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Synergistic Effect of 18-Crown-6 Derivatives on Chelate Extraction of Lanthanoids(III) into an Ionic Liquid with 2-Thenoyltrifluoroacetone

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The synergistic effect of 18-crown-6 derivatives, such as 18-crown-6 (18C6), *cis*-dicyclohexano-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6), on the extraction of trivalent lanthanoids (Ln^{3+}) into an ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, with 2-thenoyltrifluoroacetone (Htta) was investigated. The extractability of lighter Ln^{3+} was enhanced by adding 18C6 or DC18C6, whereas no enhancement of the extractability was observed by adding DB18C6. Moreover, the synergistic effect by the crown ether (CE) was increased along with the decrease in the atomic number of Ln. In the synergistic extraction system, Ln^{3+} was extracted as cationic ternary complexes $Ln(tta)_2(CE)^+$ and $Ln(tta)(CE)^{2+}$, and it was suggested that the formation of the $Ln(tta)(CE)^{2+}$ complex as an extracted species results in the large synergistic effect. This synergistic effect originated in a size-fitting effect of CE on complexation to Ln^{3+}.

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Introduction

Solvent extraction methods have been widely applied to the separation of trivalent lanthanoids (Ln^{3+}) in the fields of analytical chemistry and nuclear technology. In spite of many studies, the mutual separation of Ln^{3+} is difficult due to their remarkable chemical similarity, *e.g.*, ionic diameter, electric charge in a solution and hardness as a Lewis acid. In chelate extraction, which is extensively studied in analytical chemistry, heavier lanthanoids generally show superior extractability compared to lighter ones due to their relatively strong electrostatic interaction ability.[1,2] Conversely, the extractive separation of the lighter ones from the heavier is very difficult. In order to improve the mutual separation ability on the extraction system, several studies have been investigated; it has been found that co-use of a neutral ligand as a synergist in a chelate extraction system often results in an enhancement not only of its extractability, but also of its extractive selectivity.[1-8] Especially, the use of a crown ether (CE), having a size-recognition ability on forming complexes with metal cations, as a synergist, has received much attention in the mutual extractive separation of Ln^{3+}.[6-8] Kitatsuji *et al*. reported a unique synergistic extraction system using 2-thenoyltrifluoroacetone (Htta) and 18-crown-6 (18C6) as extractants and 1,2-dichloroethane as an extraction solvent under the coexistence of a perchlorate anion (ClO_4^-), in which lighter Ln^{3+} is extracted selectively as ion-pair $Ln(tta)_2(18C6)^+\cdot ClO_4^-$.[8]

Recently, ionic liquids (ILs) have attracted increasing attention as an alternative to conventional organic solvents in a variety of synthetic,[9,10] catalytic,[10-14] electrochemical[15] and analytical applications.[16-19] They have unique properties such as negligible volatility and non-flammability. Their chemical and physical properties, such as viscosity, polarily and hydrophobicity, are tunable because they depend on the combination of a cation and an anion in the constituents of an IL.[20,21] Especially, hydrophobic ILs have potential as extraction solvents in solvent extraction. The extraction behavior and selectivity of metals in the IL solvent extraction systems may differ from conventional organic solvent systems because ILs have affinity to both neutral and ionic species.[22]

Many studies have investigated the possible use of an IL as an extraction solvent on the extraction of metal cations,[23-49] organic compounds[22,50,51] and biomolecules.[52,53] In the use of an IL for metal cation extraction, the IL shows remarkably high performance for the extraction of alkali metals,[23-27] alkaline earth metals,[25-30] transition metals[31-38] and lanthanoids.[39-46] Most studies on this IL extraction system consist of the ion-exchange process with the IL cation using neutral extractants, firstly reported by Dietz and Dzielawa.[29] They also reported the synergistic extraction of strontium ion into several imidazolium-

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type ILs, in which the extraction efficiency of the ion is enhanced by adding tri-*n*-butyl phosphate to the ILs containing *cis*-dicyclohexano-18-crown-6 (DC18C6).[27] Many IL extraction systems, however, have serious problems involving the recovery of the extracted metals and the solubility of the extractants into the extraction solvent. For these reasons, the use of an anionic (Brønsted acid-type) chelating agent as an extractant seems to be more favorable for practical applications, and several researchers have investigated the nature of this IL chelate extraction system.[33-35] However, the possible use of a synergist in the IL chelate extraction system has not been investigated.

