

Synergistic Extraction and Solution Structures of Ternary Complexes of Lanthanoids with 2-Thenoyltrifluoroacetone and Linear Poly(oxyethylene) in 1,2-Dichloroethane

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Synergistic extraction of thenoyltrifluoroacetone (tta) complexes of 14 trivalent lanthanoids (Ln^{3+}) into 1,2-dichloroethane with linear poly(oxyethylene) compounds (POE) was investigated at 25.0 °C, where the linear POE [$\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$] are monodispersed DEOn ($\text{R} = \text{C}_{12}\text{H}_{25}$; $n = 4, 6, \text{ and } 8$) and polydispersed TX-100 ($\text{R} = \text{octylphenyl}$; $n_{\text{ave}} = 9.6$). Equilibrium studies showed a 1:1 adduct complex with POE compound, $\text{Ln}(\text{tta})_3 \cdot (\text{POE})$, formed in the organic phase. The adduct formation constant, β_{add} , increased as the ionic radius of lanthanoid increased for any kind of POE. The very high stability of the 18-crown-6 adducts is explained by the incorporation of Ln^{3+} ion into the cavity of the crown ether. Adduct formation constants of the POE having short ethylene oxide (EO) chain, such as DEO4 and 12-crown-4, were fairly small; thus, it was estimated that those coordinate to the metal ion as a bidentate or tridentate ligand. Relatively large values of β_{add} of long chain POE ($n \geq 6$) indicate the indirect outer-sphere interaction of the uncoordinated residual EO units with the metal ion. Adduct formation with linear POEs significantly reduced the difference in extraction constants among the lanthanoid ions. Therefore, this synergistic extraction system is advantageous for the separation of lanthanoid ions as a group from other metal ions.

There has been a growing interest in lanthanoid (Ln) coordination chemistry, because of the increasing industrial, chemical, medical, and sensor applications of rare-earth ions and their compounds.^{1,2} β -Diketones, represented by thenoyltrifluoroacetone (Htta), have been widely used as an effective extractant for the separation and determination of rare-earth elements.^{3–7} Addition of an electrically neutral lipophilic ligand or Lewis base enhances the extractability of the metal ions and the mutual separation of the lanthanoid ions. The synergistic effects on Htta extraction of Ln^{3+} ions have been extensively studied for monodentate and polydentate ligands, such as phosphoric esters, phosphine oxides, 1,10-phenanthroline, and polyethers.^{8–11} This effect is explained by the formation of a hydrophobic adduct through the displacement of residual water molecules coordinated to the β -diketonato–lanthanoid complex with the neutral ligand.⁸

Poly(oxyethylene) derivatives (POE compounds), which consist of repeating units of ethylene oxide (EO), form cationic complexes with alkali, alkaline-earth and rare-earth metal ions.^{12–22} Because of this peculiar nature, POEs have been used for the separation, concentration, and determination of metal ions.^{23–25} Particularly, cyclic POE compounds (crown ethers) incorporate metal ions within their cavity. In other words, they have very high selectivity for metal ions by the size-fitting effect.^{26–29}

Synergistic extraction of the lanthanoid ions with crown ethers has been studied for various extraction systems and organic solvents;^{30–33} however, systematic data have rarely been reported on the adduct formation of Htta complexes of Ln^{3+} ions with crown ethers. Thus, in our previous paper, we have

reported the synergistic extraction of a series of lanthanoid ions with Htta and various crown ethers and have estimated the structure of the adduct complexes formed in the organic phase.³⁴ Non-cyclic poly(oxyethylene)s (linear POEs) react with metal ions in the same manner as crown ethers. Linear POEs have been widely used for analytical and industrial purpose, because they are nontoxic and inexpensive compared to crown ethers.³⁵ Although the selectivity of metal ion complexation of linear POEs is inferior to the crown ethers, linear POEs have flexible structures, and long-chain derivatives are also available.^{35–39} These properties are advantageous for efficient simultaneous extraction of metal ions as a group.

In the present paper, the synergistic extraction of 14 lanthanoid complexes of Htta with linear POEs having various ethylene oxide chain lengths is reported. The formation constants and structures of the adduct complexes of the linear POEs in organic phase (1,2-dichloroethane) are compared to those of the crown ether adducts.

Experimental

Reagents. Stock solutions of lanthanoid nitrates were prepared by dissolving appropriate amounts of their metal oxides, Ln_2O_3 ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$; Shinetsu), in 6 M HNO_3 , followed by evaporation of the solvent and dissolution of the residue in distilled water. Thenoyltrifluoroacetone (Htta, Dojindo) was used as received. Monodispersed monododecyl ethers (DEOn; $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$, where $\text{R} = \text{C}_{12}\text{H}_{25}$ and number of EO units $n = 4, 6, \text{ and } 8$) and polydispersed octylphenyl ether (TX-100; $\text{R} = \text{octylphenyl}$ and average number of EO units³⁹ ($n_{\text{ave}} = 9.6$)) were obtained from Nikko

Chemicals and Wako Pure Chemicals, respectively, and were used without further purification. 1,2-Dichloroethane (Nacalai Tesque, AR grade) was washed twice with distilled water prior to use. All other reagents used were of analytical reagent grade.

