 

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

**Gene Frederick Gagabe,[1] Yuta Satoh,[1] Keiichi Satoh,[2] and Kiyoshi Sawada*[1]**

[1]Graduate School of Science and Technology, Niigata University, Ikarashi 2-Nocho, Niigata 950-2181

[2]Department of Chemistry, Faculty of Science, Niigata University, Ikarashi 2-Nocho, Niigata 950-2181

Received June 12, 2007; E-mail: sawada@sc.niigata-u.ac.jp

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 [HO–($CH_2CH_2O$–)$_n$R] are monodispersed DEO$n$ (R = $C_{12}H_{25}$; $n$ = 4, 6, and 8) and polydispersed TX-100 (R = octylphenyl; $n_{ave}$ = 9.6). Equilibrium studies showed a 1:1 adduct complex with POE compound, $Ln(tta)_3$·(POE), formed in the organic phase. The adduct formation constant, $\beta_{add}$, 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 $\beta_{add}$ 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] $\beta$-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 $\beta$-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, $Ln_2O_3$ (Ln = 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 (DEO$n$; HO–($CH_2CH_2O$–)$_n$R, where R = $C_{12}H_{25}$ and number of EO units $n$ = 4, 6, and 8) and polydispersed octylphenyl ether (TX-100; R = octylphenyl and average number of EO units[39] ($n_{ave}$) = 9.6) were obtained from Nikko

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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 thenoyltrifluoroacetonate (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 $5.0 \times 10^{-7}$ M (M = mol dm$^{-3}$). The aqueous solution (20 cm$^3$) thus prepared was mixed with an equivolume of an 1,2-dichloroethane solution containing $1.0 \times 10^{-2}$ M Htta and $1.0 \times 10^{-2}$ M POE in a centrifuge tube (50 cm$^3$). The mixture was shaken for 30 min at $25.0 \pm 0.1$ °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 $1.0 \times 10^{-2}$ M Htta and various concentrations of POE ($3.0 \times 10^{-7}$–$1.0 \times 10^{-2}$ 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 ($K_d = [12C4]_{org}/[12C4]_{aq}$) 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

$$D = \frac{C_{Ln,org}}{C_{Ln,aq}}, \tag{1}$$

where $C_{Ln,org}$ and $C_{Ln,aq}$ 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

$$Ln^{3+}{}_{aq} + 3Htta_{org} \overset{K_{ex}}{\rightleftharpoons} [Ln(tta)_3]_{org} + 3H^+{}_{aq}, \tag{2}$$

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

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 $[Ln(tta)_3 \cdot m(POE)]$ in the organic phase, the extraction equilibrium is given by

$$Ln^{3+}{}_{aq} + 3Htta_{org} + mPOE_{org} \overset{K_{ex,add}}{\rightleftharpoons} [Ln(tta)_3 \cdot m(POE)]_{org} + 3H^+{}_{aq} \tag{4}$$

The extraction constant of adduct complex is

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

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

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

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

$$[Ln(tta)_3]_{org} + mPOE_{org} \overset{\beta_{add}}{\rightleftharpoons} [Ln(tta)_3 \cdot m(POE)]_{org} \tag{7}$$

and the adduct formation constant, $\beta_{add}$, is defined as

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

Consequently, the distribution ratio in Eq. 6 becomes

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

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

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

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

Taking the logarithm of Eq. 11 yields

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

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 $[Ln(tta)_3 \cdot m(POE)]$.

Equation 12 can be simplified as

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

where $\log D_0 = \log K_{ex} + 3\log[Htta]_{org} + 3\ pH$, 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