Recently, we reported a novel IL synergistic cation-exchange system for the extractive separation of La^{3+} from Eu^{3+} and Lu^{3+} using Htta as a chelating agent, 18C6 as a synergist and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide ([bmim][Tf_2N]) as an IL extraction solvent.[41] As shown in the rapid communication, La^{3+} was effectively extracted as cationic ternary complexes, whereas the extractability of Eu^{3+} and Lu^{3+} was not enhanced by adding 18C6. Based on these results, in the present study, we performed a detailed investigation concerning the synergistic effect in the Htta-CE IL cation-exchange systems with using 18-crown-6 derivatives including 18C6, DC18C6 and dibenzo-18-crown-6 (DB18C6), and 15-crown-5 (15C5). Being more concrete, the extraction behavior of all trivalent lanthanoids (except Pm^{3+}) in the systems was studied, and the synergistic effect by using CE, possible extraction equilibria and the possible mechanism of extraction enhancement were discussed.

Experimental

Reagents

The extractant Htta (Dojindo Laboratories) and the CEs, DC18C6 (a mixture of the *cis-syn-cis* and *cis-anti-cis* isomers), 18C6, DB18C6 (Kanto Chemical Co.) and 15C5 (Aldrich Chemical Co.), were used without further purification. All other chemicals were of analytical or guaranteed reagent-grade, and were used as received. Ionic liquid [bmim][Tf_2N] was synthesized according to a published method.[54] Distilled deionized water (18 MΩ) was used throughout.

Apparatus

A Jasco U-570 UV/VIS/NIR spectrophotometer and a Hewlett Packard HP 4500 inductively coupled plasma mass spectrometer were used for the determination of the concentration of Ln^{3+} in aqueous solutions. A Horiba Model F-52 pH meter equipped with a Horiba 9611-10D combined glass electrode was used to determine the pH values.

Distribution of the lanthanoids(III)

In a centrifuge tube, an aliquot (1 cm^3) of [bmim][Tf_2N] containing 1×10^{-2} mol dm^{-3} of Htta and a CE (18C6, DC18C6, DB18C6 or 15C5) and an aqueous phase (5 cm^3) containing 1×10^{-5} – 1×10^{-4} mol dm^{-3} of Ln^{3+}, 1×10^{-1} mol dm^{-3} of lithium chloride and 1×10^{-2} mol dm^{-3} of acetate buffer were shaken mechanically at 25 ± 1°C for 30 – 90 min to reach equilibration. After the two phases were separated by centrifugation, the pH value in the aqueous phase was measured. The Ln^{3+} concentration in the aqueous phase and that in the extraction phase (after back-extraction into hydrochloric or nitric acid solution) were determined by a spectrophotometric method using Arsenazo III[55] or inductively coupled plasma mass spectrometry. All extraction experiments were performed with a single species of Ln^{3+}. The percent extraction (*%E*) of the Ln^{3+} was calculated as $100 \times [Ln(III)]_e V_e/([Ln^{3+}]_{aq,ini} V_{aq})$ and the distribution ratio (*D*) was calculated as $[Ln(III)]_e/[Ln^{3+}]_{aq}$, where *V* denotes the volume and the subscripts e, aq and ini denote the extraction phase, the aqueous phase and the initial condition, respectively.

