

Highly Selective Synergism for the Extraction of Lanthanoid(III) Ions with β -Diketones and Trioctylphosphine Oxide in an Ionic Liquid

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Selective synergism for the extraction of lanthanoids(III) (Ln) with β -diketones such as 2-thenoyltrifluoroacetone, 2-naphthoyltrifluoroacetone, and benzoylacetone has been investigated in the presence of trioctylphosphine oxide as a hydrophobic neutral ligand in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide as an ionic liquid. The extractability of heavier Ln was remarkably enhanced, resulting in a significant improvement in the separation of Ln. It was found that the present synergism is ascribed to the formation of cationic ternary complexes, followed by ion exchange into the ionic liquid.

Keywords Ionic liquid, synergistic effect, lanthanoid(III), β -diketone, trioctylphosphine oxide

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Ionic liquids (ILs) are still receiving growing interest in wide fields of chemistry and industry.^{1,2} ILs are more attractive than conventional organic solvents because they have unique properties, such as extremely low vapor pressure, non-flammability, and proper electrical conductivity.³ Moreover, since their chemical and physical properties depend on the combination of a cation and an anion,⁴⁻⁶ the solvent properties of an IL, such as polarity, hydrophobicity, and miscibility with other solvents, are tunable by changing the ionic components.

Over the last decade, water-immiscible hydrophobic ILs have been extensively investigated as novel solvents for the replacement of conventional organic diluents in solvent extraction.⁷⁻⁹ Because ILs can also act as liquid ion exchangers, not only neutral but also charged complexes are extractable into the IL phase by ion exchange with the cationic or anionic constituent of the ILs.¹⁰⁻¹³ Thus, the extractability and separability of metal ions in the IL extraction system are expected to differ from those of the usual organic solvent systems.^{14,15}

Recently, the present authors have reported on the synergistic ionic-liquid extraction of lanthanoids(III) (Ln(III)) with 2-thenoyltrifluoroacetone (Htta) as an acidic chelating extractant and several neutral ligands in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₄mim][Tf₂N]).¹⁶⁻¹⁸ In the Htta-18-crown-6 derivative (CE) systems,¹⁷ a synergistic enhancement of the extractability was found for only light Ln(III) from La to Eu, leading to selective extraction of the lighter Ln, while in the Htta-trioctylphosphine oxide (TOPO) system,¹⁸ the synergistic effect increased with an increase in the atomic number, leading to an improvement in the selectivity

among Ln(III) ions. The synergism mentioned above has been ascribed to the ion-exchange extraction of specific cationic ternary complexes such as Ln(tta)₂(CE)⁺ and Ln(tta)(CE)²⁺¹⁷ or Ln(tta)₂(TOPO)₃⁺ and Ln(tta)(TOPO)₃²⁺¹⁸ into the IL.

In the present work, the synergistic ionic-liquid extraction of Ln(III) with several β -diketones (HA) having different acidities and molar volumes, benzoylacetone (Hba), 2-naphthoyltrifluoroacetone (Hnta), and Htta for comparison, in the presence of a hydrophobic neutral ligand, TOPO, in [C₄mim][Tf₂N] was studied to clarify the effect of the acidic chelating extractant in synergistic IL systems. The extraction behavior of La(III), Eu(III), and Lu(III) was investigated to discuss the extractability and the separability of Ln(III). Furthermore, a unique complex extractable into IL was demonstrated by equilibrium analysis in the Eu(III)-Hba-TOPO system.

