Synergistic Extraction Equilibrium of Lanthanide(III) Ions with Benzoylacetone and a Neutral Ligand in an Ionic Liquid

Mizuki HATAKEYAMA¹, Yoshio NISHIYAMA^{1,*}, Hirohisa NAGATANI¹,
Hiroyuki OKAMURA² and Hisanori IMURA^{1,*}

¹*Division of Material Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan;* ²*Advance Science Research Center, Japan Atomic Energy Agency (JAEA), 2-4, Shirakawa, Tokai-mura, Ibaraki 319-1195, Japan*

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The synergistic extraction of trivalent lanthanide ions (Ln(III)) with benzoylacetone (Hba) and trioctylphosphine oxide (TOPO) in an ionic liquid (IL), 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][Tf₂N]), has been investigated. The extractability of Ln(III) with Hba was significantly enhanced in the presence of TOPO. The composition and extraction constants of the extracted species for each Ln(III) in the presence or absence of TOPO were determined by 3-dimensional equilibrium analysis. It was found that all Ln(III) were extracted as cationic ternary complexes such as Ln(ba)₂(TOPO)₂⁺ or Ln(ba)(TOPO)₄²⁺ with Hba and TOPO, while Ln(III) was extracted as a neutral or cationic species such as Ln(ba)₃ or Ln(ba)₂⁺ with Hba alone. The formation constants of the cationic ternary complexes in the IL were calculated from the corresponding extraction constants obtained, indicating that Lu(ba)(TOPO)₄²⁺ is the most stable complex in the IL. Separation efficiency between different Ln(III) was also discussed on the basis of the extraction constants. The result demonstrated that the Hba-TOPO-[Bmim][Tf₂N] system presented here is superior in the separation between heavier Ln(III).

1. Introduction

Ionic liquids (ILs) have attracted much attentions as alternative extraction solvents to conventional organic solvents in solvent extraction [1]. ILs are classified into novel types of molten salts that are liquids at below 100 °C [2]. They have unique properties such as low vapor pressure, low flammability, and moderate electric conductivity that are advantageous for a variety of synthetic, catalytic, electrochemical and analytical applications. In the field of solvent extraction, ILs of an ionic nature act as not only extraction solvents but also ion-exchangers that allow for the extraction of charged species into the IL phase. Jensen et al. reported that neodymium(III) and europium(III) were extracted as not only neutral species but also anionic species in a water-IL system with a β-diketone [3]. Due to the unique extraction behavior, the IL system has the potential to achieve separation among chemical species that are not separable with conventional organic solvent systems.

Trivalent lanthanide ions (Ln(III)) are difficult to be separated mutually due to their remarkable chemical similarity, e.g. ionic diameter, coordination number, hydrolysis behavior in solution, and hardness as Lewis acids. We investigated the synergistic extraction of Ln(III) with β-diketones and several neutral

ligands in a water-IL system [4-6]. The synergistic enhancement of the extractability depends largely on the type of the neutral ligand, e.g. selective extraction of lighter Ln(III) was achieved with 18-crown-6 as a synergist [5] while heavier Ln(III) were extracted selectively with trioctylphosphine oxide (TOPO) as a synergist [6]. It was also found that the separation efficiency of Ln(III) varied with the acidity of the β -diketones using as the extractants, e.g. the separation factor between Eu(III) and Lu(III) in the synergistic extraction system using benzoylacetone (Hba) with a higher pK_a is significantly larger than those with other β -diketones [6]. Although synergistic extraction of Ln(III) in ILs has been investigated by a variety of groups [7-10], comprehensive understanding of the unique extraction mechanism in ILs has not yet been achieved. For that purpose, it is quite important to identify the extracted species and determine their extraction constants because all types of neutral and charged complexes may be extracted into ILs.

In the present paper, the composition and extraction constants of Ln(III) species in the chelate extraction with Hba alone and the synergistic extraction with Hba and TOPO in an ionic liquid 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][Tf₂N]) were determined by 3-dimensional (3D) equilibrium analysis. The formation constants of the adducts or ternary complexes of Ln(III) with ba⁻ and TOPO in IL as well as the separation factors between Ln(III) were determined using the extraction constants obtained in order to characterize the IL extraction systems.

2. Experimental

2.1 Reagents

Hba (Wako, 99% purity), acetylacetone (abbreviated as Hacac, SIGMA-ALDRICH, 98% purity), dibenzoylmethane (abbreviated as Hdbm, Nakalai, guaranteed grade), and TOPO (SIGMA-ALDRICH, 98.5% purity) were used without further purification. All other chemicals used were of analytical or guaranteed reagent-grade, and were used as received. [Bmim][Tf₂N] was synthesized and purified in the same manner as previously reported [11].

2.2 Apparatus

A high speed shaker (ASONE, ASCM-1) was used for the agitation of the aqueous and ionic liquid phase. A pH meter (HORIBA, F-71) equipped with a micro glass combined electrode (HORIBA, 9618-10D) was calibrated with standard pH buffer solutions. An inductively coupled plasma mass spectrometer (ICP-MS, Seiko Instruments SPQ 9000) was used for the determination of Ln(III) in aqueous solutions. A Milli-Q system (Millipore, Direct-Q3UV) was used for preparation of high purity water (18.2 M Ω).

