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Crown Ethers as Synergist in the 2-Thenoyltrifluoroacetone Extraction of Lanthanoids in 1,2-Dichloroethane

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Summary. The solvent extraction of 14 trivalent lanthanoid ions (Ln^{3+}) from a nitrate medium into 1,2-dichloroethane containing 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (H*TTA*) was investigated at 25.0°C. The extraction of $Ln(TTA)_3$ species was confirmed and the extraction constants were determined. The extraction of *Ln* with the synergistic mixture of H*TTA* and a crown ether (*CE*: 12-crown-4, 18-crown-6, cyclohexano-18-crown-6 or benzo-18-crown-6) was also investigated at 25.0°C. The 1:1 adducts of the complex and crown ether, $Ln(TTA)_3{\cdot}(CE)$ are formed for all the lanthanoid ions and the *CE*s used in this study. The formation constants, β_{add}, of the adduct $Ln(TTA)_3{\cdot}(CE)$ from $Ln(TTA)_3$ in the organic phase were determined by nonlinear least-squares method. The stabilities and structures of the formed adducts were discussed with respect to the cavity size, steric effect, and basicity of the *CE*.

Keywords. Adduct formation constant; Crown ethers; ICP-MS; Lanthanoids; Synergistic extraction.

Introduction

Liquid–liquid extraction with β-diketones has been widely used in the intra- and inter-group separation of metal ions. One of the β-diketones that has been a subject of steady interest in the separation of metal ions since its introduction is 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (2-thenoyltrifluoroacetone, H*TTA*) [1]. *Reid* and *Calvin* have studied the keto-enol tautomerism of some β-diketones containing trifluoromethyl group [2]. The strong inductive effect of the trifluoromethyl group in H*TTA* and other related compounds kinetically and thermodynamically favors the enolization process. The enol-form of β-diketones forms stable complexes with metal ions. Particularly, the short O-to-O distance of the enolic H*TTA* (about 2.5 Å) was found to play an important role in the selective extraction of metal ions with similar sizes [3].

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Lanthanoids (*Ln*), which exist ordinarily in the trivalent state in aqueous solution, have a hard acid property and predominantly exhibit ionic interaction. Ln^{3+} ions from various media have been extracted with H*TTA* into various kinds of solvents [1, 4–6]. The tris(thenoyltrifluoroacetonato)lanthanoid(III) complex extracted into an organic phase has a strong tendency to form more lipophilic adduct complexes with electrically neutral ligands or *Lewis* bases. This adduct formation tends to significantly enhance the extraction of *Ln* from the aqueous phase through the displacement of residual water molecules coordinated to the *Ln*-chelate complex [7]. Mixtures of H*TTA* and various synergists such as organophosphorus esters, 1,10-phenanthroline, quaternary ammonium salts, polyethers, and coordinately saturated metal chelates were used in the solvent extraction of *Ln* [7–11].

For the past decades, crown ethers have found various applications in processes of separation and purification. The trivalent rare-earth metal ions were found to be scarcely extracted from nitrate medium by the18-crown-6 or its derivatives alone [12]. However, it has been reported that the efficiency for the extraction of actinides and lanthanides with chelating agents are significantly improved by the addition of crown ether. Due to its ability to provide oxygen coordination to metal ions and its unique size-fitting feature, crown ethers have been used with H*TTA* for selective extraction of *Ln* [12–16]. Moreover, synergism was also observed in the extraction of *Ln* with the combination of crown ethers and other chelating agents such as pyrazolones and alkylated phosphoric acid [17, 18].

Although many studies have been conducted in the H*TTA* extraction of Ln^{3+} ions with crown ethers, the adduct formation constant for the entire lanthanoid series with crown ethers of various cavity sizes and substituents was not yet reported. In the present study, the extraction of a series of lanthanoid ions with H*TTA* and the synergistic extraction of the complex with a crown ether, 12-crown-4 (*12C4*), 18-crown-6 (*18C6*), cyclohexano-18-crown-6 (*C18C6*), or benzo-18-crown-6 (*B18C6*), were investigated.

Results and Discussion

Extraction of Ln with HTTA

The distribution ratio (*D*) of the metal ion between the organic and aqueous phases is defined by Eq. (1) where $C_{Ln,\,\mathrm{org}}$ and $C_{Ln,\,\mathrm{aq}}$ are the total concentrations of the Ln^{3+} ion in the organic and aqueous phases, respectively.