[C₄mim][Tf₂N] was synthesized and purified in the same manner as previously used.¹³ All other chemicals used were of analytical or guaranteed reagent-grade, and were used as received. High purity deionized water (18.2 M Ω cm) was used throughout this study. An aliquot (3 cm³) of an aqueous phase containing 3.0×10^{-5} M (1 M = 1 mol dm⁻³) Ln(III), 1.0×10^{-1} M NaCl, and 1.0×10^{-3} M pH buffer was shaken for 1 h with a [C₄mim][Tf₂N] phase (1 cm³) containing 1.0×10^{-3} – 1.0×10^{-2} M β -diketone (Htta, Hnta, or Hba) and 1.0×10^{-3} – 1.0×10^{-2} M TOPO at $25 \pm 1^\circ\text{C}$. After centrifugation, the equilibrium pH value in the aqueous phase was measured. The Ln(III) concentration in the aqueous phase was determined by spectrophotometry using Arsenazo III,¹⁹ atomic absorption spectrophotometry, or inductively coupled plasma mass spectrometry. The Ln(III) concentration in the [C₄mim][Tf₂N] phase was determined in the same manner after back-extraction with 0.1 M HCl. The distribution ratio (*D*) of Ln(III) was calculated from the concentrations in both phases.

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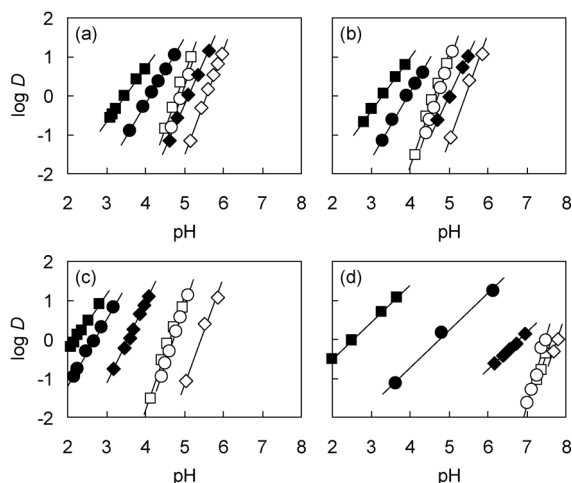


Fig. 1 Plots of $\log D$ -pH for the extraction of lanthanum(III), europium(III), and lutetium(III) with 1.0×10^{-3} M Htta and 1.0×10^{-3} M TOPO (a), 1.0×10^{-3} M Hnta and 1.0×10^{-3} M TOPO (b), 1.0×10^{-3} M Hnta and 1.0×10^{-2} M TOPO (c), and 1.0×10^{-3} M Hba and 1.0×10^{-2} M TOPO (d) in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$. $[\text{Ln}^{3+}] = 3.0 \times 10^{-5}$ M, $[(\text{Na}, \text{H})\text{Cl}] = 1.0 \times 10^{-1}$ M, $V_{\text{IL}}/V_{\text{aq}} = 1/3$. HA alone: \diamond , La; \circ , Eu; \square , Lu. HA-TOPO: \blacklozenge , La; \bullet , Eu; \blacksquare , Lu.

Figure 1 shows the variation in $\log D$ for La(III), Eu(III), and Lu(III) obtained with 1.0×10^{-3} M Htta (a), Hnta (b and c), and Hba (d) in the presence or absence of TOPO in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ as a function of the pH in the aqueous phase. The extraction behavior of Ln(III) with Htta or Hnta alone is quite similar to each other, while being very different from that with Hba alone; every Ln(III) ion is extracted with Hba in a much higher pH region. The extraction capability of these β -diketones can be explained by the substituent effect of a CF_3 group that is well recognized in the conventional organic solvent systems.²⁰ On the other hand, the extraction of Ln(III) was markedly enhanced by the addition of 1.0×10^{-3} M (a and b) or 1.0×10^{-2} M (c and d) TOPO, *i.e.*, a large synergistic effect developed in IL. The synergistic enhancement for each Ln(III) in the Htta-TOPO and the Hnta-TOPO system is similar to each other, while being quite different from that in the Hba-TOPO system. Consequently, a noticeable steric effect by the substituent of HA was not observed.