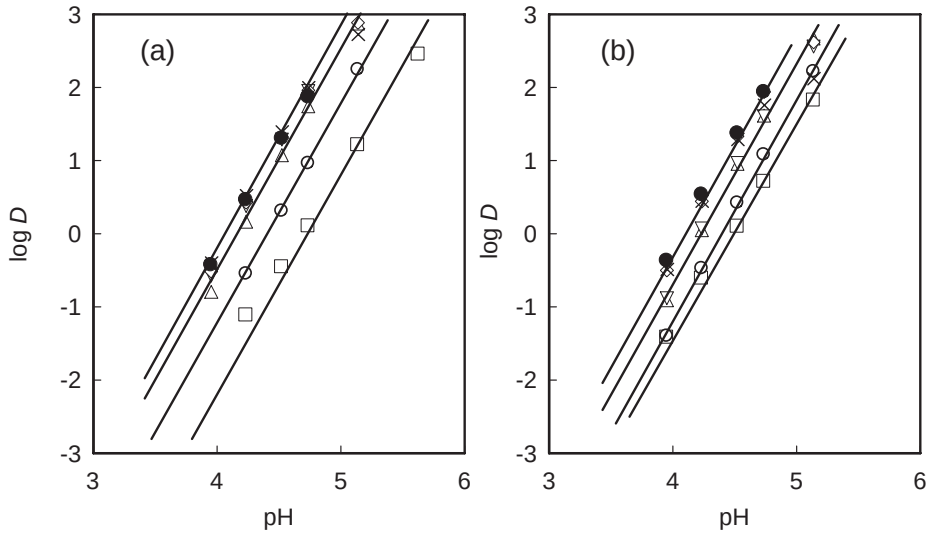


Fig. 1. Plots of log $D$ vs. pH in the extraction of $Ln^{3+}$ with $1.0 \times 10^{-2}$ M Htta and $1.0 \times 10^{-2}$ M DEO6. (a) Odd-atomic number Ln: □ = La, ○ = Pr, △ = Eu, ▽ = Tb, ◇ = Ho, × = Tm, ● = Lu; (b) Even-atomic number Ln: □ = Ce, ○ = Nd, △ = Sm, ▽ = Gd, ◇ = Dy, × = Er, ● = Yb. The slopes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

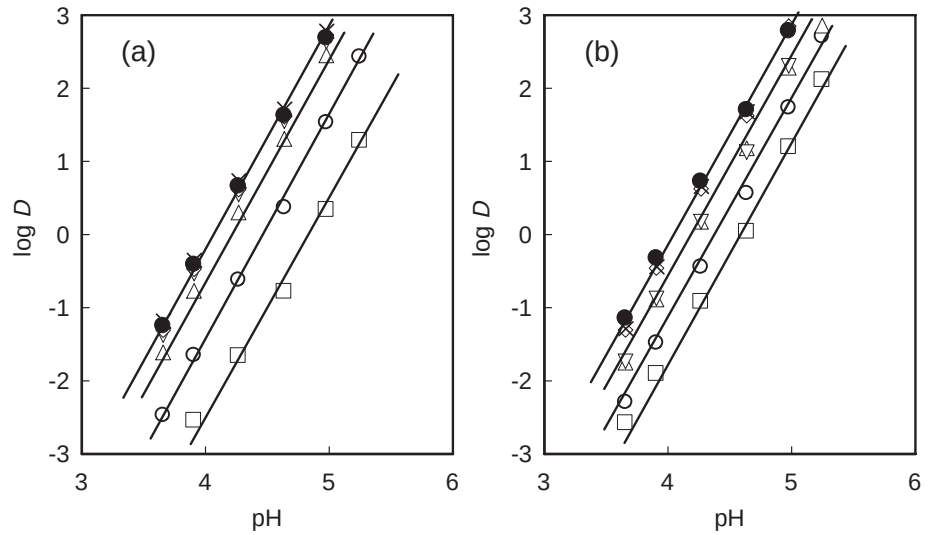


Fig. 2. Plots of log $D$ vs. pH in the extraction of $Ln^{3+}$ with $1.0 \times 10^{-2}$ M Htta and $1.0 \times 10^{-2}$ M TX-100. (a) Odd-atomic number Ln, and (b) Even-atomic number Ln. Symbols are the same as those in Fig. 1. The slopes of solid lines are 3.

determined from the slope of the plot of log $D$ vs. log $[POE]_{org}$. The distribution coefficient of DEO$n$ 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, $[POE]_{org}$, 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 $[POE]_{org}$ at pH 4.9 and $1.0 \times 10^{-2}$ M Htta. The slopes of the plots approached unity in higher $[POE]_{org}$ 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 $[Ln(tta)_3]$ 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 $[Ln(tta)_3 \cdot (POE)]$.