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

The equilibrium in the extraction of Ln^{3+} with H*TTA* is generally given by Eq. (2).

$$Ln^{3+}{}_{,\,\mathrm{aq}} + 3\mathrm{H}TTA_{,\,\mathrm{org}} \overset{K_{\mathrm{ex}}}{\rightleftharpoons} Ln(TTA)_{3,\,\mathrm{org}} + 3\mathrm{H}^{+}{}_{,\,\mathrm{aq}} \tag{2}$$

With the assumption that the only extracted complex into the organic phase is the neutral $Ln(TTA)_3$, then $C_{Ln,\,\mathrm{org}} = [Ln(TTA)_3]$. The formation of TTA^- complexes of Ln^{3+}, $Ln(TTA)_n{}^{(3-n)+}$, and hydroxo complexes, $Ln(OH)_n{}^{(3-n)+}$, in the aqueous phase can be neglected under the present experimental conditions [7, 9]. Thus, the total concentration of *Ln* in the aqueous phase is equal to the free Ln^{3+} ions, *i.e.*, $C_{Ln,\mathrm{aq}} = [Ln^{3+}]_{\mathrm{aq}}$. Thus, the distribution ratio for the H*TTA* extraction of trivalent *Ln* is given by Eq. (3) where the subscript "0" for *D* refers to the system without the synergistic agent, crown ether.

$$D_0 = \frac{[Ln(TTA)_3]_{\mathrm{org}}}{[Ln^{3+}]_{\mathrm{aq}}} \tag{3}$$

The extraction constant, K_{ex}, for Eq. (2) is defined by Eq. (4).

$$K_{\mathrm{ex}} = \frac{[Ln(TTA)_3]_{\mathrm{org}}[\mathrm{H}^+]^3_{\mathrm{aq}}}{[Ln^{3+}]_{\mathrm{aq}}[\mathrm{H}TTA]^3_{\mathrm{org}}} \tag{4}$$

Substitution of Eq. (3) into Eq. (4) leads to Eq. (5).

$$K_{\mathrm{ex}} = \frac{D_0[\mathrm{H}^+]^3_{\mathrm{aq}}}{[\mathrm{H}TTA]^3_{\mathrm{org}}} \tag{5}$$

The distribution of H*TTA* into the aqueous phase was found to be negligible under the present experimental conditions, and the total concentration of H*TTA*, $C_{\mathrm{H}TTA}$, is much higher than the total concentration of the *Ln*. Thus, the equilibrium concentration of H*TTA*, $[\mathrm{H}TTA]_{\mathrm{org}}$, can be approximated as $C_{\mathrm{H}TTA}$. Substituting $C_{\mathrm{H}TTA}$ to Eq. (5) and taking the logarithm of the equation upon subsequent rearrangement yields Eq. (6).

$$\log D_0 = \log K_{\mathrm{ex}} + 3\log C_{\mathrm{H}TTA} + 3pH \tag{6}$$

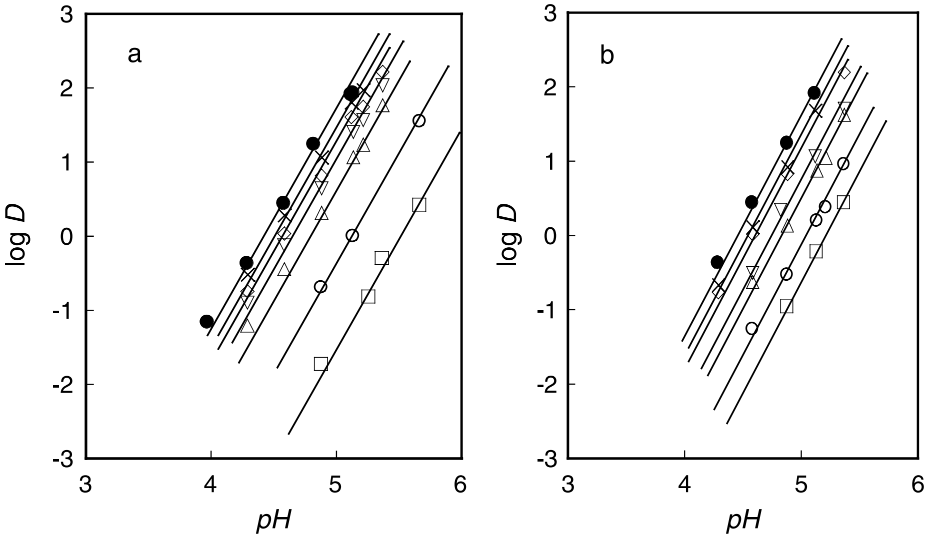

Fig. 1. Plots of log D_0 *vs*. *pH* for the extraction of 14 *Ln* with 1.0×10^{-2} *M* H*TTA* into 1,2-dichloroethane; a) odd-atomic number *Ln*: □ = La, ○ = Pr, Δ = Eu, ∇ = Tb, ◇ = Ho, × = Tm, ● = Lu; b) even-atomic number *Ln*: □ = Ce, ○ = Nd, Δ = Sm, ∇ = Gd, ◇ = Dy, × = Er, ● = Yb; the slopes of solid lines are 3