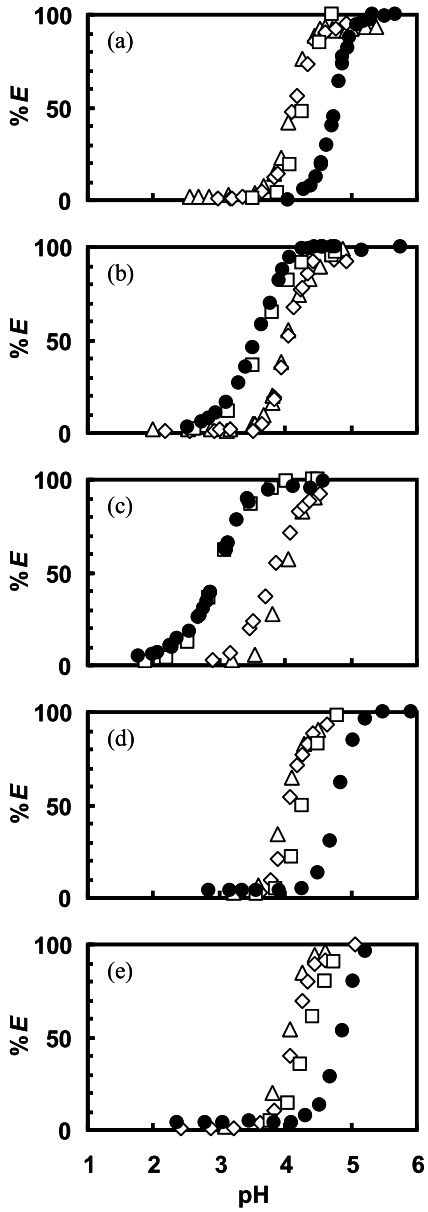

Fig. 1 Plots of *%E* for several trivalent lanthanoids (Ln^{3+}) into the [bmim][Tf_2N] phase as a function of the aqueous phase pH in the Htta alone (a), Htta-18C6 (b), Htta-DC18C6 (c), Htta-DB18C6 (d) and Htta-15C5 (e) systems. The initial Htta and CE concentrations in the [bmim][Tf_2N] phase were 1×10^{-2} mol dm^{-3}. The initial Ln^{3+} concentration in the aqueous phase was 1×10^{-4} mol dm^{-3}. ●, La^{3+}; □, Nd^{3+}; ◇, Eu^{3+}; △, Lu^{3+}.

Results and Discussion

Extraction behavior of Ln^{3+}

The *%E* values of several Ln^{3+} (La^{3+}, Nd^{3+}, Eu^{3+} and Lu^{3+}) into the [bmim][Tf_2N] phase with Htta alone, Htta and 18C6, Htta and DC18C6, Htta and DB18C6, and Htta and 15C5 are plotted

Table 1 Obtained $pH_{D=1}$ and $\Delta pH_{D=1}$ values and their standard errors for the extraction of trivalent lanthanoids (Ln^{3+}) into the [bmim][Tf_2N] phase