2.3 Extraction procedure

An aliquot (0.7 cm³) of an aqueous phase containing $(0.50 - 3.0) \times 10^{-5}$ mol dm⁻³ Ln(III), 1.0×10^{-1} mol dm⁻³ NaCl, and 1.0×10^{-2} mol dm⁻³ pH buffer (sulfanilic acid, acetic acid, MES, and HEPES) and an aliquot (0.7 cm³) of an IL phase containing $(0.010 - 1.0) \times 10^{-1}$ mol dm⁻³ β -diketone and $(0.10 - 1.0) \times 10^{-2}$ mol dm⁻³ TOPO were shaken mechanically at 25 °C. The shaking time was 1 h for La(III), Nd(III), and Eu(III) and 2 h for Dy(III) and Lu(III). After the two phases were separated by centrifugation, the pH in the aqueous phase was measured. The metal concentration in the aqueous and the IL phase (after back-extraction into an equal volume of 0.1 mol dm⁻³ hydrochloric acid solution by shaking for 2 h) was determined by ICP-MS. The extraction percentage (%*E*) and distribution ratio (*D*) were calculated from the concentrations of Ln(III) in both phases.

To determine the distribution constant of Hba, an aliquot (1.0 cm³) of the IL phase containing (0.10 – 1.0) × 10⁻² mol dm⁻³ Hba and an aliquot (5.0 cm³) of the aqueous phase containing 1.0 × 10⁻¹ mol dm⁻³ NaCl and 5.0 × 10⁻³ mol dm⁻³ pH buffers (monochloroacetic acid, sodium dihydrogenphosphate, CHES, and CAPS) were shaken mechanically for 1 h at 25 °C. The pH of the aqueous phase was adjusted to 1 – 12 with 1.0 × 10⁻¹ mol dm⁻³ HCl and 1.0 × 10⁻¹ mol dm⁻³ NaOH. After the two phases were separated by centrifugation, the pH value of the aqueous phase was measured and diluted 1.25 times with 1.0 × 10⁻¹ mol dm⁻³ HCl and 1.0 × 10⁻¹ mol dm⁻³ NaCl. Then the absorbance of the solution at pH < 2 was measured at 310 nm. The concentration of Hba in the aqueous phase was determined from the absorbance measured and the molar absorption coefficient of Hba determined separately as 5.0 × 10³ dm³ mol⁻¹ cm⁻¹. The distribution ratio of Hba was calculated according to the following equation.

$$D_{\text{HA}} = \frac{c_{\text{HA}} V_{\text{IL}} - c_{\text{aq}} V}{c_{\text{aq}} V_{\text{IL}}}, \quad (1)$$

where c_{HA} , c_{aq} , V , and V_{IL} are the initial concentration of Hba, the total concentration of Hba in the aqueous phase, the volumes of the aqueous phase, and the volumes of the IL phase, respectively.

3. Theoretical background for extraction equilibrium analysis

As mentioned above, Ln(III) can be extracted as not only neutral species but also cationic and anionic species into the IL phase. To identify the extracted species, the experimental distribution ratio data was analyzed according to the following extraction equilibria. In the extraction with Hba alone, the extraction equilibria and the extraction constants are expressed as follows.

For neutral species,

$$K_{\text{ex},3} = \frac{[\text{Ln}(\text{ba})_3]_{\text{IL}} [\text{H}^+]^3}{[\text{Ln}^{3+}] [\text{Hba}]_{\text{IL}}^3}. \quad (3)$$

For cationic species ($m < 3$),

$$K_{\text{ex},m} = \frac{[\text{Ln}(\text{ba})_m^{(3-m)+}]_{\text{IL}} [\text{H}^+]^m [\text{Bmim}^+]_{\text{IL}}^{(3-m)}}{[\text{Ln}^{3+}] [\text{Hba}]_{\text{IL}}^m [\text{Bmim}^+]_{\text{IL}}^{(3-m)}}. \quad (5)$$

For anionic species ($m > 3$),

$$K_{\text{ex},m} = \frac{[\text{Ln}(\text{ba})_m^{(m-3)-}]_{\text{IL}} [\text{H}^+]^m [\text{Tf}_2\text{N}^-]_{\text{IL}}^{(m-3)}}{[\text{Ln}^{3+}] [\text{Hba}]_{\text{IL}}^m [\text{Tf}_2\text{N}^-]_{\text{IL}}^{(m-3)}}, \quad (7)$$

where the subscript IL denotes the IL phase. Here, $[\text{Bmim}^+]$, $[\text{Bmim}^+]_{\text{IL}}$, $[\text{Tf}_2\text{N}^-]$, and $[\text{Tf}_2\text{N}^-]_{\text{IL}}$ can be

regarded as a constant. Thus, the following apparent equilibrium constants were derived from Eqs. (5) and (7):