Table 1. Extraction constants of $Ln(TTA)_3$, K_{ex}, and formation constant of the crown ether adduct $Ln(TTA)_3 \cdot (CE)$, β_{add}, in 1,2-dichloroethane

Ln^{3+}	atomic no.	ionic radii[a]	$\log K_{ex}$	$\log \beta_{add}$			
		Å		*12C4*	*18C6*	*B18C6*	*C18C6*
La^{3+}	57	1.216	−10.09	3.50	6.06	5.67	6.58
Ce^{3+}	58	1.196	−9.42	3.53	6.20	5.84	6.71
Pr^{3+}	59	1.179	−9.12	3.56	6.25	5.87	6.77
Nd^{3+}	60	1.163	−8.92	3.50	6.22	5.87	6.67
Sm^{3+}	62	1.132	−8.23	3.46	6.13	5.86	6.58
Eu^{3+}	63	1.120	−8.08	3.46	6.12	5.78	6.56
Gd^{3+}	64	1.107	−8.08	3.34	6.04	5.68	6.43
Tb^{3+}	65	1.095	−7.63	3.27	5.96	5.67	6.35
Dy^{3+}	66	1.083	−7.48	3.21	5.86	5.59	6.26
Ho^{3+}	67	1.072	−7.45	3.21	5.86	5.54	6.29
Er^{3+}	68	1.062	−7.35	3.13	5.78	5.48	6.18
Tm^{3+}	69	1.052	−7.16	3.04	5.67	5.38	6.03
Yb^{3+}	70	1.042	−7.03	2.92	5.46	5.19	5.85
Lu^{3+}	71	1.032	−7.02	2.85	5.39	5.11	5.81

[a] Coordination number is 9, taken from Ref. [20]

Experimentally determined logarithmic distribution ratio, $\log D_0$, is plotted as a function of *pH* in Fig. 1. The slope of the plots for each *Ln*, which has a value of three, implies that Ln^{3+} from nitrate medium are extracted into 1,2-dichloroethane with three TTA^- ions, $Ln(TTA)_3$. The extraction constant, K_{ex}, evaluated from the results shown in Fig. 1 are listed in Table 1. The K_{ex} values are in reasonable agree-

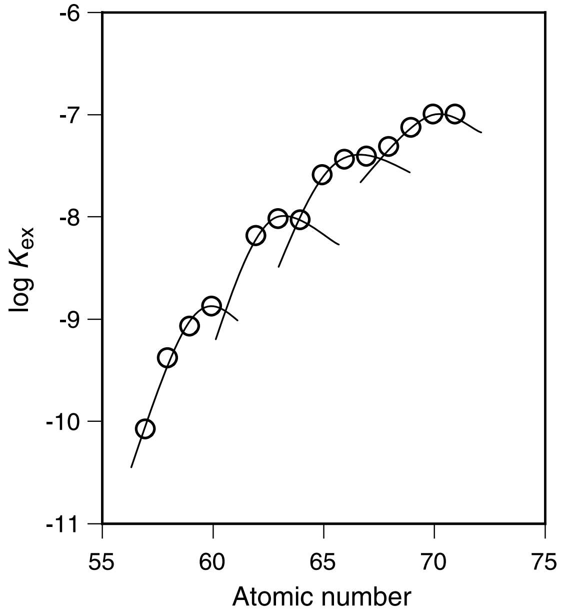

Fig. 2. Plot of log K_{ex} as a function of atomic number of *Ln*

ment with that previously reported by *Kitatsuji et al.* in their study on the extraction of Ln^{3+} ions from perchlorate medium into 1,2-dichloroethane [14].

The logarithmic values of K_{ex} are plotted as a function of atomic number in Fig. 2. This plot distinctly shows the division of the series of *Ln* into four smooth curves with the Gd point common to the second and the third tetrads, and the extended smooth curves of the first and second tetrads, and the third and fourth tetrads intersect at the atomic number 60–61 and 67–68 regions, respectively. This is consistent with the tetrad hypothesis formulated by *Peppard et al.* [19]. Similar effect has been observed in the H*TTA* extraction of Ln^{3+} into different organic solvents such as that reported with carbon tetrachloride [1].