Procedure. The number of thenoyltrifluoroacetate (Htta) involved in the extracted adduct complexes was determined by the following procedure. The pH of an aqueous solution containing 14 lanthanoid ions was adjusted to the desired value (3.5 to 5.5) with 0.01 M acetic acid–potassium acetate buffer. It has been shown that the acetate ion has no effect on the extraction of the lanthanoid ions. The ionic strength was maintained at 0.1 M with potassium nitrate. The initial concentration of each lanthanoid was 5.0×10^{-7} M ($M = \text{mol dm}^{-3}$). The aqueous solution (20 cm^3) thus prepared was mixed with an equivolume of an 1,2-dichloroethane solution containing 1.0×10^{-2} M Htta and 1.0×10^{-2} M POE in a centrifuge tube (50 cm^3). The mixture was shaken for 30 min at $25.0 \pm 0.1^\circ \text{C}$ in a thermostated mechanical shaker. This shaking time was sufficient to attain equilibrium. To determine the chemical form of the adduct and its formation constant, a portion of the aqueous phase (20 cm^3 , pH 4.9) was shaken with an equivolume of organic phase containing 1.0×10^{-2} M Htta and various concentrations of POE (3.0×10^{-7} – 1.0×10^{-2} M). After phase separation through centrifugation, the pH of the aqueous phase was measured by using a pH meter (DKK PHL-40). The concentrations of lanthanoid ions remaining in the aqueous phases were determined with an inductively coupled plasma-mass spectrometer (HP4500 ICP-MS, Yokogawa Agilent). The Ln^{3+} concentrations in the organic phase were determined in the same manner as that in the aqueous phase after back-extraction of Ln^{3+} into 0.1 M HNO_3 .

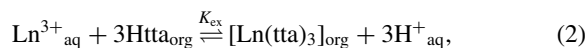
The distribution coefficient, K_d , of 12-crown-4 (12C4, Aldrich) between 1,2-dichloroethane and water was determined by the following procedure. A 1,2-dichloroethane (15 cm^3) solution containing an appropriate amount of 12C4 was mixed with an equivolume of aqueous phase in a centrifuge tube. The mixture was shaken for 30 min. After phase separation, the solvents were evaporated under low pressure. The amount of 12C4 in each phase was then determined by weighing. The distribution coefficient of 12C4 ($K_d = [\text{12C4}]_{\text{org}}/[\text{12C4}]_{\text{aq}}$) was determined to be 0.83. It has been confirmed that the potassium ion is not extracted by the nitrate ion under the present experimental conditions. MM2 calculations of the molecular structures were performed by using SPARTAN software.⁴⁰

Results

The distribution ratio (D) of a lanthanoid ion is defined as

$$D = \frac{C_{\text{Ln,org}}}{C_{\text{Ln,aq}}}, \quad (1)$$

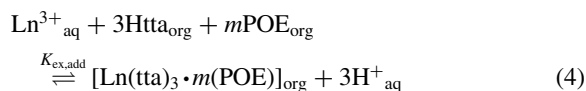
where $C_{\text{Ln,org}}$ and $C_{\text{Ln,aq}}$ are the total concentrations of the Ln ions in the organic and aqueous phases, respectively. The extraction equilibrium and extraction constant, K_{ex} , of trivalent lanthanoid ions (Ln^{3+}) with Htta have been determined^{30,34} as



$$K_{\text{ex}} = \frac{[\text{Ln}(\text{tta})_3]_{\text{org}}[\text{H}^+]^3_{\text{aq}}}{[\text{Ln}^{3+}]_{\text{aq}}[\text{Htta}]^3_{\text{org}}}. \quad (3)$$

The extraction of Ln^{3+} with Htta is significantly enhanced by the addition of linear POE in the same manner as the crown ether system.³⁴ This result indicates the formation of the

adduct complex with linear POE in the organic phase. By assuming the formation of $[\text{Ln}(\text{tta})_3 \cdot m(\text{POE})]_{\text{org}}$ in the organic phase, the extraction equilibrium is given by



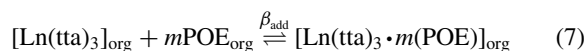
The extraction constant of adduct complex is

$$K_{\text{ex,add}} = \frac{[\text{Ln}(\text{tta})_3 \cdot m(\text{POE})]_{\text{org}}[\text{H}^+]^3_{\text{aq}}}{[\text{Ln}^{3+}]_{\text{aq}}[\text{Htta}]^3_{\text{org}}[\text{POE}]^m_{\text{org}}}. \quad (5)$$

As the total concentration of each Ln^{3+} ion in the organic phase is the sum of the concentrations of $[\text{Ln}(\text{tta})_3]$ and $[\text{Ln}(\text{tta})_3 \cdot m(\text{POE})]_{\text{org}}$, the distribution ratio of Ln^{3+} in the presence of POE is given as

$$D = \frac{[\text{Ln}(\text{tta})_3]_{\text{org}} + [\text{Ln}(\text{tta})_3 \cdot m(\text{POE})]_{\text{org}}}{[\text{Ln}^{3+}]_{\text{aq}}}. \quad (6)$$

According to extraction equilibria (2) and (4), the formation of the adduct $[\text{Ln}(\text{tta})_3 \cdot m(\text{POE})]_{\text{org}}$ in the organic phase is given by



and the adduct formation constant, β_{add} , is defined as

$$\beta_{\text{add}} = \frac{[\text{Ln}(\text{tta})_3 \cdot m(\text{POE})]_{\text{org}}}{[\text{Ln}(\text{tta})_3]_{\text{org}}[\text{POE}]^m_{\text{org}}}. \quad (8)$$

Consequently, the distribution ratio in Eq. 6 becomes

$$D = \frac{[\text{Ln}(\text{tta})_3]_{\text{org}} + [\text{Ln}(\text{tta})_3]_{\text{org}}\beta_{\text{add}}[\text{POE}]^m_{\text{org}}}{[\text{Ln}^{3+}]_{\text{aq}}} \quad (9)$$

$$= \frac{[\text{Ln}(\text{tta})_3]_{\text{org}}(1 + \beta_{\text{add}}[\text{POE}]^m_{\text{org}})}{[\text{Ln}^{3+}]_{\text{aq}}}. \quad (10)$$