$$K'_{\text{ex},m} = \frac{K_{\text{ex},m} [\text{Bmim}^+]_{\text{IL}}^{(3-m)}}{[\text{Bmim}^+]_{\text{IL}}^{(3-m)}} = \frac{[\text{Ln}(\text{ba})_m^{(3-m)+}]_{\text{IL}} [\text{H}^+]^m}{[\text{Ln}^{3+}] [\text{Hba}]_{\text{IL}}^m} \quad (m < 3) \quad (8)$$

$$K'_{\text{ex},m} = \frac{K_{\text{ex},m} [\text{Tf}_2\text{N}^-]_{\text{IL}}^{(m-3)}}{[\text{Tf}_2\text{N}^-]_{\text{IL}}^{(m-3)}} = \frac{[\text{Ln}(\text{ba})_m^{(m-3)-}]_{\text{IL}} [\text{H}^+]^m}{[\text{Ln}^{3+}] [\text{Hba}]_{\text{IL}}^m} \quad (m > 3). \quad (9)$$

From Eqs. (3), (8), and (9), when the amount of Ln-ba complexes in the aqueous phase is negligible, the distribution ratio of Ln(III) between the two phases that was determined experimentally is expressed as follows.

$$D = \frac{\sum_{m<3} [\text{Ln}(\text{ba})_m^{(3-m)+}]_{\text{IL}} + [\text{Ln}(\text{ba})_3]_{\text{IL}} + \sum_{m>3} [\text{Ln}(\text{ba})_m^{(m-3)-}]_{\text{IL}}}{[\text{Ln}^{3+}]} \\ = \sum_{m<3} \frac{[\text{ba}^-]^m K'_{\text{ex},m} K_{\text{D,HA}}^m}{K_a^m} + \frac{[\text{ba}^-]^3 K_{\text{ex},3} K_{\text{D,HA}}^3}{K_a^3} + \sum_{m>3} \frac{[\text{ba}^-]^m K'_{\text{ex},m} K_{\text{D,HA}}^m}{K_a^m}, \quad (10)$$

where $[\text{ba}^-]$, $K_{\text{D,HA}}$, and K_a represent the concentration of ba^- in the aqueous phase, the distribution constant of Hba between the two phases, and the acid dissociation constant of Hba in the aqueous phase, respectively. $K_{\text{D,HA}}$ and K_a are given by

$$K_{\text{D,HA}} = \frac{[\text{Hba}]_{\text{IL}}}{[\text{Hba}]} \quad (11)$$

$$K_a = \frac{[\text{ba}^-][\text{H}^+]}{[\text{Hba}]} \quad (12)$$

The concentration of ba^- in the aqueous phase is calculated by the following equation:

$$[\text{ba}^-] = \frac{c_{\text{HA}} K_a}{(K_{\text{D,HA}} + 1)[\text{H}^+] + (K_{\text{D,A}} + 1)K_a}, \quad (13)$$

where c_{HA} is the initial concentration of Hba in the IL phase, and $K_{\text{D,A}}$ is the apparent distribution constant of ba^- that is given by

$$K_{\text{D,A}} = \frac{[\text{ba}^-]_{\text{IL}}}{[\text{ba}^-]}. \quad (14)$$

Actually, the ba^- transfers between the aqueous and IL phases by ion exchange with Tf_2N^- can affect $[\text{Tf}_2\text{N}^-]$. However, under the present conditions where $[\text{ba}^-]$ (at most $1.6 \times 10^{-3} \text{ mol dm}^{-3}$) is much smaller than $[\text{Tf}_2\text{N}^-]$ ($1.6 \times 10^{-2} \text{ mol dm}^{-3}$ [12]), ion exchange between ba^- and Tf_2N^- hardly affect $[\text{Tf}_2\text{N}^-]$ and thus $K_{\text{D,A}}$ can be regarded as a constant. Similarly, the extraction of Ln(III) with Hba and TOPO is expressed as follows.

For neutral species,

$$K_{\text{ex},s3n} = \frac{[\text{Ln}(\text{ba})_3(\text{TOPO})_{n(\text{IL})}]_{\text{IL}} [\text{H}^+]^3}{[\text{Ln}^{3+}] [\text{Hba}]_{\text{IL}}^3 [\text{TOPO}]_{\text{IL}}^n}. \quad (16)$$

For cationic species ($m < 3$),

$$K'_{\text{ex},smn} = \frac{[\text{Ln}(\text{ba})_m(\text{TOPO})_n^{(3-m)+}]_{\text{IL}} [\text{H}^+]^m}{[\text{Ln}^{3+}] [\text{Hba}]_{\text{IL}}^m [\text{TOPO}]_{\text{IL}}^n} \quad (18)$$

For anionic species ($m > 3$),

$$K'_{\text{ex},smn} = \frac{[\text{Ln}(\text{ba})_m(\text{TOPO})_n^{(m-3)-}]_{\text{IL}} [\text{H}^+]^m}{[\text{Ln}^{3+}] [\text{Hba}]_{\text{IL}}^m [\text{TOPO}]_{\text{IL}}^n} \quad (20)$$