Synergistic Extraction of Ln Complex of HTTA with Crown Ether

The distribution ratio of *Ln* extracted with H*TTA* increases by the addition of crown ether (*CE*). This is attributable to the formation of a more lipophilic adduct with the *CE*. The overall reaction of the generally accepted synergistic extraction of lanthanoid ions is given by Eq. (7) where x and m correspond to the number of TTA^- and *CE*, respectively, in the extracted adduct, $\mathrm{Ln}(TTA)_x \cdot m(CE)$.

$$Ln^{3+}{}_{,\mathrm{aq}} + x\mathrm{H}TTA_{,\mathrm{org}} + mCE_{,\mathrm{org}} \rightleftharpoons Ln(TTA)_x{\cdot}m(CE)_{,\mathrm{org}} + x\mathrm{H}^+{}_{,\mathrm{aq}} \qquad (7)$$

To determine the number of TTA^- involved in the extracted adduct, the variation of the distribution ratio of *Ln* with respect to the concentration of H^+ at constant concentrations of H*TTA* and *CE* was investigated. The log *D vs. pH* plots in the extraction of Ln^{3+} using H*TTA* and the crown ether, *B18C6*, is shown in Fig. 3. The plots show straight lines for all *Ln* with a slope of three, which implies that three

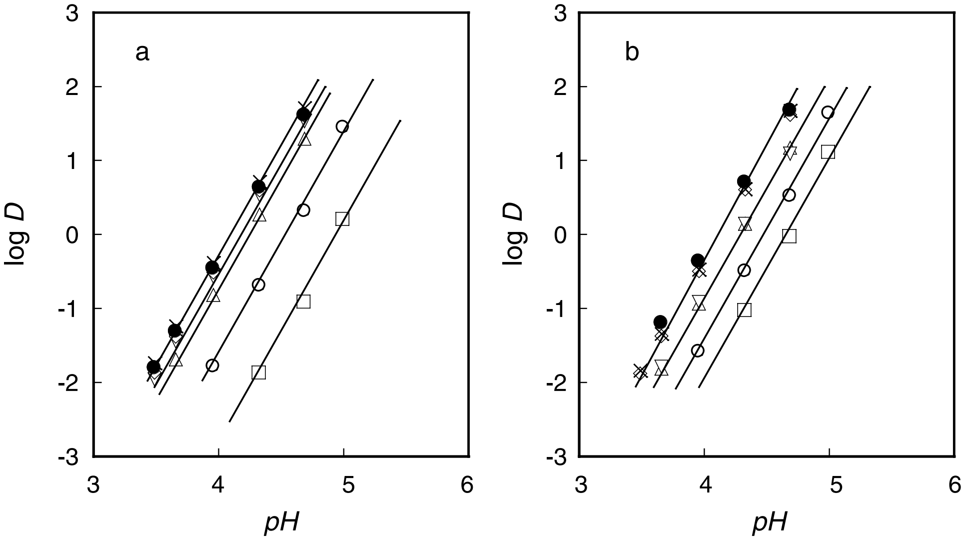

Fig. 3. Plots of log *D vs. pH* in the extraction of *Ln* with 1.0×10^{-2} *M* H*TTA* and 3×10^{-4} *M B18C6*; a) odd-atomic number *Ln*; b) even-atomic number *Ln*; symbols are the same as those in Fig. 1; the slopes of the solid lines are 3

H*TTA* participated in the synergistic extraction of Ln^{3+}. Thus, the synergistic extraction equilibrium in Eq. (7) can be rewritten as Eq. (8).

$$Ln^{3+}{}_{,\mathrm{aq}} + 3\mathrm{H}TTA_{,\mathrm{org}} + mCE_{,\mathrm{org}} \rightleftharpoons Ln(TTA)_3{\cdot}m(CE)_{,\mathrm{org}} + 3\mathrm{H}^{+}{}_{,\mathrm{aq}} \tag{8}$$

According to the extraction equilibria (Eqs. (2) and (8), the formation of adduct in the organic phase is written by the following equilibrium (Eq. (9)).

$$Ln(TTA)_{3,\mathrm{org}} + mCE_{,\mathrm{org}} \overset{\beta_{\mathrm{add}}}{\rightleftharpoons} Ln(TTA)_3{\cdot}m(CE)_{,\mathrm{org}} \tag{9}$$

The adduct formation constant, β_{add}, is given by Eq. (10).

$$\beta_{\mathrm{add}} = \frac{[Ln(TTA)_3{\cdot}m(CE)]_{\mathrm{org}}}{[Ln(TTA)_3]_{\mathrm{org}}[CE]^{m}{}_{\mathrm{org}}} \tag{10}$$

If it is assumed that the dominant species in the organic phase are only $Ln(TTA)_3$ and $Ln(TTA)_3{\cdot}m(CE)$, then the total concentration of *Ln* in the organic phase is given by Eq. (11).

$$C_{Ln,\mathrm{org}} = [Ln(TTA)_3]_{\mathrm{org}} + [Ln(TTA)_3{\cdot}m(CE)]_{\mathrm{org}} \tag{11}$$

