Extraction Ability of 4-Benzoyl-3-phenyl-5-isoxazolone towards 4f-Ions into Ionic and Molecular Media

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The distribution constants of 4-benzoyl-3-phenyl-5-isoxazolone (HPBI) and deprotonated one (PBI⁻) between hydrophobic ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₁C₄im][Tf₂N]) and aqueous phases were determined, together with the acid-dissociation constant of HPBI. The solvent extraction of three selected lanthanoid ions (La³⁺, Eu³⁺, and Lu³⁺) with HPBI from aqueous nitrate phase into [C₁C₄im][Tf₂N] has been investigated. Application of the ionic liquid as the extracting phase greatly enhanced the extraction performance of HPBI for lanthanoid ions compared with that in the chloroform system. A slope analysis was conducted in order to compare the results of the solution 4f-ion coordination chemistry in ionic and molecular media. The composition of the extracted species was established to be anionic tetrakis entities, Ln(PBI)₄⁻, for light, middle, and heavy lanthanoid ions in an ionic environment (Ln denotes lanthanoid ion). Nevertheless, the typical neutral chelate lanthanoid complexes of the type Ln(PBI)₃ have been detected when the conventional molecular diluent chloroform was applied as an organic phase.

Keywords Lanthanoids, 4-benzoyl-3-phenyl-5-isoxazolone, ionic liquid, extraction

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Introduction

Nowadays, rare-earth elements are being evaluated as critical materials due to their vital role in advanced materials and cutting-edge technologies. The intragroup separation of lanthanoids (Lns) is an extremely difficult task because of their similar chemical properties. Additionally, there is some concern about a shortage of these metals with no viable substitutes demonstrating identical performance worldwide.

In the last two decades, ionic liquids (ILs) have emerged as unique and versatile compounds possessing a number of advantageous tunable properties; as a consequence they have succeeded to gain tremendous attention from the separation-science community.¹⁻⁴ As a matter of fact, the extraction of metal ions including Lns can be drastically enhanced by applying ILs to organic phases as alternatives to traditional systems, implicating classical molecular diluents, when enormous varieties of ligands have been studied in this regard during recent years. Nevertheless, that aforesaid ionic character really gives rise to a high extraction ability, which permits ion-exchange mechanism incorporating an IL cation or anion. Unlike conventional molecular systems, where metals generally form neutral hydrophobic complexes, in IL systems the situation is remarkably different in view of intensive ion exchange that sometimes creates atypical complexes *via* multiple mechanism

processes.⁵⁻⁹ A variety of ligands developed to operate in molecular media have nowadays proven to be effective in ILs too, such as crown ethers,^{7,10,11} *N,N,N',N'*-tetraoctyldiglycolamide (TODGA),¹² octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO),^{5,13,14} β -diketones,^{6,7,9,15-18} calix[n]-arenes¹⁹⁻²² and other compounds. This has a supplemental advantage, so that researchers may draw on the massive library of known compounds, many of which are highly specific for a given group of metallic species, in order to design new ones.

The solvent extraction of Lns by the 4-benzoyl-3-phenyl-5-isoxazolone (HPBI, Fig. 1) molecule has been extensively studied by Atanassova and co-researchers in a range of conventional molecular diluents (CHCl₃, C₆H₆, CCl₄,

Fig. 1 Chemical structures of the chelating extractant and ionic liquid employed in this study.

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1,2-dichloroethane), including combinations with a wide variety of ligands, like crown ethers,²³ *p*-*tert*-butylcalix[4]arenes,^{24,25} alkylammonium salts²⁶ including Aliquat 336 in its perchlorate form too.²⁷ Strong acidity due to the electron delocalization induced by the isoxazolone moiety makes 4-acyl-5-isoxazolones an interesting class of analogs to β -diketones with potential application at strong acidic media for developing a separation process for both lanthanoids and actinoids.^{28–32} However, the complexation performance of this powerful chelating agent towards metallic species has not been evaluated in IL surroundings.