Ln	Htta alone	Htta-18C6		Htta-DC18C6		Htta-DB18C6		Htta-15C5	
	$pH_{D=1}$	$pH_{D=1}$	$\Delta pH_{D=1}$[a]	$pH_{D=1}$	$\Delta pH_{D=1}$	$pH_{D=1}$	$\Delta pH_{D=1}$	$pH_{D=1}$	$\Delta pH_{D=1}$
La	4.54 ± 0.19	3.15 ± 0.12	1.39 ± 0.23	2.49 ± 0.21	2.05 ± 0.28	4.54 ± 0.07	0.00 ± 0.20	4.58 ± 0.14	–0.05 ± 0.24
Ce	4.27 ± 0.03	2.91 ± 0.18	1.36 ± 0.18	2.35 ± 0.10	1.92 ± 0.11	4.30 ± 0.05	–0.03 ± 0.06	4.26 ± 0.17	0.01 ± 0.17
Pr	4.12 ± 0.27	2.96 ± 0.14	1.16 ± 0.30	2.37 ± 0.09	1.75 ± 0.28	4.12 ± 0.13	0.00 ± 0.30	4.12 ± 0.11	0.00 ± 0.29
Nd	4.05 ± 0.02	3.26 ± 0.01	0.79 ± 0.02	2.60 ± 0.02	1.46 ± 0.02	4.05 ± 0.07	0.01 ± 0.07	4.07 ± 0.09	–0.02 ± 0.09
Pm	—	—	—	—	—	—	—	—	—
Sm	3.94 ± 0.22	3.67 ± 0.11	0.26 ± 0.25	3.03 ± 0.08	0.90 ± 0.24	3.86 ± 0.26	0.07 ± 0.34	3.87 ± 0.04	0.06 ± 0.23
Eu	3.88 ± 0.26	3.79 ± 0.14	0.09 ± 0.30	3.41 ± 0.15	0.47 ± 0.30	3.84 ± 0.11	0.04 ± 0.28	3.91 ± 0.09	–0.03 ± 0.28
Gd	3.93 ± 0.18	3.92 ± 0.21	0.01 ± 0.27	3.74 ± 0.07	0.19 ± 0.19	3.88 ± 0.08	0.05 ± 0.20	3.86 ± 0.18	0.07 ± 0.26
Tb	3.82 ± 0.18	3.64 ± 0.14	0.18 ± 0.23	3.71 ± 0.07	0.11 ± 0.19	3.79 ± 0.07	0.03 ± 0.19	3.79 ± 0.08	0.03 ± 0.20
Dy	3.77 ± 0.03	3.73 ± 0.12	0.04 ± 0.12	3.66 ± 0.08	0.11 ± 0.09	3.65 ± 0.09	0.12 ± 0.09	3.74 ± 0.05	0.03 ± 0.06
Ho	3.79 ± 0.09	3.70 ± 0.04	0.09 ± 0.10	3.69 ± 0.07	0.10 ± 0.11	3.76 ± 0.09	0.03 ± 0.12	3.75 ± 0.18	0.04 ± 0.20
Er	3.77 ± 0.05	3.66 ± 0.19	0.11 ± 0.20	3.68 ± 0.18	0.09 ± 0.19	3.70 ± 0.04	0.07 ± 0.06	3.72 ± 0.10	0.05 ± 0.11
Tm	3.70 ± 0.10	3.69 ± 0.09	0.02 ± 0.13	3.64 ± 0.11	0.06 ± 0.15	3.67 ± 0.08	0.03 ± 0.13	3.68 ± 0.12	0.02 ± 0.16
Yb	3.75 ± 0.10	3.68 ± 0.19	0.06 ± 0.22	3.69 ± 0.19	0.06 ± 0.21	3.70 ± 0.16	0.05 ± 0.19	3.68 ± 0.12	0.07 ± 0.15
Lu	3.81 ± 0.07	3.75 ± 0.09	0.07 ± 0.12	3.66 ± 0.27	0.16 ± 0.27	3.75 ± 0.18	0.06 ± 0.20	3.76 ± 0.03	0.05 ± 0.08

The initial Htta and CE concentrations in the [bmim][Tf_2N] phase were 1×10^{-2} mol dm^{-3}. The initial Ln^{3+} concentration in the aqueous phase was 1×10^{-4} mol dm^{-3}. a. $\Delta pH_{D=1} = pH_{D=1}$ (Htta alone) – $pH_{D=1}$ (Htta-CE).

as a function of the aqueous phase pH in Fig. 1 as examples. The extracted Ln^{3+} was back-extracted into acid solutions quantitatively. In addition, all of the Ln^{3+} was hardly extracted into the [bmim][Tf_2N] phase in extractant-free and in the CE alone systems ($D < 10^{-2.5}$). In the Htta alone system, Nd^{3+}, Eu^{3+} and Lu^{3+} were extracted in low-pH region, whereas light lanthanoid La^{3+} was extracted in a relatively high-pH region. In the Htta-18C6 and the Htta-DC18C6 systems, on the contrary, the extractability of La^{3+} and Nd^{3+} was enhanced compared to that in the Htta alone system, whereas the extraction behavior of middle lanthanoid Eu^{3+} and heavy lanthanoid Lu^{3+} was hardly changed, except that the extractability of Eu^{3+} was slightly enhanced in the Htta-DC18C6 system. In comparison between 18C6 and DC18C6 as a synergist, the latter was more effective for the extraction of La^{3+} and Nd^{3+} because of its high hydrophobicity and Lewis basicity than 18C6. However, the extraction behavior of Ln^{3+} was hardly changed in the Htta-DB18C6 and the Htta-15C5 systems.