Thus, the distribution ratio (*D*) of the *Ln* between the organic and aqueous phases is then expressed by Eq. (12).

$$D = \frac{[Ln(TTA)_3]_{\mathrm{org}} + [Ln(TTA)_3{\cdot}m(CE)]_{\mathrm{org}}}{[Ln^{3+}]_{\mathrm{aq}}} \tag{12}$$

By the substitution of Eqs. (3) and (10) into Eq. (12), the distribution ratio for the extraction with the synergistic mixture in terms of the concentration of *CE* is given by Eqs. (13) or (14).

$$D = \frac{[Ln(TTA)_3]_{\mathrm{org}} + [Ln(TTA)_3]_{\mathrm{org}}\beta_{\mathrm{add}}[CE]^{m}_{\mathrm{org}}}{[Ln]_{\mathrm{aq}}} = D_0(1 + \beta_{\mathrm{add}}[CE]^{m}_{\mathrm{org}} \tag{13}$$

$$\log D = \log D_0 + \log\,(1 + \beta_{\mathrm{add}}[CE]^{m}_{\mathrm{org}}) \tag{14}$$

Thus, a plot of log *D* as a function of log [*CE*] will give a curve, the slope of which approaches to *m* at higher *CE* concentration region.

Plots of log *D vs*. log [*CE*] in the extraction of Ln^{3+} from nitrate medium at *pH* 4.90 into 1,2-dichloroethane with H*TTA* and crown ethers are shown in Fig. 4. As seen from Fig. 4, the slopes of the curves for the Ln^{3+} ions approach to unity at higher [*CE*] region, irrespective of the kind of *CE* used. Only representative lanthanoids are shown in Fig. 4, but the extraction behavior of all other lanthanoid ions was found to be the same. These results indicate that the $Ln(TTA)_3$ complex forms an adduct with one molecule of the *CE*, that is, the 1:1 adducts, $Ln(TTA)_3{\cdot}(CE)$, are extracted for any crown ethers used in this study. This is in conformity with the results obtained by other authors [14]. Although the formation of a 1:2 adduct, $Ln(TTA)_3{\cdot}2(18C6)$, was reported in the extraction of Eu and Gd into chloroform [15], the formation of this type of adduct was not observed in the present extraction with 1,2-dichloroethane.