In the present study, the employment of a stronger chelating agent, HPBI, for the solvent extraction of 4f-ions into an IL was studied. The ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, hereafter referred to as [C₁C₄im][Tf₂N] (Fig. 1), was used as the extracting medium because it is a water-immiscible hydrophobic IL with low viscosity. In an attempt to investigate the influence of the organic chemical ambience *i.e.* ionic *vs.* molecular nature on the extraction process, the extraction test was performed in chloroform by applying the identical protocol. An effort was made to explore/understand the equilibrium mechanism with the main goal being to elucidate the nature of the complexes formed in the organic phase in order to propose a definitive explanation for metal-ion transfer into ILs.

Experimental

Reagents and chemicals

The commercial product HPBI (purity > 99%, Fluka) was used as received. La(NO₃)₃·6H₂O, Eu(NO₃)₃·6H₂O, and Lu(NO₃)₃·3H₂O were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). The ionic liquid, [C₁C₄im][Tf₂N], was synthesized and purified with 82.9% yield, as described previously,³³ and the quality was checked by ¹H NMR in acetone-*d*₆. The applied molecular diluent was chloroform (HPLC grade, 99.7% Wako). Metal stock solutions containing each Ln(III) ion at a concentration of 10 mM (1 M = 1 mol dm⁻³) were prepared by dissolving their nitrate salts in nitric acid, pH 2. High-purity deionized water (18.2 MΩ·cm) was used throughout this study. All other commercially available analytical-grade reagents were used without any further purification.

Distribution of HPBI

The aqueous phases were prepared by the addition of either 0.1 M HCl or 0.1 M NaOH to a 0.1 M 2-morpholinoethanesulfonic acid (MES) buffer. The [C₁C₄im][Tf₂N] phases were prepared by dissolving HPBI to give a concentration of 10 mM. Equal volumes (0.7 cm³) of the aqueous and IL solutions were mixed and shaken mechanically at 25°C for 30 min to attain distribution equilibrium. After phase separation by centrifugation, the pH in the aqueous phase at equilibrium was measured by a pH meter (Horiba F-72) with an accuracy 0.01 pH unit. The equilibrated aqueous phases were diluted with 1 M NaOH, and then the absorbance at 310 nm corresponding to the maximum absorption wavelength for PBI⁻ was measured by using a UV/Vis spectrophotometer (JASCO V-550) to determine the ligand concentration in the aqueous phase. The ligand concentration in the [C₁C₄im][Tf₂N] phase was determined in the same manner after dilution with 1 M NaOH in methanol-H₂O (1:1). The values of the molar absorptivity of PBI⁻ in a 1 M NaOH aqueous solution and in a 1 M NaOH methanol-H₂O (1:1) solution were 9.0 × 10³ and 9.2 × 10³ dm³ mol⁻¹ cm⁻¹, respectively. The

recovery of the ligand for each sample was checked to confirm that the determination method of the ligand was appropriate. The distribution of the MES buffer components into the IL phase and the effect of the MES buffer on the distribution of ligand were regarded as being negligible. The distribution ratio of HPBI (*D*_{HPBI}) was calculated as:

$$D_{\text{HPBI}} = \frac{[\text{HPBI}]_{\text{IL}} + [\text{PBI}^-]_{\text{IL}}}{[\text{HPBI}]_{\text{aq}} + [\text{PBI}^-]_{\text{aq}}}, \quad (1)$$

where the subscripts IL and aq denote the IL phase and the aqueous phase, respectively.