The values of the adduct formation constant, $\beta_{add}$, 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 $\beta_{add}$, thus obtained are listed in Table 1. The values of log $\beta_{add}$ for some crown ether adducts[34] 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 $[Ln(tta)_3 \cdot nH_2O]$, where $n = 2$ or 3.[42] In synergistic systems, the extract-

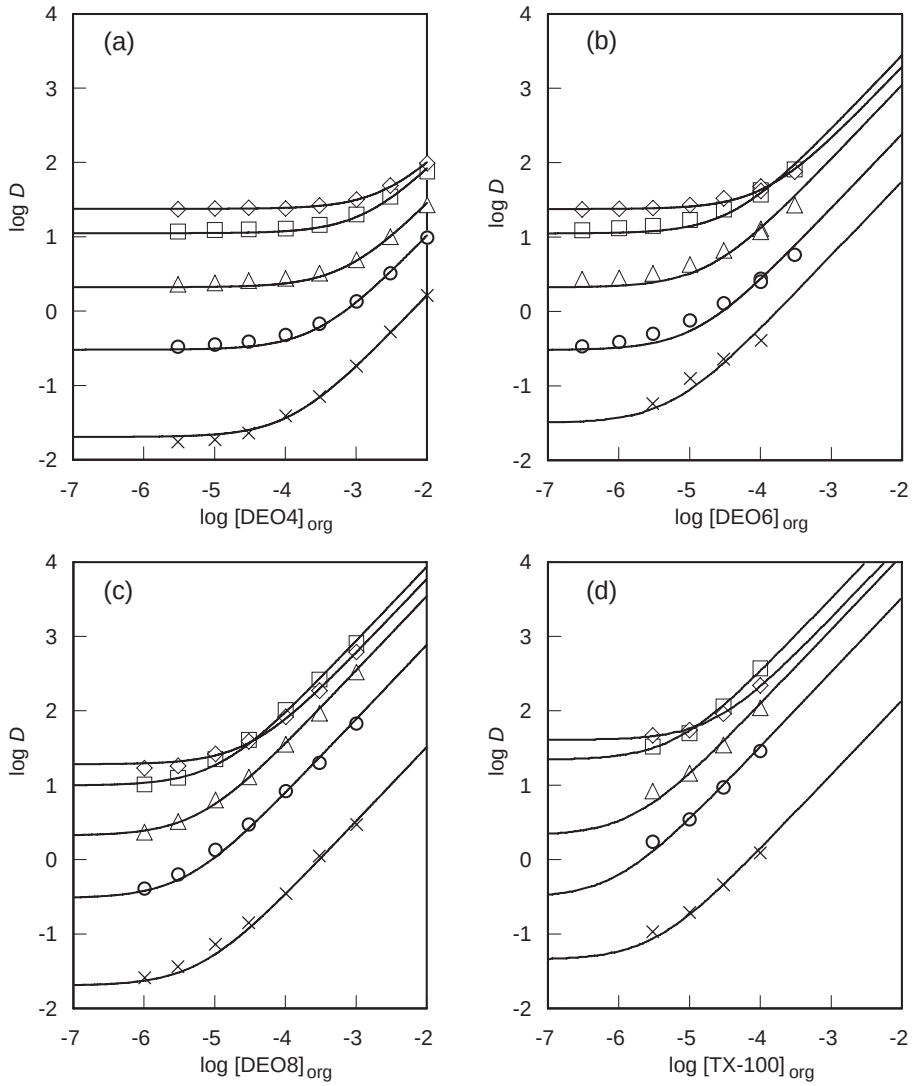


Fig. 3. Plots of $\log D$ vs. $\log [\mathrm{POE}]_{org}$ in the extraction of $Ln^{3+}$ with $1.0 \times 10^{-2}$ M Htta at pH 4.9. POE: (a) DEO4, (b) DEO6, (c) DEO8, (d) TX-100; Ln: × = La, ○ = Nd, △ = Gd, □ = Er, ◇ = Lu. Solid lines are calculated curves; see text.

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

| $Ln^{3+}$ | Ionic radii /Å | $\log K_{ex}$ [a)] | $\log \beta_{add}$ | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 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 $\beta_{add}$ for 12C4 and 18C6 were corrected by taking into consideration the distribution coefficient of crown ethers.