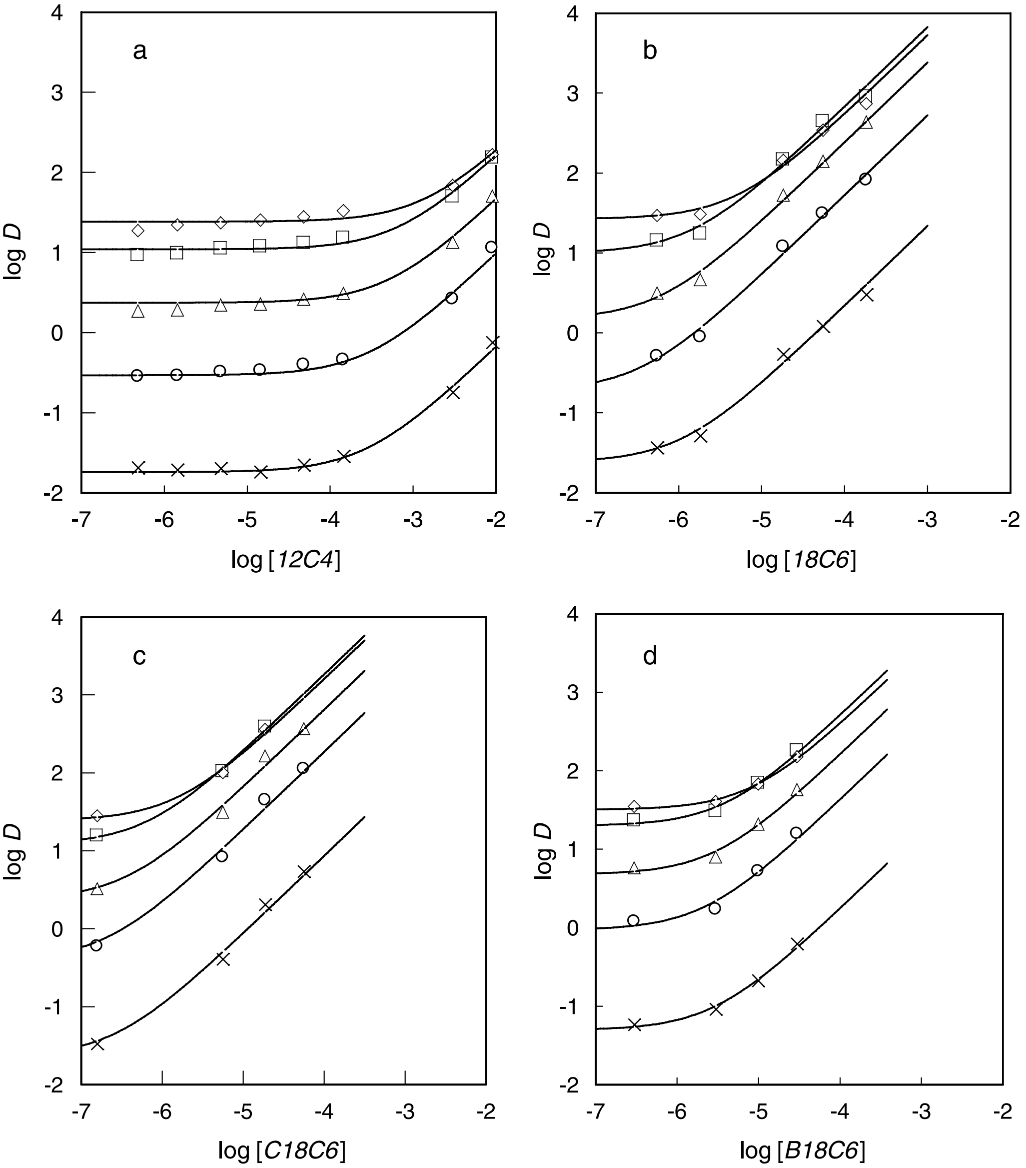

Fig. 4. Plots of log *D* *vs*. log [*CE*] in the extraction of *Ln* with 1.0×10^{-2} *M* H*TTA* at $pH = 4.90$; *CE*: a) *12C4*, b) *18C6*, c) *C18C6*, d) *B18C6*; *Ln*: × = La, ○ = Nd, Δ = Gd, □ = Er, ◇ = Lu; solid lines are calculated curves; see text

By applying nonlinear least-squares method to the plots of Fig. 4, the values of β_{add} were calculated based on Eq. (13). The calculated regression curves are depicted by solid lines in Fig. 4. These curves show good agreement with the experimental data. The values of log β_{add} for the adduct formed with each *CE* are listed in Table 1. The logarithmic adduct formation constants are plotted against ionic radii of *Ln* [20] in Fig. 5.

The log β_{add} for *18C6* is more than two orders of magnitude higher than that for *12C4*. The accepted value of the effective radius of *12C4* cavity is 0.72 Å [21], which is smaller than the ionic radii of the trivalent *Ln* ions. Consequently, the

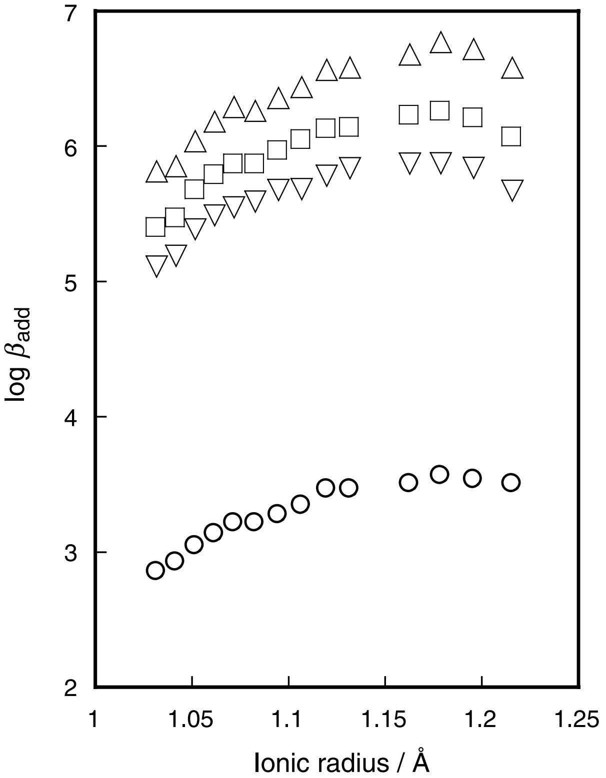

Fig. 5. The plots of logarithmic formation constants of adducts as a function of ionic radii of *Ln*; crown ethers: *C18C6*, Δ; *18C6*, $\square$; *B18C6*, ∇; *12C4*, ○

12C4 cannot accommodate the *Ln*$^{3+}$ ion inside its cavity, *i.e.*, the metal ion can only coordinate with the oxygen donors above the plane of the *CE*. On the other hand, the effective radius of the *18C6* cavity, which is 1.45 Å [21], is large enough to accommodate the *Ln*$^{3+}$ ion. This size-fitting effect accounts for the large differ-