Liquid-liquid extraction of lanthanoids

The pH of the aqueous solutions was adjusted by the addition of either HNO₃ or NaOH to a 0.1 M MES buffer. To prepare each aqueous phase, a stock solution containing each Ln ion was added to the aqueous solutions to give Ln ion concentrations of 0.01 mM. Extracting phases containing HPBI in [C₁C₄im][Tf₂N] were prepared at concentrations of 1 mM for the pH dependency test or 0.2 to 5 mM for the HPBI concentration dependency test. For a comparison with the performance of IL, a conventional organic diluent, chloroform, containing HPBI was also prepared by the same procedure. Equal volumes (0.5 cm³) of the aqueous and extracting solutions were mixed and shaken mechanically at 25°C for 60 min (1800 rpm) to attain equilibrium. After separation of the two layers by 3 min centrifugation (5000 rpm), the concentration of Ln(III) in the aqueous phase was determined by using an inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer NexION 300X). The metal concentration in the extracting phase was determined in the same manner after back-extraction with 1 M HNO₃. The recovery of Ln(III) ions for each sample was checked to confirm no loss of metals into the interface and/or tube surface. The acidity of the aqueous phase at equilibrium was measured by a pH meter. The distribution ratio of Ln(III) (*D*) was calculated as

$$D = \frac{[\text{Ln}^{3+}]_{\text{aq,back}}}{[\text{Ln}^{3+}]_{\text{aq,f}}}, \quad (2)$$

where [Ln³⁺]_{aq,f} is the concentration of Ln³⁺ ion in the aqueous phase after extraction and [Ln³⁺]_{aq,back} is its concentration after back-extraction. The extractability (*E*) was evaluated as

$$E = \frac{[\text{Ln}^{3+}]_{\text{aq,back}}}{[\text{Ln}^{3+}]_{\text{aq,f}} + [\text{Ln}^{3+}]_{\text{aq,back}}} \times 100. \quad (3)$$

Results and Discussion

Distribution equilibria of HPBI

The distribution behavior of HPBI between the [C₁C₄im][Tf₂N] phase and the aqueous phase was investigated as a function of the pH in the aqueous phase. Figure 2 shows the relationship between log *D*_{HPBI} and the aqueous phase pH in the [C₁C₄im][Tf₂N] system. In the lower pH region, the log *D*_{HPBI} value approaches a constant value with decreasing pH in the aqueous phase. Furthermore, the log *D*_{HPBI} value can be assumed to become constant in the higher pH region, as reported previously.³⁴ It was, therefore, indicated that the neutral HPBI and the deprotonated anionic PBI⁻ distribute into the IL phase. The distribution equilibrium of neutral HPBI is represented as follows:

Fig. 2 Logarithmic distribution ratio of HPBI ($\log D_{\text{HPBI}}$) as a function of the equilibrium pH value of the aqueous phase in the $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ system. The initial concentration of HPBI was 10 mM. The solid line was obtained by a non-linear least-squares fitting.

and the distribution constant of HPBI ($K_{\text{D,HPBI}}$) is defined as

$$K_{\text{D,HPBI}} = \frac{[\text{HPBI}]_{\text{IL}}}{[\text{HPBI}]_{\text{aq}}} \quad (5)$$

In contrast, the distribution equilibrium of anionic PBI^- can be represented by the following anion-exchange reaction:

The equilibrium constant can be defined as

$$K_{\text{D,PBI}} = \frac{[\text{PBI}^-]_{\text{IL}}[\text{Tf}_2\text{N}^-]_{\text{aq}}}{[\text{PBI}^-]_{\text{aq}}[\text{Tf}_2\text{N}^-]_{\text{IL}}} \quad (7)$$

Given that the variation of $[\text{Tf}_2\text{N}^-]_{\text{aq}}$ by the anion-exchange reaction is negligibly small compared with the solubility of $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ in water (17.0 mM),³⁵ and $[\text{Tf}_2\text{N}^-]_{\text{aq}}$ and $[\text{Tf}_2\text{N}^-]_{\text{IL}}$ are constant under the stated conditions, the following equation for the apparent distribution constant of PBI^- ($K'_{\text{D,PBI}}$) can be derived:

$$K'_{\text{D,PBI}} = \frac{[\text{PBI}^-]_{\text{IL}}}{[\text{PBI}^-]_{\text{aq}}} \quad (8)$$