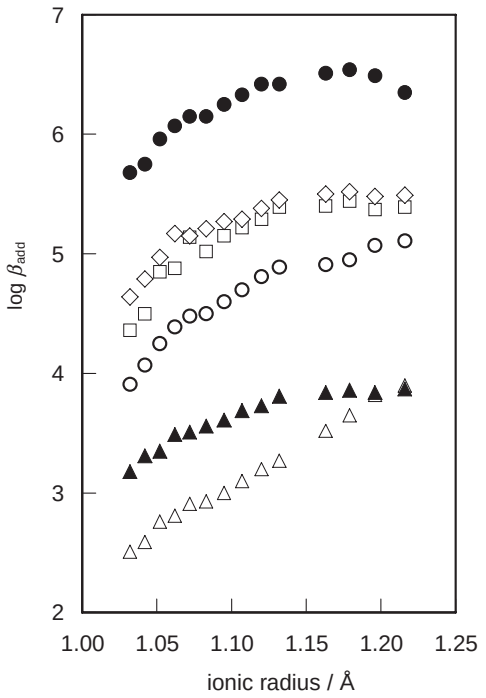


Fig. 4. The plots of logarithmic formation constants of adducts as a function of ionic radii of Ln. POE: △ = DEO4, ○ = DEO6, □ = DEO8, ◇ = TX-100, ▲ = 12C4, ● = 18C6.

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 $[Ln(tta)_3 \cdot (POE)]$ of the linear POEs, $\log \beta_{add}$, are plotted as a function of ionic radii of lanthanoids[43] in Fig. 4, where the results for crown ethers are also shown. Similar to the results for crown ethers, the value of $\beta_{add}$ 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 $[Ln(tta)_3 \cdot (TBP)]$ or $[Ln(tta)_3 \cdot (TOPO)]$ show an opposite trend with the present results for POEs, that is, $\log \beta_{add}$ 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 oligoglymes 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 $\log \beta_{add}$ 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 $\beta_{add}$ 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 $[Ln(tta)_2 \cdot (18C6)]$ 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 $[Ln(tta)_2 \cdot (18C6)]$ 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 $[Ln(tta)_2 \cdot (18C6)]^+(tta^-)$. On the basis of the preceding information, the structure of $[Ln(tta)_2 \cdot (18C6)]^+(tta^-)$ 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 $\beta_{add}$ values for 12C4 adducts are significantly lower than those of 18C6. Thus, the 12C4 may coordinate to the metal ion of the complex $[Ln(tta)_3]$ as a bidentate or tridentate ligand. The structure of $[Ln(tta)_3 \cdot (12C4)]$ 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 $\beta$-diketones, and is coordinated by four oxygen donor atoms of the tetraglyme to form a 10-coordinate complex.[46] The structure of the adduct $[Ln(tta)_3 \cdot (DEO4)]$ 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