Synergistic effect by using CE

In order to research the synergistic effect of CEs in detail, the pH values ($pH_{D=1}$) at which D is 1 (%E = 17%) in the Htta alone system and the four Htta-CE systems were determined under a fixed extractant concentration (1×10^{-2} mol dm^{-3}), and the values of $\Delta pH_{D=1}$ in the Htta-CE systems (defined as $pH_{D=1}$ (Htta alone) – $pH_{D=1}$ (Htta-CE)) were calculated. The obtained $pH_{D=1}$ and $\Delta pH_{D=1}$ values are listed with their standard errors in Table 1. In the Htta alone system, the $pH_{D=1}$ values lowered with an increase in the atomic number from La^{3+} to Sm^{3+}, and the middle and heavier Ln^{3+} (Sm^{3+} – Lu^{3+}) showed similar $pH_{D=1}$ values. On the contrary, the $pH_{D=1}$ values for lighter Ln^{3+} from La^{3+} to Nd^{3+} in the Htta-18C6 system and lighter and middle Ln^{3+} from La^{3+} to Eu^{3+} in the Htta-DC18C6 system lowered compared to those in the Htta alone system. The values of $\Delta pH_{D=1}$ for Ln^{3+} increased along with the decrease in the atomic number. Namely, the highest value of $\Delta pH_{D=1}$ was obtained for La^{3+} in both the Htta-18C6 and the Htta-DC18C6 systems. As a result, the extraction selectivity order between lighter Ln^{3+} and heavier ones was inverted by adding 18C6 or DC18C6. On the contrary, no enhancement of the extractability for Ln^{3+} by adding CE was observed when using the Htta-DB18C6 ($|\Delta pH_{D=1}| < 0.12$) and the Htta-15C5 ($|\Delta pH_{D=1}| < 0.07$) systems. The order of the synergistic effect by adding CE was DC18C6 > 18C6 >> DB18C6 = 15C5.

Extracted species and extraction mechanism

In IL extraction systems, as mentioned above, not only neutral complexes, but also positively or negatively charged complexes, can be extracted into the IL phase competitively. In these Ln^{3+}-extraction systems, therefore, a variety of possible extracted species, abbreviated as $Ln(tta)_x(CE)_y^{(3-x)+}$, should be considered. In this case, the following extraction equilibria can be considered:

(i) Cationic complexes ($x < 3$):

$$Ln^{3+} + x\mathrm{Htta}_{(e)} + y\mathrm{CE}_{(e)} + (3 - x)\mathrm{bmim}^+_{(e)} \rightleftharpoons Ln(tta)_x(CE)_y^{(3-x)+}{}_{(e)} + x\mathrm{H}^+ + (3 - x)\mathrm{bmim}^+ \quad (1)$$

(ii) Neutral complexes ($x = 3$):

$$Ln^{3+} + 3\mathrm{Htta}_{(e)} + y\mathrm{CE}_{(e)} \rightleftharpoons Ln(tta)_3(CE)_{y(e)} + 3\mathrm{H}^+ \quad (2)$$

(iii) Anionic complexes ($x > 3$):

$$Ln^{3+} + x\mathrm{Htta}_{(e)} + y\mathrm{CE}_{(e)} + (x - 3)\mathrm{Tf_2N}^-_{(e)} \rightleftharpoons Ln(tta)_x(CE)_y^{(x-3)-}{}_{(e)} + x\mathrm{H}^+ + (x - 3)\mathrm{Tf_2N}^- \quad (3)$$

where the subscript (e) shows the extraction phase. In the Htta alone system, as reported previously,[39–41] Ln^{3+} was extracted as neutral $Ln(tta)_3$ ($x = 3$, $y = 0$) and anionic $Ln(tta)_4^-$ ($x = 4$, $y = 0$) competitively. In the Htta-18C6 system,[41] furthermore, La^{3+} was extracted as cationic $La(tta)_2(18C6)^+$ ($x = 2$, $y = 1$) and $La(tta)(18C6)^{2+}$ ($x = 1$, $y = 1$), and the former was the predominant species.

