | 4.35 | $2.16\times10^{4}$ | 1.00 | 0.09 | 0.00 |
| Eu | 2 : 1 | 4.34 | $2.18\times10^{4}$ | 1.00 | 0.09 | 0.00 |
| Gd | 2 : 1 | 4.35 | $2.21\times10^{4}$ | 1.32 | 0.09 | 0.04 |
| Dy | 2 : 1 | 4.47 | $2.93\times10^{4}$ | 1.46 | 0.05 | 0.06 |
| Ho | 2 : 1 | 4.63 | $4.26\times10^{4}$ | 2.07 | -0.01 | 0.11 |
| Y | 2 : 1 | 4.95 | $8.91\times10^{4}$ | 1.15 | -0.12 | 0.02 |
| Er | 2 : 1 | 5.01 | $1.02\times10^{5}$ | -* | -0.14 | 0.63 |
| Lu | 1 : 1 | 4.31 | $2.05\times10^{4}$ |  | -0.77 |  |

* no meaning due to different stoichiometries

(b)

| REE | Stoichiometry (Ligand:REE) | log $K_{ex}$ | $K_{ex}$ | $\beta$ | $pH_{1/2}$ | $\Delta pH_{1/2}$ |
|---|---|---|---|---|---|---|
| La | 3 : 1 | -1.91 | $1.24\times10^{-2}$ | 4.27 | 2.46 | 0.21 |
| Ce | 3 : 1 | -1.28 | $5.27\times10^{-2}$ | 1.51 | 2.25 | 0.06 |
| Pr | 3 : 1 | -1.10 | $7.98\times10^{-2}$ | 1.41 | 2.19 | 0.05 |
| Nd | 3 : 1 | -0.95 | $1.13\times10^{-1}$ | 8.51 | 2.14 | 0.31 |
| Sm | 3 : 1 | -0.02 | $9.59\times10^{-1}$ | 2.00 | 1.83 | 0.10 |
| Eu | 3 : 1 | 0.28 | 1.91 | 2.14 | 1.73 | 0.11 |
| Gd | 3 : 1 | 0.61 | 4.09 | 10.5 | 1.62 | 0.34 |
| Dy | 3 : 1 | 1.63 | $4.28\times10^{1}$ | 2.63 | 1.28 | 0.14 |
| Ho | 3 : 1 | 2.05 | $1.13\times10^{2}$ | 1.41 | 1.14 | 0.05 |
| Y | 3 : 1 | 2.20 | $1.59\times10^{2}$ | 1.41 | 1.09 | 0.05 |
| Er | 3 : 1 | 2.35 | $2.25\times10^{2}$ | 13.8 | 1.04 | 0.38 |
| Lu | 3 : 1 | 3.49 | $3.10\times10^{3}$ |  | 0.66 |  |

The separation factor, $\beta$, is defined by Eq. (7),

$$\beta = \frac{D_{\text{Heavier REE}}}{D_{\text{Lighter REE}}} = \frac{K_{\text{ex, Heavier REE}}}{K_{\text{ex, Lighter REE}}} \quad (7)$$

Comparison of $K_{ex}$ and $\beta$ for Lu and other REEs with different stoichiometries is senseless. Thus, the half pH values ($pH_{1/2}$), the difference between the half pH values ($-\Delta pH_{1/2}$), were further estimated. The half pH value, $pH_{1/2}$, is defined as the pH value at which half of the metal ions are extracted under the experimental conditions used in this study. The difference between the half pH values, $\Delta pH_{1/2}$, is calculated from the difference in the $pH_{1/2}$ values between the lighter and heavier metal ions.

For the REE extraction with ⁸None{1}CH₂OP(O)(OEt)OH, the stoichiometry was 3:1, the extraction reaction of all REEs is expressed in Eq. (8);

$$REE^{3+} + 3HR \xleftrightarrow{K_{ex}} REE \cdot R_3 + 3H^+ \quad (8)$$

where HR represents ⁸None{1}CH₂OP(O)(OEt)OH.

The equation for extraction equilibrium constant, $K_{ex}$ was obtained as Eq.(9).

$$K_{ex} = \frac{\left[REE \cdot R_3\right]\left[H^+\right]^3}{\left[REE^{3+}\right]\left[HR\right]^3} \quad (9)$$

The Eq. (9) can be rewritten as Eq. (10);

$$\log D_{REE} = 3pH + 3\log\left[HR\right] + \log K_{ex} \quad (10)$$

The extraction equilibrium constants ($K_{ex}$), the separation factors ($\beta$), half pH values ($pH_{1/2}$), difference half pH values ($\Delta pH_{1/2}$) for extraction of REEs with both reagents are listed in Table 1.

## CONCLUSION

Tripodal extraction reagent with three phosphoric acid groups and the corresponding monopodal molecule have been prepared to investigate the extraction behavior of trivalent rare earth elements together with other ions. Tripodal reagent exhibited extremely high selectivity for metals with high valency such as Zr(IV), In(III), Lu(III), and Fe(III). Tripodal reagent also exhibited exceptionally high extraction ability compared with the corresponding monopodal one in the extraction of trivalent rare earths due to structural effects based on its specific pseudo-cyclic structure. The result for the stoichiometry of tripodal reagent to heavy rare earths showed the inflexion point between Er (2:1 for ligand with ion) and Tm (1:1), which can be optimized for better separation at a certain point on lanthanide series. The extraction reactions were determined for all rare earths with both reagents. The extraction equilibrium constants ($K_{ex}$), the separation factors ($\beta$), half pH values ($pH_{1/2}$), difference half pH values ($\Delta pH_{1/2}$) for extraction of REEs with both reagents were estimated. Tripodal ⁸None{3}CH₂OP(O)(OEt)OH has a potential as a new framework for metal separation due to effect of functional group together with structural one.

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