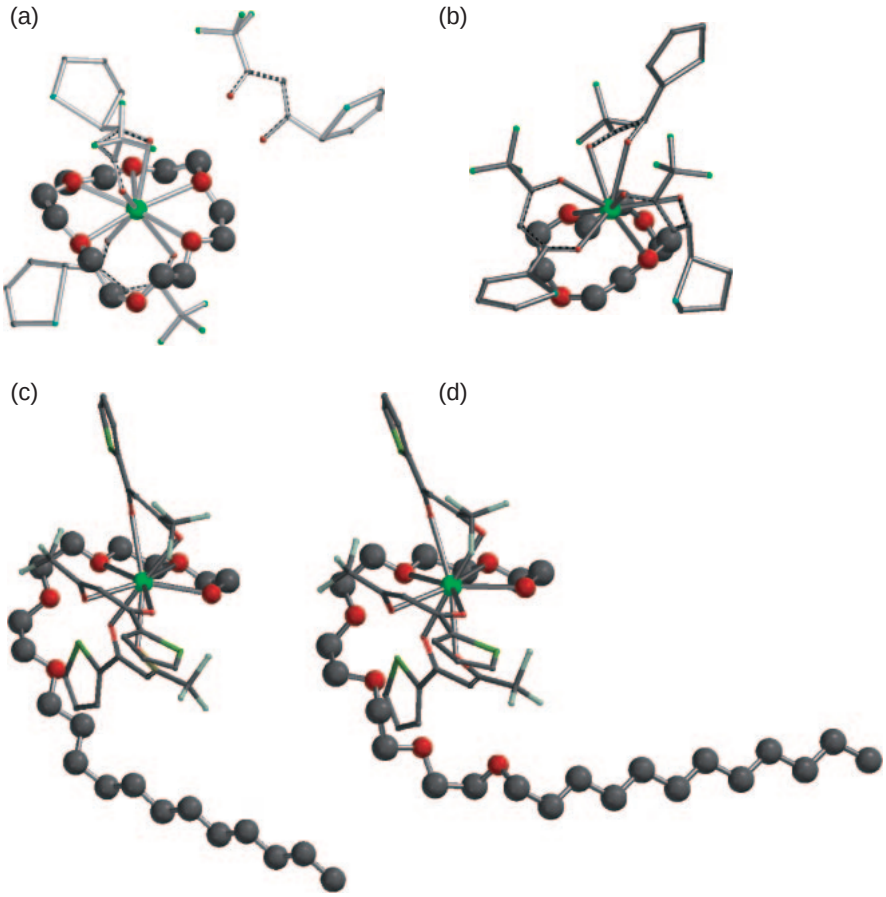


Fig. 5. Proposed structures of the adduct complexes of [La(tta)$_3$·(POE)], POE: (a) 18C6, (b) 12C4, (c) DEO4, and (d) DEO6. Optimized by MM2 calculations; see text. La = green, O = red, C = dark gray, H is omitted for simplicity, tta is given by stick frame.

[Ln(tta)$_3$·(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, [Nd(NO$_3$)$_3$·(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 [K(DEO6)](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 [Ln(tta)$_3$] complex. However, the $\beta_{add}$ 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 [Ln(tta)$_3$·(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 $\log \beta_{add}$ values between DEO6 and DEO8, and between DEO8 and TX-100 ($n_{ave} = 9.6$) 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 [Ln(tta)$_3$] complex.

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

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

The values of $\log K_{ex,add}$ thus obtained are listed in Table 2. The $\log K_{ex,add}$ is plotted as a function of ionic radius of $Ln^{3+}$ in Fig. 6 together with $\log K_{ex}$ and $\log \beta_{add}$, 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 $\log K_{ex}$ value decreases as the size of $Ln^{3+}$

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

| $Ln^{3+}$ | $\log K_{ex,add}$ | | | | | |
|---|---|---|---|---|---|---|
| | 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 |

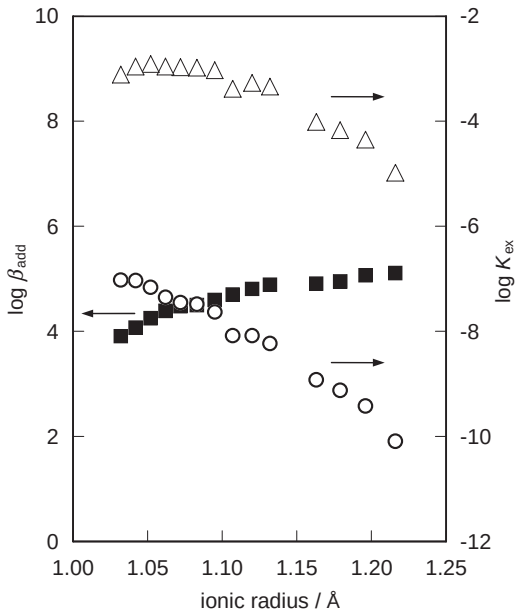


Fig. 6. Plots of extraction constant of $[Ln(tta)_3]$, and extraction and adduct formation constants of $[Ln(tta)_3 \cdot (DEO6)]$ as a function of ionic radius. ○ = $\log K_{ex}$; △ = $\log K_{ex,add}$; ■ = $\log \beta_{add}$.

ion increases. On the other hand, the $\log \beta_{add}$ increases as the ionic radius of lanthanoid increases. These opposite trends between the $\log K_{ex}$ and $\log \beta_{add}$ resulted in the leveling of the range of equilibrium constants of the synergistic extraction, $\log K_{ex,add}$. In particular, the values of $K_{ex,add}$ 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 $[Ln(tta)_3 \cdot (POE)]$ 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: 18C6 $\gg$ TX-100 $\approx$ DEO8 > DEO6 $\gg$ 12C4 $\geq$ 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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