Substitution of Eq. 3 into Eq. 10 results in the following:

$$D = \frac{K_{\text{ex}}[\text{Htta}]^3_{\text{org}}(1 + \beta_{\text{add}}[\text{POE}]^m_{\text{org}})}{[\text{H}^+]^3_{\text{aq}}}. \quad (11)$$

Taking the logarithm of Eq. 11 yields

$$\log D = \log K_{\text{ex}} + 3 \log [\text{Htta}] + 3 \text{ pH} + \log(1 + \beta_{\text{add}}[\text{POE}]^m_{\text{org}}). \quad (12)$$

To make sure that number of Htta molecules involved in the adduct is three, the distribution ratio, D , was determined as a function of pH with the concentrations of Htta and POE kept constant. The plots of $\log D$ vs. pH thus obtained are shown in Figs. 1 and 2, where the results of extraction with DEO6 and TX-100 are depicted as examples. The plots were straight lines with a slope of three for all Ln^{3+} , and the same results were obtained for the other POEs. Thus, it is confirmed that the adduct complex also involves three tta molecules, that is, the adduct $[\text{Ln}(\text{tta})_3 \cdot m(\text{POE})]_{\text{org}}$.

Equation 12 can be simplified as

$$\log D = \log D_0 + \log(1 + \beta_{\text{add}}[\text{POE}]^m_{\text{org}}), \quad (13)$$

where $\log D_0 = \log K_{\text{ex}} + 3 \log [\text{Htta}]_{\text{org}} + 3 \text{ pH}$, and D_0 is the distribution ratio of Ln^{3+} in the absence of POE. The value of D_0 is constant when the pH and concentration of Htta are fixed. Thus, the number of POE in the extracted adduct, m , can be

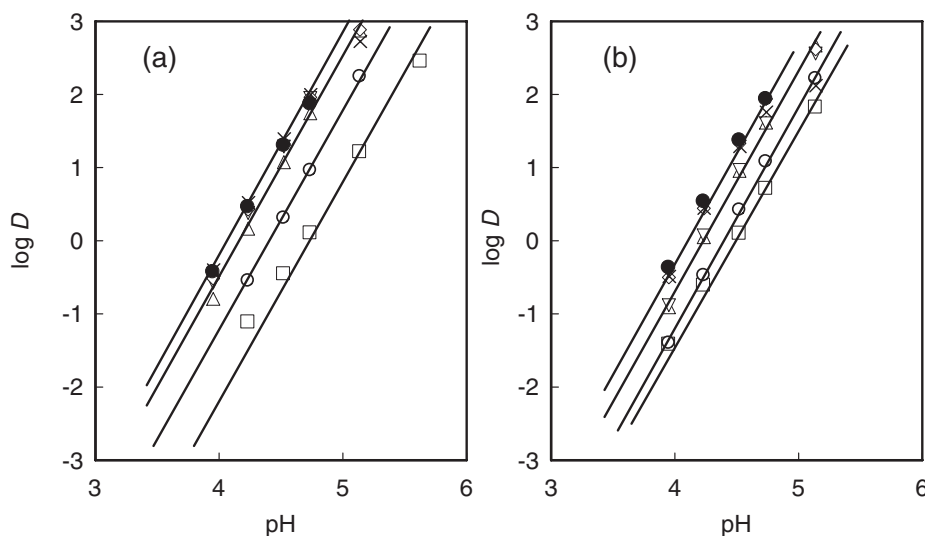


Fig. 1. Plots of $\log D$ vs. pH in the extraction of Ln^{3+} with 1.0×10^{-2} M Htta and 1.0×10^{-2} M DEO6. (a) Odd-atomic number Ln: \square = La, \circ = Pr, \triangle = Eu, ∇ = Tb, \diamond = Ho, \times = Tm, \bullet = Lu; (b) Even-atomic number Ln: \square = Ce, \circ = Nd, \triangle = Sm, ∇ = Gd, \diamond = Dy, \times = Er, \bullet = Yb. The slopes of solid lines are 3.

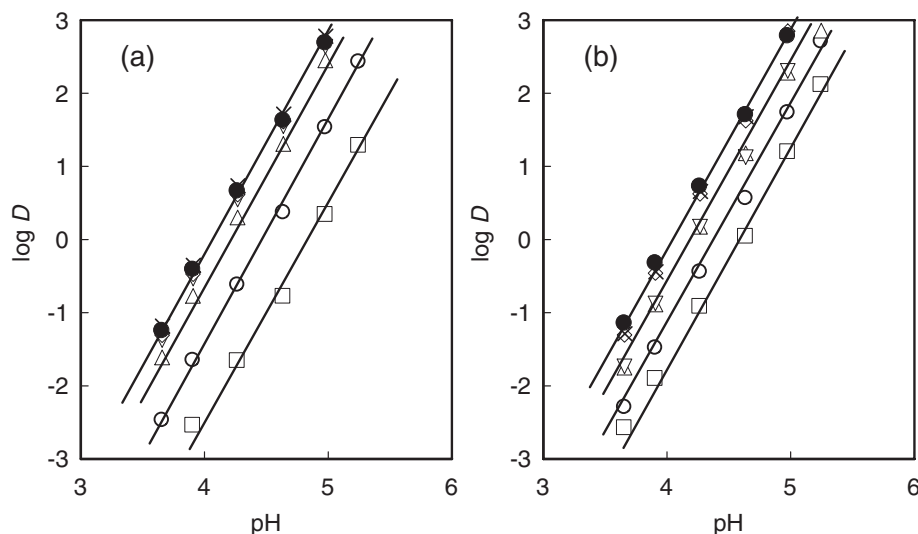


Fig. 2. Plots of $\log D$ vs. pH in the extraction of Ln^{3+} with 1.0×10^{-2} M Htta and 1.0×10^{-2} M TX-100. (a) Odd-atomic number Ln, and (b) Even-atomic number Ln. Symbols are the same as those in Fig. 1. The slopes of solid lines are 3.