To determine the x and y values for La^{3+}, Nd^{3+} and Eu^{3+} in the Htta-DC18C6 system, the relationships between log D for Ln^{3+} and the logarithmic initial Htta concentration in the [bmim][Tf_2N] phase (log C_e(Htta)) and the logarithmic initial DC18C6 concentration in the [bmim][Tf_2N] phase (log C_e(DC18C6)) were investigated. These plots are shown in Fig. 2. For La^{3+} and Nd^{3+}, the slope of the log D *vs.* log C_e(Htta) plots increased from *ca.* 1 to 2 along with an increase in

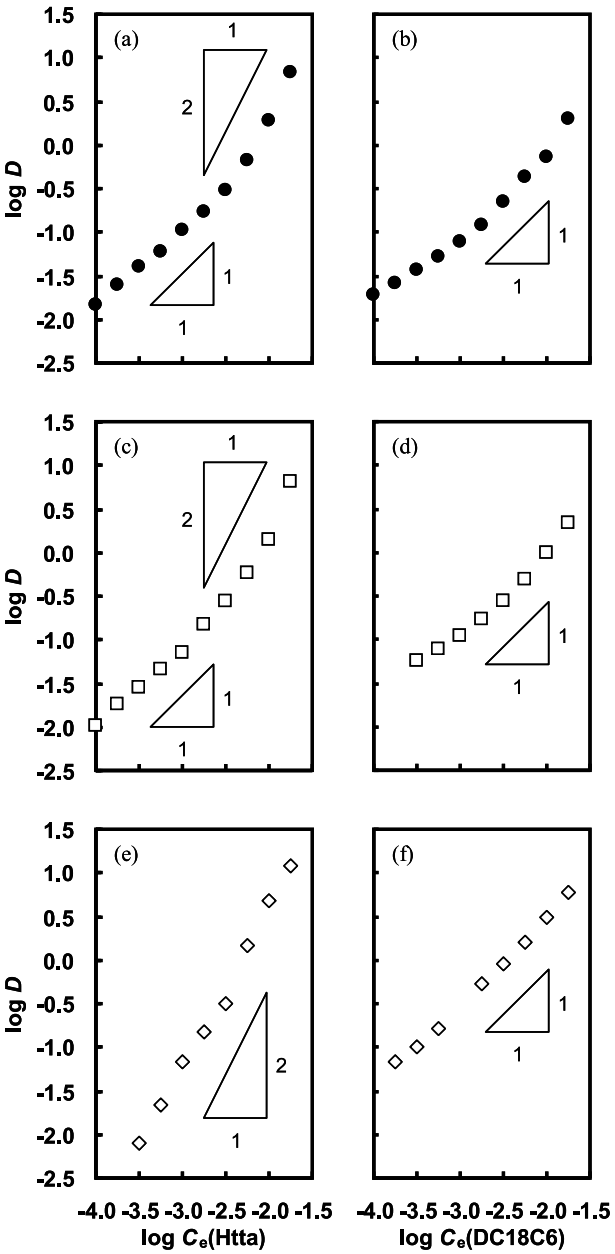

Fig. 2 Plots of log D for La^{3+} ((a) and (b), ●), Nd^{3+} ((c) and (d), □), and Eu^{3+} ((e) and (f), ◇) into the [bmim][Tf_2N] phase in the Htta-DC18C6 system as a function of log C_e(Htta) ((a), (c) and (e)) and those as that of log C_e(DC18C6) ((b), (d) and (f)). The initial DC18C6 concentration in the [bmim][Tf_2N] phase was 1×10^{-2} mol dm^{-3} on (a), (c) and (e), the initial Htta concentration in the [bmim][Tf_2N] phase was 1×10^{-2} mol dm^{-3} on (b), (d) and (f), and the aqueous phase pH was 3.0, 2.8, 2.8, 2.7, 3.3 and 3.2 for (a) – (f), respectively. The initial Ln^{3+} concentration in the aqueous phase was 1×10^{-5} mol dm^{-3}.