The distribution ratio between both phases in the synergistic extraction is expressed as

$$D = \frac{\sum_{m<3} \sum_n [\text{Ln}(\text{ba})_m(\text{TOPO})_n^{(3-m)+}]_{\text{IL}} + \sum_n [\text{Ln}(\text{ba})_3(\text{TOPO})_n]_{\text{IL}} + \sum_{m>3} \sum_n [\text{Ln}(\text{ba})_m(\text{TOPO})_n^{(m-3)-}]_{\text{IL}}}{[\text{Ln}^{3+}]} \\ = \sum_{m<3} \sum_n \frac{[\text{ba}^-]^m [\text{TOPO}]_{\text{IL}}^n K'_{\text{ex},smn} K_{\text{D,HA}}^m}{K_{\text{a}}^m} + \sum_n \frac{[\text{ba}^-]^3 [\text{TOPO}]_{\text{IL}}^n K'_{\text{ex},s3n} K_{\text{D,HA}}^3}{K_{\text{a}}^3} \\ + \sum_{m>3} \sum_n \frac{[\text{ba}^-]^m [\text{TOPO}]_{\text{IL}}^n K'_{\text{ex},smn} K_{\text{D,HA}}^m}{K_{\text{a}}^m} \quad (21)$$

4. Results and Discussion

4.1 Extraction behavior of Ln(III) with β -diketones and TOPO

Figure 1(a) shows the extractability of Ln(III) with Hba in the presence or absence of TOPO in [Bmim][Tf₂N] as a function of pH in the aqueous phase. With Hba alone, the Ln(III) were barely extractable

Figure 1. Extractability of Ln(III) with β -diketones in the presence or absence of TOPO in [Bmim][Tf₂N]. Hba, Hacac, and Hdbm are used as β -diketones in panel (a), (b), and (c), respectively. The concentrations of β -diketones, TOPO, and Ln(III) are $1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $1.0 \times 10^{-2} \text{ mol dm}^{-3}$, and $5.0 \times 10^{-6} - 3.0 \times 10^{-5} \text{ mol dm}^{-3}$, respectively. β -diketones alone system: $\diamond$ La(III), $\triangle$ Nd(III), $\circ$ Eu(III), $\square$ Lu(III). β -diketones-TOPO system ; $\blacklozenge$ La(III), $\blacktriangle$ Nd(III), $\bullet$ Eu(III), $\blacktriangledown$ Dy(III), $\blacksquare$ Lu(III).

or partially extracted at high pH into the IL phase. On the other hand, Ln(III) can be extracted at lower pH values with Hba and TOPO, indicating that the extraction of Ln(III), especially the heavier ones, was significantly enhanced due to the synergistic effect in this system. A similar synergistic effect was observed for the extraction with other β -diketones such as Hacac or Hdbm (Figure 1(b) and (c)).

4.2 Determination of the distribution constant of Hba in the water-IL system

The distribution of Hba between the aqueous and the IL phase is an important factor affecting the extraction efficiency of Ln(III). The distribution ratio (D_{HA}) of Hba between both phases was determined as a function of pH (shown in Figure 2). The pH dependence can be explained by the phase transfer of neutral Hba and anionic ba^- , as reported for 2-thenoyltrifluoroacetone (Htta) [13]. At lower pH regions, $\log D_{\text{HA}}$ was almost constant because neutral Hba is mainly formed and distributed between both phases. At a medium region of pH, i.e. 8 to 11, the D_{HA} value decreases with increasing of pH due to the formation of anionic ba^- that is relatively stable in the aqueous phase compared with neutral Hba. At higher pH values, the D_{HA} value was almost constant again because anionic ba^- is mainly formed and distributed into the IL by an ion-exchange mechanism. The experimentally determined D_{HA} value was expressed as follows.

$$D_{\text{HA}} = \frac{[\text{Hba}]_{\text{IL}} + [\text{ba}^-]_{\text{IL}}}{[\text{Hba}] + [\text{ba}^-]} \quad (22)$$

Using Eqs. (11), (12), and (14), Eq. (22) is rewritten as follows.

$$D_{\text{HA}} = \frac{K_{\text{D,HA}} + (K_{\text{D,A}} K_{\text{a}} / [\text{H}^+])}{1 + (K_{\text{a}} / [\text{H}^+])} \quad (23)$$

By fitting the $\log D_{\text{HA}}$ curve in Figure 2 by a nonlinear least-squares method based on Eq. (23), the values of $\log K_{\text{D,HA}}$, $\log K_{\text{D,A}}$, and $\text{p}K_{\text{a}}$ were determined as 2.67 ± 0.04 , -0.84 ± 0.13 , and 8.54 ± 0.07 , respectively. The calculated results (the solid line in Figure 2) reproduced the experimental data well, and the value of $\text{p}K_{\text{a}}$ is consistent with the reported values (8.39 [14] and 8.96 [15] at $I = 0.1 \text{ mol dm}^{-3}$ and 25°C). The value of $\log K_{\text{D,HA}}$ in the present IL is smaller than that in benzene (3.02), indicating that Hba with a high hydrophobicity has a higher affinity for benzene than for the IL.