determined from the slope of the plot of $\log D$ vs. $\log [\text{POE}]_{\text{org}}$. The distribution coefficient of DEOn and TX-100 in 1,2-dichloroethane is larger than 10^3 ,^{37,38} and the concentration of POE is much higher than that of metal complexes. Thus, the concentration of POE in the organic phase, $[\text{POE}]_{\text{org}}$, can be assumed to be equal to its total concentration, C_{POE} . Figure 3 shows the plots of $\log D$ as a function of $\log [\text{POE}]_{\text{org}}$ at pH 4.9 and 1.0×10^{-2} M Htta. The slopes of the plots approached unity in higher $[\text{POE}]_{\text{org}}$ region irrespective of the kind of POE. The other lanthanoids, not depicted in Fig. 3, also showed the same results. These results indicate that the $[\text{Ln}(\text{tta})_3]$ complex forms an adduct with one molecule of POE, that is, $m = 1$. Thus, the chemical form of the adduct formed in the synergistic extraction with the linear POEs was determined to be $[\text{Ln}(\text{tta})_3 \cdot (\text{POE})]$.

The values of the adduct formation constant, β_{add} , were calculated based on Eq. 13 by applying nonlinear least-square

regression to the plots of Fig. 3. The solid lines in Fig. 3 depict the calculated regression curves, and these are in good agreement with the experimental results. The logarithmic values of adduct formation constant, $\log \beta_{\text{add}}$, thus obtained are listed in Table 1. The values of $\log \beta_{\text{add}}$ for some crown ether adducts³⁴ are also listed in this table for comparison. The values of the adduct formation constants of the crown ethers listed in this table were corrected for the distribution of the crown ether into the aqueous phase by using K_d values of 1.05 and 0.83 (present work) for 18-crown-6 (18C6)⁴¹ and 12-crown-4 (12C4), respectively.

Discussion

Trend in Adduct Formation Constants Across the Lanthanoid Series. Lanthanoid complexes of Htta are extracted into the organic phase as the hydrated complex $[\text{Ln}(\text{tta})_3 \cdot n\text{H}_2\text{O}]$, where $n = 2$ or 3 .⁴² In synergistic systems, the extract-

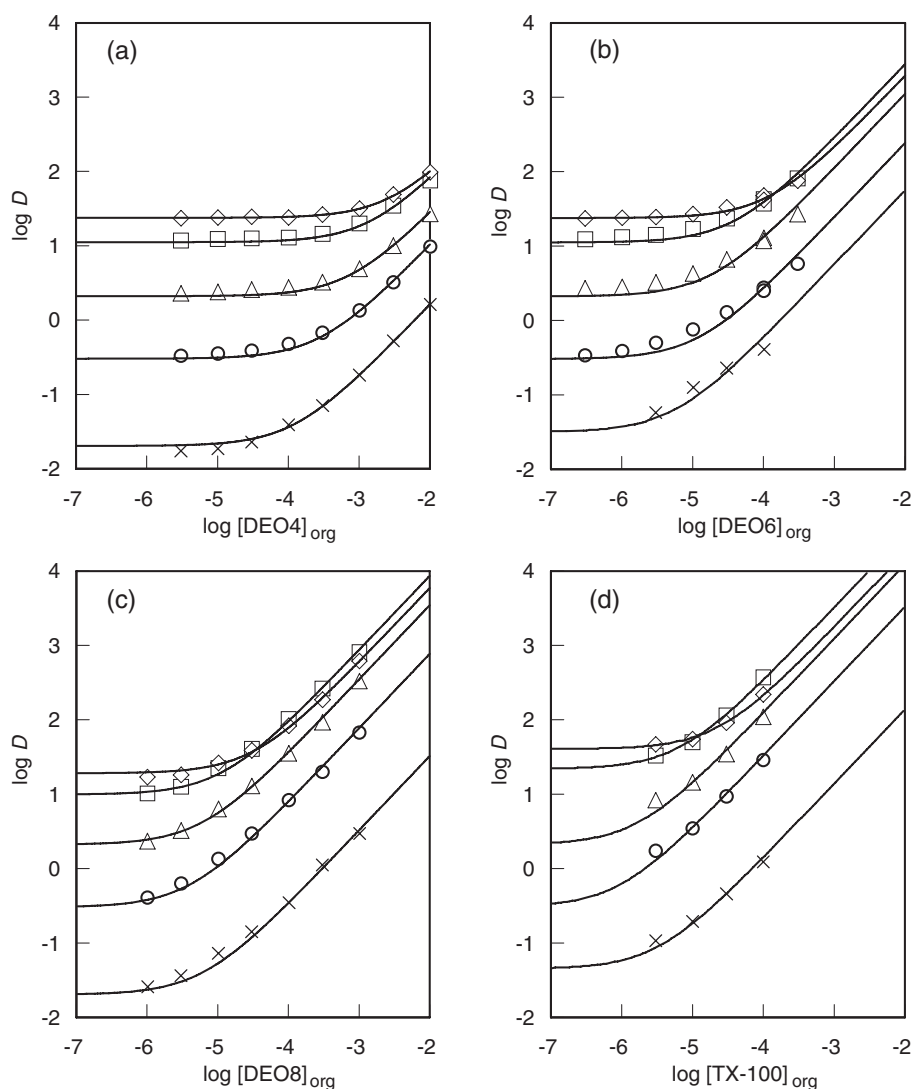


Fig. 3. Plots of $\log D$ vs. $\log [\text{POE}]_{\text{org}}$ in the extraction of Ln^{3+} with $1.0 \times 10^{-2} \text{ M}$ Htta at pH 4.9. POE: (a) DEO4, (b) DEO6, (c) DEO8, (d) TX-100; Ln: $\times = \text{La}$, $\circ = \text{Nd}$, $\triangle = \text{Gd}$, $\square = \text{Er}$, $\diamond = \text{Lu}$. Solid lines are calculated curves; see text.