The distribution ratio, D_{HPBI} , as shown in Eq. (1), can be rewritten using the distribution constant, $K_{\text{D,HPBI}}$, the apparent distribution constant, $K'_{\text{D,PBI}}$, and the acid dissociation constant (K_{a}) of HPBI as follows:

$$D_{\text{HPBI}} = \frac{K_{\text{D,HPBI}} + K'_{\text{D,PBI}}(K_{\text{a}}/[\text{H}^+]_{\text{aq}})}{1 + (K_{\text{a}}/[\text{H}^+]_{\text{aq}})} \quad (9)$$

The values of $K_{\text{D,HPBI}}$, $K'_{\text{D,PBI}}$, and K_{a} were determined by a non-linear least-squares fitting of the plots in Fig. 2 based on Eq. (9). The obtained values for the distribution constants in the $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ system were $\log K_{\text{D,HPBI}} = 2.88 \pm 0.01$ and $\log K'_{\text{D,PBI}} = 0.88 \pm 0.01$. The $K_{\text{D,HPBI}}$ value in the $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ system is higher than $K_{\text{D,HTTA}}$ ($\log K_{\text{D,HTTA}} = 1.61 \pm 0.05$; HTTA denotes 2-thenoyltrifluoroacetone),³⁴ whereas the $K'_{\text{D,PBI}}$ value is comparable to $K'_{\text{D,TTA}}$ ($\log K'_{\text{D,TTA}} = 0.96 \pm 0.10$).³⁴ In addition, the $\text{p}K_{\text{a}}$ value obtained by the fitting was 0.65 ± 0.01 ,

Fig. 3 Dependence of the Ln(III) ion extractability on the equilibrium pH value of the aqueous phase using 1 mM HPBI in $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ or CHCl_3 .

which is in good agreement with the reported value ($\text{p}K_{\text{a}} = 0.68$).³⁶ This result indicates that HPBI is a powerful acidic chelating ligand compared with HTTA ($\text{p}K_{\text{a}} = 6.33$).³⁷ It should be noted that the HPBI concentration in the IL phase after the equilibration with the aqueous phase decreases with increasing pH due to the strong acid dissociation of HPBI in the aqueous phase. The HPBI concentration in the IL phase at equilibrium ($[\text{HPBI}]_{\text{IL}}$) can be calculated using the obtained $K_{\text{D,HPBI}}$, $K'_{\text{D,PBI}}$, and K_{a} values as follows:

$$[\text{HPBI}]_{\text{IL}} = \frac{[\text{HPBI}]_{\text{IL,ini}} K_{\text{D,HPBI}}}{K_{\text{D,HPBI}} + K'_{\text{D,PBI}}(K_{\text{a}}/[\text{H}^+]_{\text{aq}}) + (1 + K_{\text{a}}/[\text{H}^+]_{\text{aq}})} \quad (10)$$

where $[\text{HPBI}]_{\text{IL,ini}}$ is the initial concentration of HPBI in the IL phase. The calculation of the HPBI concentration in the IL phase was applied in the slope analysis discussed later.

Extraction behavior of lanthanoids in ionic and molecular diluents

The extraction performance of the chelating agent HPBI in ionic and molecular diluents was assessed towards La^{3+} , Eu^{3+} , and Lu^{3+} ions as representatives of light, middle, and heavy 4f-series, *ceteris paribus*. The degree of Lns extraction was compared with the two studied diluents IL vs. CHCl_3 by applying the same protocol. The extractability of Lns by HPBI in $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ as a function of the pH value of the aqueous phase, compared with that in chloroform system, can be seen in Fig. 3. The extraction % of metal ions increases with increasing pH in the aqueous phase in the pH range of 1.4 – 3.1 as well as 2.2 – 5.0, considering the ionic and molecular systems, respectively. As a result, the extraction efficiency of Ln(III) ions reached approximately 100% at pH 3 in the IL and pH 4 in molecular medium. At a lower pH (< 1) the extraction in IL is nil, whereas at a slightly higher pH (> 2) more than 90% of the extraction could be achieved. Furthermore, it is worth noting that HPBI exhibited a very similar selectivity facing the target metals in the two systems transferring Ln ions in the same order: $\text{Lu}^{3+} \approx \text{Eu}^{3+} > \text{La}^{3+}$. This order was expected following the atomic number of the metals due to their decreasing ionic radii from La^{3+} to Lu^{3+} . With increasing atomic number, the ionic radii decrease at constant charge ($3+$), and consequently the charge densities increase, and the formation of an extractable