4.3 Determination of extraction constants for Ln(III) extraction with Hba alone

To evaluate the extracted species for the extraction of Ln(III) with Hba alone, the distribution ratio was determined at various pH values in the aqueous phase and Hba concentration in the IL phase. In Figure 3, the logarithmic distribution ratio was plotted as a function of the logarithmic concentration of ba^- that was calculated using Eq. (13). Among the Ln(III) investigated here, the slopes of the plots vary from two to three according to $[\text{ba}^-]$, indicating that Ln(III) was extracted as $\text{Ln}(\text{ba})_2^+$ at lower $[\text{ba}^-]$ and as $\text{Ln}(\text{ba})_3$ at higher $[\text{ba}^-]$. Therefore, Eq. (10) is rewritten as follows.

$$D = \frac{[\text{ba}^-]^2 K'_{\text{ex},2} K_{\text{D,HA}}^2}{K_{\text{a}}^2} + \frac{[\text{ba}^-]^3 K_{\text{ex},3} K_{\text{D,HA}}^3}{K_{\text{a}}^3} \quad (24)$$

Figure 2. Distribution ratio of Hba as a function of pH in the aqueous phase. Initial concentration of Hba is $1.0 \times 10^{-3} - 1.0 \times 10^{-2} \text{ mol dm}^{-3}$. The solid line shows the calculated values.

The extraction constants $K'_{\text{ex},2}$ and $K_{\text{ex},3}$ for each Ln(III) were determined by fitting the $\log D - \log [\text{ba}^-]$ plots using Eq. (24) (shown in Table 1). As shown in Table 1, the values of $K'_{\text{ex},2}$ and $K_{\text{ex},3}$ increase with an increase in the atomic number of the Ln(III). This tendency was also reported for most Ln(III) extractions [16], and can be interpreted from the electrostatic interactions between Ln(III) and ba^- because basic ligands have stronger electrostatic interactions with heavier Ln(III) with smaller ionic radius. The values of $K_{\text{ex},3}$ for La(III), Eu(III), and Lu(III) in IL are higher than those reported in benzene [17]. The extraction constant $K_{\text{ex},3}$ is related to the distribution constant ($K_{\text{D},\text{M}3}$) of the neutral chelate $\text{Ln}(\text{ba})_3$ between both phase as follows.

$$K_{\text{D},\text{M}3}\beta_3 = \frac{K_{\text{ex},3}K_{\text{D},\text{HA}}^3}{K_{\text{a}}^3}. \quad (25)$$

Here β_3 is the formation constant of $\text{Ln}(\text{ba})_3$ in the aqueous phase and thus independent of the extraction solvent. The values of $K_{\text{D},\text{M}3}\beta_3$, which were obtained with Eq. (25), were higher in the IL than those in benzene (shown in Table 1) in spite of a lower $K_{\text{D},\text{HA}}$ value in IL than in benzene ($K_{\text{D},\text{HA}}(\text{IL}) < K_{\text{D},\text{HA}}(\text{benzene})$), indicating that the $\text{Ln}(\text{ba})_3$ chelates have higher affinities for IL that is more polar than benzene (e.g. $\epsilon_r = 14.0$ for [Bmim][Tf₂N] [18] and 2.27 for benzene [19]) and has the donating property of Tf₂N⁻ [20].

Figure 3. Distribution ratio of Ln(III) as a function of the ba^- concentration in the aqueous phase. The solid line shows the calculated values. $1.0 \times 10^{-2} - 3.0 \times 10^{-1} \text{ mol dm}^{-3}$ Hba, $1.0 \times 10^{-5} - 3.0 \times 10^{-5} \text{ mol dm}^{-3}$ Ln(III). pH 4.4 – 7.1. $\diamond$ La(III), $\triangle$ Nd(III), $\circ$ Eu(III), ∇ Dy(III), $\square$ Lu(III).

Table 1. Extraction constants of Ln(III) in the Hba-[Bmim][Tf₂N] system at 25°C.

Ln(III)	[Bmim][Tf ₂ N]			Benzene ^a	
	$\log K'_{\text{ex},2}$	$\log K_{\text{ex},3}$	$\log K_{\text{D},\text{M}3}\beta_3$	$\log K_{\text{ex},3}$	$\log K_{\text{D},\text{M}3}\beta_3$
La(III)	-12.65 ± 0.05	-18.03 ± 0.03	15.63	-20.46	14.70
Nd(III)	-11.11 ± 0.08	-16.69 ± 0.14	16.97	—	—
Eu(III)	-10.85 ± 0.05	-15.61 ± 0.06	18.05	-18.90	16.26
Dy(III)	-10.08 ± 0.08	-15.35 ± 0.15	18.31	—	—
Lu(III)	-9.68 ± 0.21	-13.62 ± 0.13	20.04	-15.21	19.95

a : Ref. 17

4.4 Determination of extraction constants for Ln(III) extraction with Hba and TOPO

The distribution ratio for Ln(III) in the synergistic extraction was determined at varying pH and concentrations of Hba and TOPO. The 3D plot of $\log D$ for Eu(III) as a function of $\log [\text{ba}^-]$ and $\log [\text{TOPO}]_{\text{IL}}$ is shown in Figure 4, where two types of 2D plots, the $\log D - \log [\text{ba}^-]$ plot at fixed $\log [\text{TOPO}]_{\text{IL}}$ and the $\log D - \log [\text{TOPO}]_{\text{IL}}$ plot at fixed $\log [\text{ba}^-]$, are also shown. From the slope of the $\log D - \log [\text{ba}^-]$ plots,