To compare the magnitude of the synergistic effect or the selectivity for respective Ln(III) ions in the β -diketone-TOPO systems, the $\text{pH}_{D=1}$ values which are the pH at $D = 1$ (extractability = 25%) were determined. The values obtained for each Ln(III) are plotted in Fig. 2, where the lower $\text{pH}_{D=1}$ value means a higher extraction efficiency of Ln(III). The magnitude of the synergistic effect of TOPO can be evaluated based on the difference in the $\text{pH}_{D=1}$ values between the HA alone and the HA-TOPO system. In all of the IL systems studied, the magnitudes of the synergistic effect increased in the order of La(III) < Eu(III) < Lu(III), which is in contrast to that of the conventional solvent systems. It is well known that the synergistic enhancement of the extractability can be ascribed to the adduct formation of Ln(III) β -diketonates with neutral ligands in the organic phase, and lowered with an increase in the atomic number of Ln(III) in the β -diketone-TOPO^{21,22} or -TBP²³ conventional solvent systems. Therefore, the present synergistic effect in IL is selective for the heavier Ln(III).

An additional singular effect can be observed in the extraction of Ln(III) with 1.0×10^{-3} M Hba and 1.0×10^{-2} M TOPO in

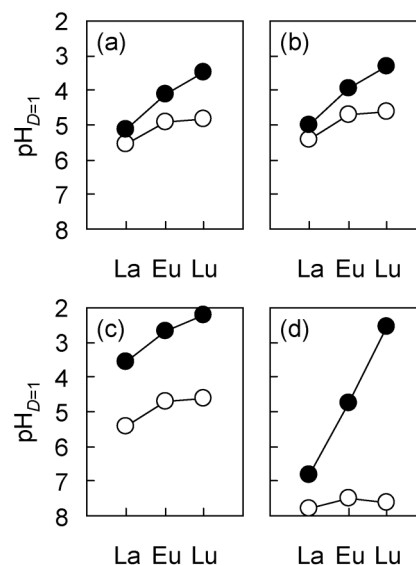
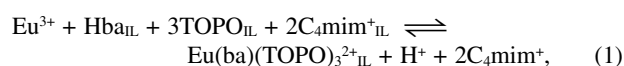


Fig. 2 Values of $\text{pH}_{D=1}$ for the extraction of lanthanoids(III) with 1.0×10^{-3} M Htta and 1.0×10^{-3} M TOPO (a), 1.0×10^{-3} M Hnta and 1.0×10^{-3} M TOPO (b), 1.0×10^{-3} M Hnta and 1.0×10^{-2} M TOPO (c), and 1.0×10^{-3} M Hba and 1.0×10^{-2} M TOPO (d) in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$. $[\text{Ln}^{3+}] = 3.0 \times 10^{-5}$ M, $[(\text{Na}, \text{H})\text{Cl}] = 1.0 \times 10^{-1}$ M, $V_{\text{IL}}/V_{\text{aq}} = 1/3$. \circ , HA alone; \bullet , HA-TOPO.

$[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ (Fig. 2(d)). The synergistic effect for Eu(III) and Lu(III) in the Hba-TOPO system is considerably larger than that in the Hnta-TOPO system. Furthermore, the difference in the $\text{pH}_{D=1}$ values among Ln(III) ions, *i.e.*, the selectivity, in the Hba-TOPO system, is much larger than that in the Hnta-TOPO and Htta-TOPO systems. The same is true concerning the separation factor (α), *e.g.*, the values of $\log \alpha$ between Eu(III) and Lu(III) in the Hba-TOPO and Hnta-TOPO systems are 2.2 and 0.9, respectively. The order of the selectivity, $\text{Hba} \gg \text{Hnta} \approx \text{Htta}$, is consistent with that of their $\text{p}K_{\text{a}}$. Consequently, the separability among Ln(III) ions is dependent on the acidic chelating extractants, and thus can be greatly improved by the synergistic effect in the present IL systems.