Table 1. Formation Constant of the POE Adduct $[\text{Ln}(\text{tta})_3 \cdot (\text{POE})]$, β_{add} , in 1,2-Dichloroethane

Ln^{3+}	Ionic radii / \AA	$\log K_{\text{ex}}^{\text{a)}$	$\log \beta_{\text{add}}$					
			DEO4	DEO6	DEO8	TX-100	12C4 ^{a)}	18C6 ^{a)}
La^{3+}	1.216	-10.09	3.90 ± 0.03	5.11 ± 0.06	5.39 ± 0.02	5.49 ± 0.04	3.87	6.35
Ce^{3+}	1.196	-9.42	3.82 ± 0.03	5.09 ± 0.04	5.37 ± 0.02	5.48 ± 0.03	3.84	6.49
Pr^{3+}	1.179	-9.12	3.65 ± 0.03	4.95 ± 0.04	5.44 ± 0.02	5.52 ± 0.03	3.86	6.54
Nd^{3+}	1.163	-8.92	3.52 ± 0.03	4.91 ± 0.03	5.40 ± 0.02	5.50 ± 0.03	3.84	6.51
Sm^{3+}	1.132	-8.23	3.27 ± 0.03	4.89 ± 0.02	5.39 ± 0.02	5.45 ± 0.03	3.81	6.42
Eu^{3+}	1.120	-8.08	3.20 ± 0.03	4.81 ± 0.02	5.29 ± 0.02	5.38 ± 0.03	3.73	6.42
Gd^{3+}	1.107	-8.08	3.10 ± 0.03	4.70 ± 0.02	5.22 ± 0.02	5.29 ± 0.04	3.69	6.33
Tb^{3+}	1.095	-7.63	3.00 ± 0.03	4.60 ± 0.02	5.15 ± 0.03	5.27 ± 0.04	3.61	6.25
Dy^{3+}	1.083	-7.48	2.93 ± 0.04	4.50 ± 0.03	5.02 ± 0.03	5.21 ± 0.04	3.56	6.15
Ho^{3+}	1.072	-7.45	2.91 ± 0.04	4.48 ± 0.03	5.14 ± 0.03	5.15 ± 0.04	3.51	6.15
Er^{3+}	1.062	-7.35	2.81 ± 0.04	4.39 ± 0.03	4.88 ± 0.04	5.17 ± 0.05	3.49	6.07
Tm^{3+}	1.052	-7.16	2.76 ± 0.05	4.25 ± 0.04	4.85 ± 0.04	4.97 ± 0.05	3.35	5.96
Yb^{3+}	1.042	-7.03	2.59 ± 0.05	4.07 ± 0.04	4.50 ± 0.04	4.79 ± 0.05	3.31	5.75
Lu^{3+}	1.032	-7.02	2.51 ± 0.05	3.91 ± 0.04	4.36 ± 0.04	4.64 ± 0.05	3.18	5.68

a) Cited from Ref. 34. The values of β_{add} for 12C4 and 18C6 were corrected by taking into consideration the distribution coefficient of crown ethers.

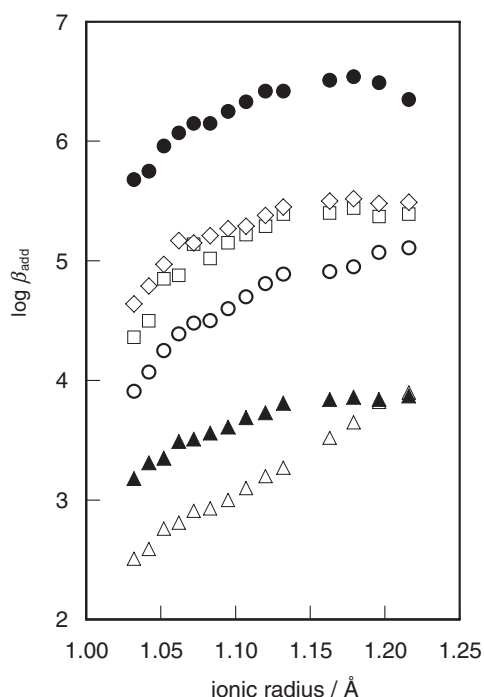


Fig. 4. The plots of logarithmic formation constants of adducts as a function of ionic radii of Ln. POE: \triangle = DEO4, \circ = DEO6, \square = DEO8, \diamond = TX-100, \blacktriangle = 12C4, \bullet = 18C6.