one or two ba^- ions were found to coordinate to Eu(III). Similarly, two to four TOPO molecules were found to be coordinated to Eu(III). Similar trends were observed in the $\log D$ plots for other Ln(III). Given that the coordination number of the Ln(III) is eight or nine, $\text{Ln}(\text{ba})(\text{TOPO})_2^{2+}$, $\text{Ln}(\text{ba})(\text{TOPO})_3^{2+}$, $\text{Ln}(\text{ba})(\text{TOPO})_4^{2+}$, $\text{Ln}(\text{ba})_2(\text{TOPO})_2^+$, $\text{Ln}(\text{ba})_2(\text{TOPO})_3^+$ and $\text{Ln}(\text{ba})_2(\text{TOPO})_4^+$ can be considered as the extracted species with Hba as a bidentate ligand and with TOPO as a unidentate ligand. According to Eq. (21), the extraction constants for the respective extracted species were determined by fitting the 3D plot of $\log D$ by a nonlinear least-squares method. Reliable fits were achieved by limiting the extracted species to $\text{Ln}(\text{ba})(\text{TOPO})_4^{2+}$ and $\text{Ln}(\text{ba})_2(\text{TOPO})_2^+$ for Ln(III) except for Lu(III), and to only $\text{Ln}(\text{ba})(\text{TOPO})_4^{2+}$ for Lu(III). As shown in Figure 4, the calculation using the extraction constants, i.e. solid curves, reproduced the experimental data. This fitting result indicates that only cationic ternary complexes were extracted in the synergistic extraction with Hba and TOPO, in contrast to the extraction with Hba alone where neutral and cationic species were extracted.

Figure 4. Distribution ratio (D) of Eu(III) as a function of the concentration of ba^- in the aqueous phase ($[\text{ba}^-]$) and/or that of TOPO in the IL phase ($[\text{TOPO}]_{\text{IL}}$). Panels (a), (b), (c) represent a 3D plot of $\log D$ against $\log [\text{ba}^-]$ and $\log [\text{TOPO}]_{\text{IL}}$, a 2D plot of $\log D$ against $\log [\text{ba}^-]$, and a 2D plot of $\log D$ against $\log [\text{TOPO}]_{\text{IL}}$, respectively. Solid symbols show the experimental values ($\blacklozenge$ $\log [\text{TOPO}]_{\text{IL}} = -2.99$, $\blacksquare$ $\log [\text{TOPO}]_{\text{IL}} = -2.00$, $\blacktriangledown$ $\log [\text{ba}^-] = -7.98$, $\blacktriangle$ $\log [\text{ba}^-] = -6.93$). Curves in panels (b) and (c) show calculated results. $1.0 \times 10^{-2} - 3.0 \times 10^{-2} \text{ mol dm}^{-3}$ Hba, $1.0 \times 10^{-3} - 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ TOPO, $5.0 \times 10^{-5} - 3.0 \times 10^{-5} \text{ mol dm}^{-3}$ Eu(III). pH 4.2 – 6.2.

Synergistic extraction proceeds via the adduct formation of Ln(III) benzoylacetate with TOPO in the IL phase. The following complexation equilibrium exists between $\text{Ln}(\text{ba})_m(\text{TOPO})_n^{(3-m)+}$ that is extracted synergistically and $\text{Ln}(\text{ba})_{m'}^{(3-m') +}$ that is extracted with Hba alone.

The adduct formation constant can be defined as

$$\beta_{m'}^{mn} = \frac{[\text{Ln}(\text{ba})_m(\text{TOPO})_n^{(3-m)+}]_{\text{IL}}}{[\text{Ln}(\text{ba})_{m'}^{(3-m') +}]_{\text{IL}} [\text{TOPO}]_{\text{IL}}^n} = \frac{K'_{\text{ex},smn} K_a^{(m'-m)} K_{\text{D,A}}^{(m'-m)}}{K'_{\text{ex},m} K_{\text{D,HA}}^{(m'-m)}} \quad (27)$$

The adduct formation constants β_2^{22} , β_3^{22} , β_2^{14} , and β_3^{14} were determined for Ln(III) except for Lu(III), while only β_2^{14} and β_3^{14} were determined for Lu(III) (listed in Table 2). For adduct formation of the cationic chelate $\text{Ln}(\text{ba})_2^+$ with two TOPO molecules, the value of the formation constant β_2^{22} is maximized for Eu(III), as shown in Figure 5. This tendency with respect to the Ln(III) series is different from that in conventional organic solvent systems where the adduct formation constant decreases monotonously as the atomic number increases [16]. Furthermore, the value of β_2^{14} increases with an increase in the atomic number and is particularly large for Lu(III). This tendency indicates that the heavier Ln(III) prefer to form the dicationic ternary complex $\text{Ln}(\text{ba})(\text{TOPO})_4^{2+}$. For both of the two adduct complexes presented here, ba^- and TOPO occupy six coordination sites of Ln(III), indicating that there is no significant difference in steric hindrance between the two complexes although a steric effect potentially has an influence on the adduct formation process for heavier Ln(III) with smaller ionic radius. Instead, preferential formation of the dicationic complex for heavier Ln(III) can be interpreted in terms of the hard-soft acid-base (HSAB) principle. The hard acid character of $\text{Ln}(\text{ba})_2^{2+}$ is greater than that of $\text{Ln}(\text{ba})_2^+$ and increases with the increase in the atomic number of Ln(III). Therefore, heavier Ln(III) have a higher affinity for TOPO than for ba^- and tends to form the dicationic ternary complex that is coordinated with hydrophobic TOPO molecules instead of ba^- in the IL.