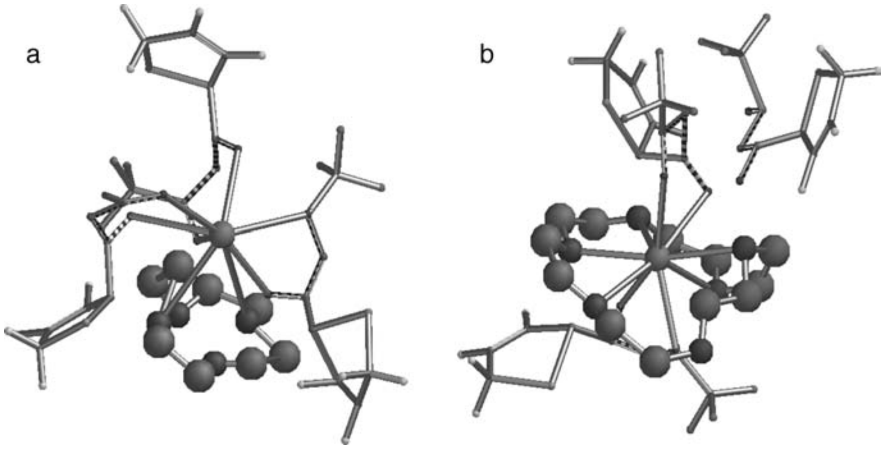

Fig. 6. Proposed structures of the adduct complexes of *Ln*(*TTA*)$_3$ with crown ethers; optimized by MM2 calculations; see text

ence in the adduct formation constants between the 18-membered *18C6* and the 12-membered *12C4*. Thus, the structure wherein the lanthanoid ion is surrounded by the ether oxygens in the cavity of *18C6* is proposed as depicted in Fig. 6.

If the 18-membered *CE*s were to form an adduct in such a manner as *12C4*, then the adduct formation constant with cyclohexano-*18C6* must be smaller than that of unsubstituted *18C6* due to steric hindrance caused by the bulky cyclohexano- substituent. Since the log β_{add} for *C18C6* is higher than *18C6*, the formed adduct must be in a configuration where the steric effect of cyclohexano-substituents with the chelating TTA^- ions is not so significant. This fact also corroborates that the Ln^{3+} ion is coordinated inside the cavity of the 18-membered *CE*s.

Formation of the ion-pair complex $[Ln(TTA)_2 \cdot CE]^+ClO_4^-$ has been reported in the extraction of lighter *Ln* from perchlorate medium into 1,2-dichloroethane [14]. Generally, the synergistic extraction of trivalent *Ln* with a mixture of monovalent chelating anion such as TTA^- and the neutral ligand, in this case *CE*, forms the adduct $Ln(TTA)_3 \cdot (CE)$. The formation of the stable *Ln-CE* complex obstructs the coordination of all three TTA^- ions with the Ln^{3+} ion. Taking into account the coordination number of Ln^{3+} as 8 or 9 and the observation that it is coordinated inside the cavity of *18C6*, only two of the TTA^- can be accommodated in the inner sphere of the complex, *i.e.*, the coordination with the third TTA^- is sterically hindered. Thus, the formation of the cationic species, $[Ln(TTA)_2 \cdot CE]^+$, might be anticipated. Because the nitrate ion is less hydrophobic than the perchlorate ion, $[Ln(TTA)_2 \cdot CE](NO_3)$ was not extracted in the present study. Consequently, since three TTA^- participate in the adduct formation, one of these anions may act as a counter ion forming the ion-pair $[Ln(TTA)_2 \cdot CE]^+(TTA)^-$. The suitable structures of $Ln(TTA)_3 \cdot 12C4$ and $Ln(TTA)_3 \cdot 18C6$ showing the coordination of *CE* and TTA^- to Ln^{3+} ion as estimated from the above discussions are depicted in Fig. 6. These structures were optimized by MM2 calculations using SPARTAN software [22].

The stability of the adduct formed as indicated by the formation constant, β_{add}, increases in the following order: $B18C6 < 18C6 < C18C6$, for any lanthanoid ion. This order agrees with the increasing basicity of the crown ether oxygen. The cyclohexano-substituent in *C18C6* increases the electron density of the oxygen atoms of the polyethylene oxide, thus increases the stability of the adduct. The lower value of the adduct formation constant for *B18C6* compared with that of the unsubstituted *18C6* is attributable to the decrease in electron density of the donor oxygen atoms resulting from the electron-withdrawing effect of the benzo-substituent in *B18C6*. The same trend has been reported for the complex formation of potassium ions with various *CE*s in 1,2-dichloroethane [23]. The order of stability has also been explained by the change in the basicity of the oxygen atoms of the polyethylene oxide.