ability of the metal complex considerably increases by the replacement of these water molecules with lipophilic POE molecules. The logarithmic formation constants of the adducts $[\text{Ln}(\text{tta})_3 \cdot (\text{POE})]$ of the linear POEs, $\log \beta_{\text{add}}$, are plotted as a function of ionic radii of lanthanoids⁴³ in Fig. 4, where the results for crown ethers are also shown. Similar to the results for crown ethers, the value of β_{add} for linear POEs generally increased as the radius of Ln^{3+} increased. The hydration energy decreases as the radius of Ln^{3+} ions increases. Because of this, the displacement of coordinated water molecules by the POE would be much easier for larger Ln^{3+} than for smaller ones. Hence, lighter Ln^{3+} ions more favorably form the adduct with the POE. In case of the adduct formation with a monodentate ligand such as tributylphosphate (TBP) or trioctylphosphine oxide (TOPO), the formation constants of the adduct $[\text{Ln}(\text{tta})_3 \cdot (\text{TBP})]$ or $[\text{Ln}(\text{tta})_3 \cdot (\text{TOPO})]$ show an opposite trend with the present results for POEs, that is, $\log \beta_{\text{add}}$ for TBP or TOPO decreases as the radius of Ln^{3+} ion increases.^{7,9,11} Lewis basicity of TBP and TOPO are stronger than water, thus the stability of the adduct increases by a decrease in ion size of the metal ion. On the other hand, POEs are much weaker bases; thus, the hydration energy of the lanthanoid ions has a greater effect on adduct formation.

The coordination number of lanthanoid ions increases from eight to nine by the increase in the ionic radius of Ln^{3+} . The usual coordination number is eight for the heavier Ln^{3+} , Tb^{3+} to Lu^{3+} , nine for the lighter Ln^{3+} , La^{3+} to Sm^{3+} , and both for Gd^{3+} and Eu^{3+} .⁴⁴ Crystal structures of the adducts of Ln^{3+} ions with hexafluoroacetylacetone and linear oligoethers have shown that the number of oxygen atoms of the polyether coordinating to the Ln^{3+} ion center increases with

ionic size.^{45–48} The increase in the number of oxygen atoms of POE coordinating to the lanthanoid ion due to the increase in the ionic radii also causes the increase in the stability of the adduct.

Comparison of Adducts Formed among Polyethers. The value of $\log \beta_{\text{add}}$ for 18C6 is about 2.5 orders of magnitude higher than that for the 12C4 adducts of the corresponding metal ion. These large values of β_{add} for 18C6 complexes are attributable to the stable structures of these complexes. The cavity size of 18C6 has been estimated as 1.45 Å and is larger than the ionic radius of any Ln^{3+} ion.⁴⁹ Thus, 18C6 forms stable complexes with Ln^{3+} by incorporating the metal ion inside of its cavity. The metal ion coordinated by 18C6 does not have enough space for the direct coordination of three bidentate tta ligands. Hence, it is thought that one tta molecule is expelled from the inner coordination sphere of the complex, and the cationic complex $[\text{Ln}(\text{tta})_2 \cdot (18\text{C6})]$ is formed. The formation of this kind of cationic complex has been reported for the extraction of Ln^{3+} ions in the presence of ClO_4^- .³⁵ Moreover, formation of $[\text{Ln}(\text{tta})_2 \cdot (18\text{C6})]$ in crystal and in organic solution has been confirmed by X-ray crystallographic and ¹H NMR spectroscopic analyses.⁵⁰ Equilibrium studies indicate the participation of three tta ions for the adduct formation. Accordingly, the third tta may form an ion pair with the cationic complex as $[\text{Ln}(\text{tta})_2 \cdot (18\text{C6})]^+(\text{tta}^-)$. On the basis of the preceding information, the structure of $[\text{Ln}(\text{tta})_2 \cdot (18\text{C6})]^+(\text{tta}^-)$ was estimated by MM2 calculations. The resulting structure is shown in Fig. 5a. Generally, the complex formation constant of the third step is much smaller than those of the first and second steps. Thus, the third tta^- coordinating the metal ion must be substituted by the 18C6, which is a multidentate ligand and can incorporate the lanthanoid ion in its cavity.

In case of 12C4 adduct, the metal ion cannot be incorporated inside of the crown ether ring, because the cavity size of 12C4 (0.72 Å)⁴⁹ is smaller than the ionic radii of the lanthanoid ions. The β_{add} values for 12C4 adducts are significantly lower than those of 18C6. Thus, the 12C4 may coordinate to the metal ion of the complex $[\text{Ln}(\text{tta})_3]$ as a bidentate or tridentate ligand. The structure of $[\text{Ln}(\text{tta})_3 \cdot (12\text{C4})]$ estimated by MM2 calculations, which is shown in Fig. 5b, reasonably explained the above results.

The adduct formation constants of DEO4 are on the same orders of magnitude as those of 12C4 adducts. The number of ethylene oxide groups in DEO4 is not enough to surround the Ln^{3+} ions; hence, the stability and structure of the DEO4 adduct must be similar to those of the 12C4 adducts. The structure of the adduct of La-hexafluoroacetylacetonate complex with the linear polyether tetraglyme has been reported for the crystalline complex. The La^{3+} ion is encapsulated by the six oxygen atoms of three β -diketones, and is coordinated by four oxygen donor atoms of the tetraglyme to form a 10-coordinate complex.⁴⁶ The structure of the adduct $[\text{Ln}(\text{tta})_3 \cdot (\text{DEO4})]$ in solution could be similar to this crystal structure. However, because of the bulkiness of the ligands, i.e., tta and DEO4, it is thought that a 9-coordinate adduct is formed, that is, three oxygen atoms of DEO4 is coordinating to the metal ion. The terminal -OH may coordinate to the metal ion, because the basicity of the hydroxy oxygen is higher than that of the ethereal oxygen.⁵¹ An optimized structure of