The present equilibrium analysis also indicates that the coordination sites of Ln(III) for the extracted species are not fully occupied by ba^- and TOPO, i.e. other molecules such as water or solvent ions are also coordinated. For the IL extraction system, it has been discussed whether the metal ions in the extracted species are hydrated or not, because ILs are capable of containing a significant amount of water molecules ($> 1 \text{ mol dm}^{-3}$) and the extractability is reduced by hydration. Luminescence lifetime measurements have been applied to estimate the number of water molecules coordinated to Eu(III). We previously demonstrated that Eu(III)-tta chelates extracted into the IL phase are dehydrated [20]. At present, we are trying to apply this method for the present extraction system and the results will be reported in the near future.

Figure 5. Variation of the adduct formation constants of Ln(III) in [Bmim][Tf₂N] across Ln series. ○ $\log \beta_3^{22}$, □ $\log \beta_3^{14}$, ● $\log \beta_2^{22}$, ■ $\log \beta_2^{14}$. $1.0 \times 10^{-2} - 3.0 \times 10^{-2} \text{ mol dm}^{-3}$ Hba, $1.0 \times 10^{-3} - 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ TOPO, $5.0 \times 10^{-6} - 3.0 \times 10^{-5} \text{ mol dm}^{-3}$ Ln(III). pH 3.9 – 7.5.

Table 2. Extraction constants of Ln(III) in the Hba-TOPO-[Bmim][Tf₂N] system and adduct formation constants of Ln(III)-Hba-TOPO in [Bmim][Tf₂N] at 25 °C

Ln(III)	$\log K'_{\text{ex},s22}$	$\log K'_{\text{ex},s14}$	$\log \beta_2^{22}$	$\log \beta_3^{22}$	$\log \beta_2^{14}$	$\log \beta_3^{14}$
La(III)	-5.69 ± 0.07	3.85 ± 0.05	6.96 ± 0.09	0.28 ± 0.08	4.43 ± 0.08	-2.24 ± 0.07
Nd(III)	-3.93 ± 0.05	5.37 ± 0.05	7.18 ± 0.10	0.70 ± 0.15	4.42 ± 0.10	-2.07 ± 0.15
Eu(III)	-2.66 ± 0.06	6.01 ± 0.06	8.19 ± 0.10	0.88 ± 0.09	4.79 ± 0.10	-2.50 ± 0.10
Dy(III)	-1.93 ± 0.14	7.11 ± 0.17	8.15 ± 0.10	1.36 ± 0.16	5.12 ± 0.12	-1.67 ± 0.17
Lu(III)	—	9.26 ± 0.05	—	—	6.87 ± 0.22	-1.25 ± 0.14

4.5 Separation between lanthanide ions using synergistic extraction system

The separation efficiency between different Ln(III) was examined in terms of separation factors that were calculated from the extraction constants determined above. The separation factor ($\alpha_{\text{Ln(III)}/\text{Ln(III)'}}$) between Ln(III) and Ln(III)' is defined as

$$\alpha_{\text{Ln(III)}/\text{Ln(III)'}} = \frac{D_{\text{Ln(III)}}}{D_{\text{Ln(III)'}}} = \frac{\frac{[\text{ba}^-][\text{TOPO}]_{\text{IL}}^4 K'_{\text{ex,s14(Ln(III))}} K_{\text{D,HA}}}{K_a} + \frac{[\text{ba}^-]^2 [\text{TOPO}]_{\text{IL}}^2 K'_{\text{ex,s22(Ln(III))}} K_{\text{D,HA}}^2}{K_a^2}}{\frac{[\text{ba}^-][\text{TOPO}]_{\text{IL}}^4 K'_{\text{ex,s14(Ln(III)')}} K_{\text{D,HA}}}{K_a} + \frac{[\text{ba}^-]^2 [\text{TOPO}]_{\text{IL}}^2 K'_{\text{ex,s22(Ln(III)')}} K_{\text{D,HA}}^2}{K_a^2}}. \quad (28)$$