The extracted species in the Hnta- and Hba-TOPO systems were investigated based on the slope of the $\log D$ -pH plots shown in Fig. 1. In the Hnta-TOPO system (Fig. 1(c)), the slopes for La(III), Eu(III), and Lu(III) were 2.09 ± 0.05 , 1.72 ± 0.06 , and 1.47 ± 0.04 , respectively. These results are in good agreement with those obtained in the Htta-TOPO- $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$,¹⁸ and thus suggested that cationic ternary complexes, *e.g.*, $\text{Ln}(\text{nta})_2^+$ and $\text{Ln}(\text{nta})_2^{2+}$ combined with TOPO, were extracted in the Hnta-TOPO system. On the other hand, quite different slopes were found in the Hba-TOPO system, which were 0.96 ± 0.02 , 0.95 ± 0.09 , and 0.96 ± 0.01 for La(III), Eu(III), and Lu(III), respectively. These results suggest the extraction of the dicationic ternary complex, $\text{Ln}(\text{ba})(\text{TOPO})_n^{2+}$. Figure 3 shows the ligand-concentration dependences of $\log D$ in the Eu(III)-Hba-TOPO system. The plots of $\log D$ - $\log[\text{Hba}]_{\text{IL}}$ and $\log D$ - $\log[\text{TOPO}]_{\text{IL}}$ give straight lines with slopes of 0.87 ± 0.08 and 3.15 ± 0.19 , respectively. These results indicate that Eu(III) is extracted by ion exchange as the dicationic ternary complex, $\text{Eu}(\text{ba})(\text{TOPO})_3^{2+}$, as follows:



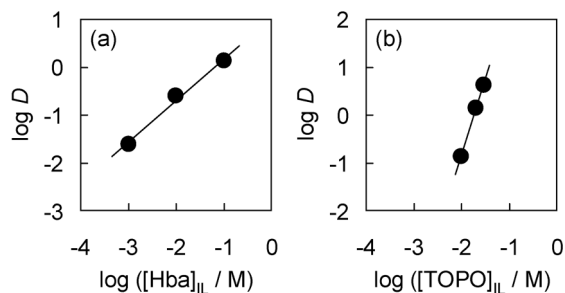


Fig. 3 Plots of $\log D$ - $\log[\text{Hba}]_{\text{IL}}$ (a), and $\log D$ - $\log[\text{TOPO}]_{\text{IL}}$ (b) for the extraction of europium(III) with Hba and TOPO in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$. $[\text{Eu}^{3+}] = 3.0 \times 10^{-5} \text{ M}$, $[(\text{Na}, \text{H})\text{Cl}] = 1.0 \times 10^{-1} \text{ M}$, $V_{\text{IL}}/V_{\text{aq}} = 1/1$. (a) $[\text{TOPO}]_{\text{IL}} = 1.0 \times 10^{-2} \text{ M}$, $\text{pH} = 3.71 - 3.73$. (b) $[\text{Hba}]_{\text{IL}} = 1.0 \times 10^{-2} \text{ M}$, $\text{pH} = 3.35 - 3.42$.

on the basis of the following equation,¹⁷

$$\log D = \text{pH} + \log[\text{Hba}]_{\text{IL}} + 3\log[\text{TOPO}]_{\text{IL}} + \text{constant}. \quad (2)$$

The $\text{Eu}(\text{ba})(\text{TOPO})_3^{2+}$ complex is assumed to be solvated with Tf_2N^- to form more stable coordinately saturated complexes in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$.¹³ Therefore, the Hba-TOPO-IL system generates such a unique and large synergism.

In conclusion, special synergism for the enhancement of not only the extractability, but also the separability of Ln(III) ions, was found using an IL containing β -diketones such as Htta, Hnta, and Hba in the presence of TOPO. When Hba was used as an acidic ligand, the extraction efficiency of only heavier Ln(III) was remarkably enhanced by the synergistic effect. These findings reveal that the combination of an appropriate acidic chelating ligand and a hydrophobic neutral ligand leads to the development of a more selective synergism, or an improvement of the mutual separation for Ln(III) ions.

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Supporting Information

Log D -pH plots at various concentrations of Hba and TOPO in the Hba-TOPO system. This material is available free of charge

on the Web at <http://www.jsac.or.jp/analsci/>.

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