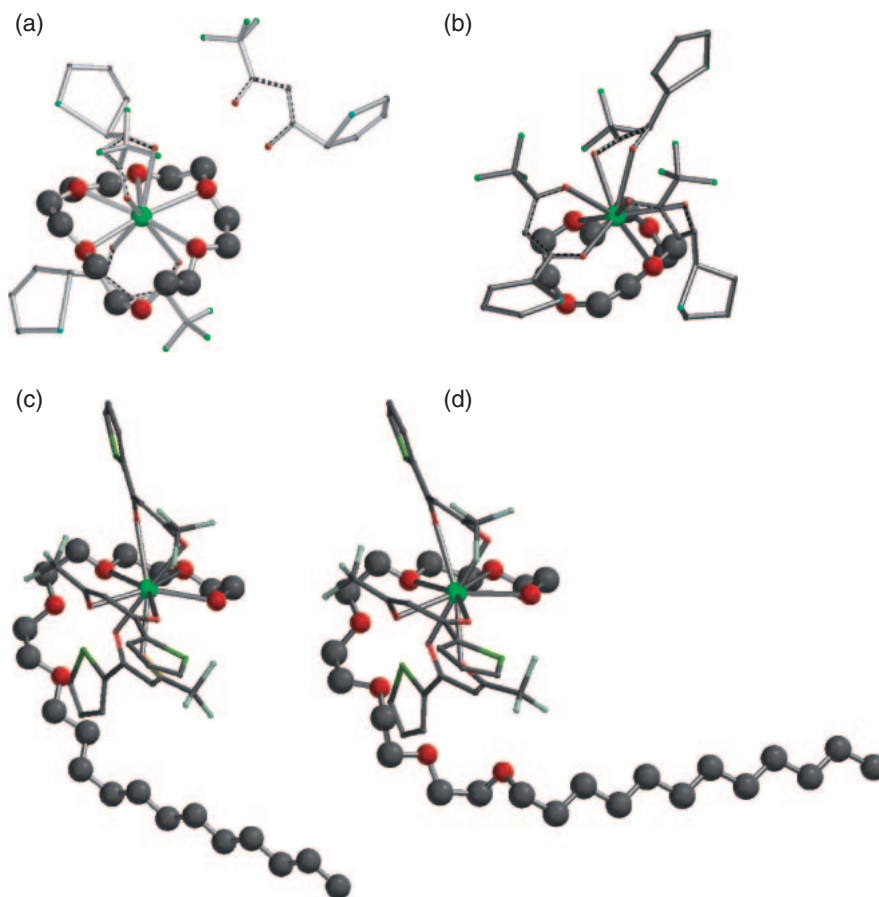


Fig. 5. Proposed structures of the adduct complexes of $[\text{Ln}(\text{tta})_3 \cdot (\text{POE})]$, POE: (a) 18C6, (b) 12C4, (c) DEO4, and (d) DEO6. Optimized by MM2 calculations; see text. La = green, O = red, C = dark gray, H is omitted for simplicity, tta is given by stick frame.

$[\text{Ln}(\text{tta})_3 \cdot (\text{DEO4})]$ adduct obtained by MM2 calculations is shown in Fig. 5c.

The adduct formation constant for DEO6 is much smaller than 18C6, although the number of ethylene oxide units is the same between them. This may indicate that the number of oxygen atoms coordinating to the metal ion in DEO6 is smaller than that of 18C6. When the counter anion of the metal complex of linear POE is a non-coordinating ion, such as picrate (pic^-) or nitrate, the metal ion center is surrounded by the oxygen atoms of the ethylene oxide chain of DEO_n . For example, in the solid-state adduct of linear pentaethylene glycol (PEG5) with neodymium nitrate, $[\text{Nd}(\text{NO}_3)_3 \cdot (\text{PEG5})]$, all of the six oxygen atoms of PEG5 coordinate to the Nd^{3+} ion by forming a ring-like configuration around the metal ion center similar to that of the crown ether complex.¹⁷ NMR studies revealed that the POE complex has similar structure even in solution. That is, in the $[\text{K}(\text{DEO6})](\text{pic})$ complex, the EO moiety of DEO6 is coordinating to the K^+ ion by wrapping around the metal ion center.^{37,51} On the other hand, DEO6 does not substitute the coordinated tta ligands in the present extraction system, since the coordinating ability of tta is higher than that of POE. This may imply that the structure of the DEO6 adduct might be similar to that of the DEO4 complex, that is, two or three oxygen atoms of DEO6 coordinate to the metal ion in $[\text{Ln}(\text{tta})_3]$ complex. However, the β_{add} values of DEO6 adduct are 30-fold higher than that of the DEO4 adduct. These results

may be attributed to some additional interactions of the DEO6 with the metal ion center. The uncoordinated oxygen atoms of the residual EO chain of DEO6 may electrostatically interact with the Ln^{3+} ion center at the outer sphere of the complex. Molecular structure of the $[\text{Ln}(\text{tta})_3 \cdot (\text{DEO6})]$ adduct optimized by MM2 calculations is shown in Fig. 5d. The outer sphere interaction of residual oxygen atoms of DEO6 is supported by the structure generated by MM2 calculation.

The differences in $\log \beta_{\text{add}}$ values between DEO6 and DEO8, and between DEO8 and TX-100 ($n_{\text{ave}} = 9.6$) are not so significant compared to that between DEO4 and DEO6. As can be seen from the structure of DEO6 complex (Fig. 5d), six ethylene oxide units are enough for the outer sphere interaction with the $[\text{Ln}(\text{tta})_3]$ complex.