log C_e(Htta), and that of the log D *vs.* log C_e(DC18C6) plots increased to *ca.* 1 along with an increase in log C_e(DC18C6) up to C_e(DC18C6) = 1×10^{-2} mol dm^{-3}. From these results, it was found that cationic $Ln(tta)(DC18C6)^{2+}$ ($x = 1$, $y = 1$) and $Ln(tta)_2(DC18C6)^+$ ($x = 2$, $y = 1$) for La^{3+} and Nd^{3+} can be extracted competitively as ternary complexes at C_e(DC18C6) $\leq 1 \times 10^{-2}$ mol dm^{-3}. For Eu^{3+}, on the contrary, the log D *vs.* log C_e(Htta) plots showed a straight line with a slope of *ca.* 2, whereas the log D *vs.* log C_e(DC18C6) plots were similar to that for La^{3+} and Nd^{3+}, showing that only cationic $Eu(tta)_2(DC18C6)^+$ ($x = 2$, $y = 1$) was extracted as a ternary complex (interestingly, it was also found that neutral ternary complexes $Ln(tta)_3(DC18C6)_n$ are not also extracted in the Htta-DC18C6 system). From the above-mentioned results, in the Htta-CE systems, it was suggested that the formation of the $Ln(tta)(CE)^{2+}$ ($x = 1$, $y = 1$) ternary complex as an extracted species results in a large $\Delta pH_{D=1}$ value.

Possible mechanism of synergistic effect by using CE

As mentioned above, lighter Ln^{3+} showed a remarkable synergistic effect upon co-using DC18C6 or 18C6 as a synergist. Furthermore, it was found that one CE molecule coordinates to Ln^{3+} in the cationic ternary complexes as extracted species. These facts indicate that a size-fitting effect of 18C6 (cavity diameter = 0.268 – 0.286 nm)[56] or DC18C6 on complexation to lighter Ln^{3+} (ionic diameter = 0.243 nm for La^{3+} at the coordination number 9)[57] would contribute to an extraction enhancement. In fact, the co-use of 15C5, having a relatively small cavity diameter (0.172 – 0.184 nm),[56] resulted in no extraction enhancement. Therefore, it was suggested that Ln^{3+} in the cationic ternary complexes exists at the center of the CE cavity, and that 1 or 2 molecules of tta^- coordinate to the Ln^{3+} toward the axial direction. In addition, no effect on co-using DB18C6 seems to originate in a loss of flexibility by introducing an aromatic structure onto the 18-membered ring. Actually, the use of DB18C6 in the 1,2-dichloroethane system resulted in a slight synergistic effect (data not shown).

In the ion-exchange extraction of cationic complexes into ILs, low-charged and/or hydrophobic ones are preferable to be extracted. Namely, the complexation of tta^- to $Ln(CE)^{3+}$ seems to result in an enhancement of the cation-exchange extraction. Moreover, when $Ln(CE)^{3+}$ itself has high stability and suitable hydrophobicity, it is expected that not only monocationic $Ln(tta)_2(CE)^+$, but also dicationic $Ln(tta)(CE)^{2+}$ can be extracted into the IL phase, resulting in a large synergistic effect. The latter complex is favorable in the low tta^- concentration and pH regions. The actual extraction behavior mentioned above agrees with the hypothesis.

Conclusion

The synergistic effect of CEs on the extraction of trivalent lanthanoids using an IL, [bmim][Tf_2N], as an extraction solvent was investigated. The IL chelate extraction system using Htta together with CE, such as 18C6 and DC18C6, resulted in an enhancement of the extractability for lighter Ln^{3+}, whereas the extraction behavior of heavier ones was hardly changed. In the synergistic extraction system, an extraction enhancement originated in the conversion of the extracted species from neutral or anionic complex to cationic ternary complexes, $Ln(tta)_2(CE)^+$ and $Ln(tta)(CE)^{2+}$, also the formation of the dicationic $Ln(tta)(CE)^{2+}$ as the extracted species results in a large synergistic effect. Furthermore, the synergistic effect depended on the size-fitting ability of Ln^{3+} into the cavity of CE. Thus, the structure of the cationic complexes could be estimated to show that Ln^{3+} exists inside the cavity of CE.

In cation-exchange extraction with using imidazolium-type ILs (1-alkyl-3-methylimidazolium salts), it is well known that the use of the IL having a relatively short 1-alkyl chain results in an enhancement of the extraction efficiency for cationic species.[29] Therefore, it is expected that the use of such IL, *e.g.*, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide, as an extraction solvent results in the development of a more selective extraction system for lighter Ln^{3+}.

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