The 3D plots of $\log \alpha_{\text{Eu(III)}/\text{La(III)}}$ and $\log \alpha_{\text{Lu(III)}/\text{Eu(III)}}$ as functions of $\log [\text{ba}^-]$ and $\log [\text{TOPO}]_{\text{IL}}$ are shown in Figure 6. The separation factor between Eu(III) and La(III) is reduced slightly with an increase in $[\text{TOPO}]_{\text{IL}}$. On the other hand, the separation factor between Lu(III) and Eu(III) varies significantly with both $[\text{ba}^-]$ and $[\text{TOPO}]_{\text{IL}}$, and a value of $\alpha_{\text{Lu(III)}/\text{Eu(III)}}$ greater than 10^3 is achieved at lower $[\text{ba}^-]$ and at higher $[\text{TOPO}]_{\text{IL}}$. Variation of $\alpha_{\text{Lu(III)}/\text{Eu(III)}}$ according to $[\text{ba}^-]$ and $[\text{TOPO}]_{\text{IL}}$ is ascribed to the difference in the composition of predominant adduct species: both monocationic and dicationic complexes are extracted competitively for Eu(III), whereas only a dicationic complex is extracted for Lu(III). In the extraction system using β -diketones in conventional organic solvents, separation between the heavier Ln(III) is poorer than that between lighter Ln(III) [15]. The IL synergistic extraction system presented here is capable of the extraction of various charged adduct complexes, which results in large synergistic effects and superior separation efficiency for the heavier Ln(III).

Figure 6. Separation factors (a) between Eu(III) and La(III) and (b) between Lu(III) and Eu(III), calculated from the determined extraction constants.

5. Conclusion

The synergistic extraction equilibrium of Ln(III) with Hba and TOPO in $[\text{Bmim}][\text{Tf}_2\text{N}]$ was investigated, and the extracted species and their extraction constants were determined by the 3D equilibrium

analysis. In the presence of TOPO, cationic adduct complexes such as $\text{Ln}(\text{ba})(\text{TOPO})_4^{2+}$ and $\text{Ln}(\text{ba})_2(\text{TOPO})_2^+$ are found to be formed in the IL phase, in contrast to the extraction with Hba alone where neutral and cationic species are extracted. The formation constant for each adduct complex shows different trends among the Ln(III) series. The separation factors calculated from the determined extraction constants indicate that the present synergistic extraction system is capable of the selective extraction of the heavier Ln(III).

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References

- 1) S. Dai, Y. H. Ju, C. E. Barnes, *J. Chem. Soc., Dalton Trans.* 1201-1202 (1999).
- 2) T. Welton, *Chem. Rev.*, **99**, 2071-2084 (1999).
- 3) M. P. Jensen, B. J. Neufeind, S. Skanthakumar, L. Soderholm, *J. Am. Chem. Soc.*, **125**, 15466-15473 (2003)
- 4) N. Hirayama, H. Okamura, K. Kidani, H. Imura, *Anal. Sci.*, **24**, 697-699 (2008).
- 5) H. Okamura, N. Hirayama, K. Morita, K. Shimojo, H. Naganawa, H. Imura, *Anal. Sci.*, **26**, 607-611 (2010).
- 6) H. Okamura, H. Takagi, T. Isomura, K. Morita, H. Nagatani, H. Imura, *Anal. Sci.*, **30**, 323-325 (2014).
- 7) X. Sun, Y. Ji, F. Hu, J. Chen, D. Li, *Talanta*, **81**, 1877-1883 (2010)
- 8) A. N. Turanov, V. K. Karandashev, V. E. Baulin, *Solvent Extr. Ion Exch.*, **30**, 244-261 (2012).
- 9) Z. Zhao, Y. Baba, F. Kubota, N. Kamiya, M. Goto, *J. Chem. Eng. Jpn.*, **47**, 656-662 (2014).
- 10) M. Atanassova, V. Kurteva, *Sep. Purif Technol.*, **183**, 226-236 (2017).
- 11) P. Bonhoôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.*, **35**, 1168-1178 (1996).
- 12) S. Katsuta, K. Nakamura, Y. Kudo, Y. Takeda, *J. Phys. Chem. B*, **116**, 852-859 (2011)
- 13) K. Kidani, H. Imura, *Talanta*, **83**, 299-304 (2010).
- 14) T. Sekine, Y. Hasegawa, N. Ihara, *J. Inorg. Nucl. Chem.*, **35**, 3968-3970 (1973).
- 15) A. P. Zozulya, N. N. Mezentseva, V. M. Peshkova, Y. Yuriev, *Zh. Anal. Khim.*, **14**, 17(1959).
- 16) T. Shigematsu, M. Tabushi, M. Matsui, T. Honjyo, *Bull. Chem. Soc. Jpn.*, **40**, 2807-2812 (1967).
- 17) J. Stay, *Zh. Neorg. Khim.*, **4**, 2412 (1959).
- 18) M. Huang, Y. Jiang, P. Sasisanker, G. Driver, H. Weingärtner, *J. Chem. Eng. Data.*, **56**, 1494-1499 (2011).
- 19) W. M. Haynes (ed.), *CRC Handbook of Chemistry and Physics. 97th Edition*, CRC Press, Boca Raton, 2010, p. 2229.
- 20) H. Okamura, N. Aoyagi, K. Shimojo, H. Naganawa, H. Imura, *RSC Adv.*, **7**, 7610-7618 (2017).