Extraction Constant of POE Adducts. The over-all synergistic extraction constant, $K_{\text{ex,add}}$, in Eq. 5 is given by combining Eqs. 3 and 8:

$$\log K_{\text{ex,add}} = \log K_{\text{ex}} + \log \beta_{\text{add}}. \quad (14)$$

The values of $\log K_{\text{ex,add}}$ thus obtained are listed in Table 2. The $\log K_{\text{ex,add}}$ is plotted as a function of ionic radius of Ln^{3+} in Fig. 6 together with $\log K_{\text{ex}}$ and $\log \beta_{\text{add}}$, where the results for DEO6 system are shown as the example. Because of its negative charge and chelating effect, the coordination ability of the tta ligand is higher than that of the water molecule. Thus, the $\log K_{\text{ex}}$ value decreases as the size of Ln^{3+}

Table 2. Extraction Constants of the Adduct Complex $[\text{Ln}(\text{tta})_3 \cdot (\text{POE})]$, $K_{\text{ex,add}}$, into 1,2-Dichloroethane

Ln^{3+}	$\log K_{\text{ex,add}}$					
	DEO4	DEO6	DEO8	TX-100	12C4	18C6
La^{3+}	-6.19	-4.98	-4.70	-4.60	-6.22	-3.74
Ce^{3+}	-5.60	-4.35	-4.05	-3.94	-5.58	-2.93
Pr^{3+}	-5.47	-4.17	-3.68	-3.60	-5.26	-2.58
Nd^{3+}	-5.40	-4.01	-3.52	-3.42	-5.08	-2.41
Sm^{3+}	-4.96	-3.34	-2.84	-2.78	-4.42	-1.81
Eu^{3+}	-4.88	-3.27	-2.79	-2.70	-4.35	-1.66
Gd^{3+}	-4.98	-3.38	-2.86	-2.79	-4.39	-1.75
Tb^{3+}	-4.63	-3.03	-2.48	-2.36	-4.02	-1.38
Dy^{3+}	-4.55	-2.98	-2.46	-2.27	-3.92	-1.33
Ho^{3+}	-4.54	-2.97	-2.31	-2.30	-3.94	-1.30
Er^{3+}	-4.54	-2.96	-2.47	-2.18	-3.86	-1.28
Tm^{3+}	-4.40	-2.91	-2.31	-2.19	-3.81	-1.20
Yb^{3+}	-4.44	-2.96	-2.53	-2.24	-3.72	-1.28
Lu^{3+}	-4.51	-3.11	-2.66	-2.38	-3.84	-1.34

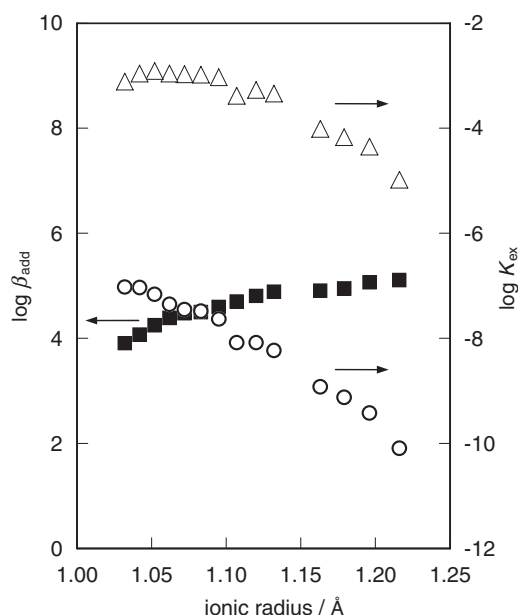


Fig. 6. Plots of extraction constant of $[\text{Ln}(\text{tta})_3]$, and extraction and adduct formation constants of $[\text{Ln}(\text{tta})_3 \cdot (\text{DEO6})]$ as a function of ionic radius. $\circ = \log K_{\text{ex}}$; $\triangle = \log K_{\text{ex,add}}$; $\blacksquare = \log \beta_{\text{add}}$.

ion increases. On the other hand, the $\log \beta_{\text{add}}$ increases as the ionic radius of lanthanoid increases. These opposite trends between the $\log K_{\text{ex}}$ and $\log \beta_{\text{add}}$ resulted in the leveling of the range of equilibrium constants of the synergistic extraction, $\log K_{\text{ex,add}}$. In particular, the values of $K_{\text{ex,add}}$ of heavy lanthanoids (Sm^{3+} to Lu^{3+}) barely change.

Usually, the synergistic extraction of lanthanoid ions has been investigated for the purpose of mutual separation among them. Recently, ICP method has become popular for the simultaneous determination of elements. Thus, the group separation is of great importance for the simultaneous analysis of metal ions.⁵² Also, group separation is quite essential since the extraction of rare-earth ions is the primary step in the partitioning of high-level liquid wastes containing fission products.⁵³ Thus,

small difference in the extraction constants of the lanthanoid ions is preferable for these purposes.

Conclusion

The synergistic extraction of thenoyltrifluoroacetone complexes of the whole series of lanthanoid ions (except promethium) with linear poly(oxyethylene) was studied and compared to that of crown ether systems. (1) The extraction of lanthanoids is significantly enhanced by the formation of the 1:1 adduct $[\text{Ln}(\text{tta})_3 \cdot (\text{POE})]$ in organic phase. (2) The adduct formation constant increased with an increase in the ionic radius of lanthanoid ion. (3) The order of the adduct formation constants among the POE compounds is as follows: $18\text{C6} \gg \text{TX-100} \approx \text{DEO8} > \text{DEO6} \gg 12\text{C4} \geq \text{DEO4}$. (5) The structures of adduct complexes were estimated from the adduct formation constants with the aid of MM2 calculation. (6) The synergistic extraction with linear POE is advantageous for the group separation of lanthanoid ions.

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