As seen from Table 1 and Fig. 5, the value of log β_{add} increases with the increase in ionic radii of *Ln*, although it shows a small decrease from Pr to La. This conforms to the reported entropy for the interaction of lanthanoid ions and *18C6*, *i.e.*, the ΔS for the formation of the 1:1 *Ln-18C6* complex increases with increasing ionic radii and eventually decreases from Pr [24]. This general trend might be primarily explained by size-fitting, *i.e.*, the increasing size of the Ln^{3+} ion approaches to the effective cavity size of the *18C6*. However, the increase in log β_{add} with increasing *Ln* ionic radii is also observed for the adduct formation with *12C4*. Thus, factors other than size-fitting may be responsible for this trend. One of these is the hydration energy of lanthanoid ions. In the extraction of Ln^{3+} ions into an organic phase with H*TTA*, the extracted neutral complex is in the hydrated form, $Ln(TTA)_3 \cdot nH_2O$ (where $n = 2$ or 3), to satisfy the coordination number of Ln^{3+} (8 or 9) [25]. These coordination water molecules are displaced by the formation of lipophilic adduct. The hydration energy decreases by the increase in ion size of Ln^{3+}. Thus, larger Ln^{3+} ions more favorably form the adduct with *CE*. The plots of log β_{add} (Fig. 5) for any *CE* also exhibit the so-called tetrad effect and the small decrease in the β_{add} from Pr^{3+} to La^{3+} may be explained by this effect.

The mono-adduct formation constants of $Tm(TTA)_3$ with the unidentate ligands tributylphosphate (*TBP*) and tri-*n*-octylphosphine oxide (*TOPO*) were reported as log $\beta_{add} = 5.2$ and 6.8, respectively [26]. These values are in the same magnitude for the $Tm(TTA)_3 \cdot CE$, even though the basicity of the *CE* is considerably lower than that of organophosphorus ligands. The enhanced β_{add} of the *CE* complexes can be explained by the multiple coordination of the oxygen atoms.

Experimental

Reagents

Nitrate solutions of the lanthanoids were prepared from their oxides by weighing appropriate amounts of each Ln_2O_3 (Shinetsu), dissolving it with 6 *M* HNO_3, evaporating the solution to dryness, and redissolving the residue with distilled water. The extractants 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (H*TTA*, Dojindo), 18-crown-6 (Aldrich), benzo-18-crown-6 (Aldrich), cyclohexano-18-crown-6 (Fluka), and 12-crown-4 (Aldrich) were used without further purification. 1,2-Dichloroethane (Nacalai Tesque, AR grade) was washed and pre-equilibrated twice with distilled water prior to use. All other reagents used were of analytical reagent grade.

Procedure

In the extraction of *Ln* with H*TTA*, aqueous solution (20 cm^3) containing a mixture of tervalent *Ln* and 1,2-dichloroethane solution (20 cm^3) containing 1.0×10^{-2} *M* H*TTA* were placed together in a centrifuge tube (50 cm^3). The initial concentration of each *Ln* was 5.0×10^{-7} *M* ($M = mol \cdot dm^{-3}$). The mixture was shaken for 30 min at 25.0 ± 0.1°C in a thermostated mechanical shaker (Taitek MM-10). This shaking time was sufficient enough to reach equilibrium. The *pH* of the aqueous solutions was adjusted from 4.0 to 5.5 by using acetic acid-potassium acetate buffer, and the ionic strength was maintained at 0.1 *M* with potassium nitrate. After phase separation through centrifugation (Kubota KN-70) for 10 min, the *pH* of the aqueous phase was measured by a *pH* meter (DKK PHL-40). The concentration of *Ln* remaining in the aqueous phases was determined with an inductively coupled plasma – mass spectrometer (HP4500 ICP-MS, Yokogawa Agilent). The concentration of *Ln* extracted into the organic phase was determined in the same manner as that in the aqueous phase after back-extraction of *Ln* into 0.1 *M* HNO_3.

In the synergistic extraction of *Ln*, the same procedure was followed as stated above. For the determination of number of TTA^- ions involved in the formed adduct, the aqueous phase with *pH* initially adjusted from 3.5 to 5.0 was shaken with an equal volume of organic phase containing 1.0×10^{-2} *M* H*TTA* and 3.0×10^{-4} *M CE*. For the determination of the chemical form of the adduct and its formation constant, an aqueous phase, the *pH* of which was adjusted to 4.9, was shaken with an equal volume of organic phase containing 1.0×10^{-2} *M* H*TTA* and various concentrations of crown ether (3.0×10^{-7}–1.0×10^{-3} *M*).

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