Fig. 4 Log D vs. $\log[\text{HPBI}]_{\text{IL}}$ plots at pH 2.3 for La^{3+} and pH 1.8 for Eu^{3+} and Lu^{3+} in $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$. The experiment was separately performed under the presence of a single metal ion in each aqueous phase.

complex is favored. Thus, an increase of the extraction efficiency is observed going from La^{3+} to Lu^{3+} . As a whole, the two systems are very efficient for Lns removing at low acidity with a HPBI compound. Additionally, the present experiments show that a complete quantitative back-extraction of Lns can be obtained easily using 1 M HNO_3 as a stripping agent with excellent recovery independently from the extracting phase nature. Another advantage is that the process is carried out at rather lower pH values of the aqueous phase in a very short region (~ 1 pH unit). The half-extraction pH values (pH_{50}) at which the extractability is 50% were 2.3 for La^{3+} , 1.8 for Eu^{3+} , and 1.8 for Lu^{3+} in the IL system and 3.6 for La^{3+} , 2.8 for Eu^{3+} , and 2.8 for Lu^{3+} in the chloroform system, respectively. A notable difference between the pH_{50} values in the IL and chloroform systems (ΔpH_{50} approximately 1.0–1.3 pH unit) demonstrates that the IL system can remarkably enhance the extraction performance of HPBI for Ln ions compared with the chloroform system. Furthermore, it is interesting to note that HPBI enables a quantitative partitioning of Lns from higher acidic solutions than typical β -diketones such as HTTA.^{7,9,15}

Mechanism of lanthanoids extraction using 4-benzoyl-3-phenyl-5-isoxazolone in ionic and molecular media

While metal ions generally exist at the form of neutral hydrophobic complexes in molecular liquids, charged metallic complexes highly soluble in the IL phase may pertain in this ionic solvation environment. Three fundamental classes of mononuclear Ln complexes with β -diketone (HL) in the IL solutions can be considered:³⁸ i) neutral tris complexes (LnL_3) involving three β -diketone molecules for a Ln ion; ii) neutral self-adduct complexes ($\text{LnL}_3\cdot\text{HL}$) including one protonated acidic molecule; iii) anionic tetrakis complexes (LnL_4^-) consisting of four β -diketone molecules and a Ln ion. Atanassova *et al.* have already demonstrated that the extraction of Ln ions using the strongly coordinating compound HPBI in a set of molecular diluents proceeds through a proton-exchange reaction, forming neutral tris complexes.^{23–27} The extraction mechanism and the extraction constant of the neutral tris complexes ($K_{\text{ex},3}$) were represented by the following equations:

$$K_{\text{ex},3} = \frac{[\text{Ln}(\text{PBI})_3]_{\text{org}}[\text{H}^+]_{\text{aq}}^3}{[\text{Ln}^{3+}]_{\text{aq}}[\text{HPBI}]_{\text{org}}^3}, \quad (12)$$

where the subscript org denotes organic phase. In this study, we confirmed that the extraction of Ln(III) ions with HPBI in the chloroform system is consistent with the previous data and can be described by Eq. (11) from slope analysis (data not shown in the figures).^{23–27} In addition, the values of $\log K_{\text{ex},3}$ for La^{3+} , Eu^{3+} , and Lu^{3+} in the chloroform system were determined to be -1.34 ± 0.10 , 0.85 ± 0.11 , and 0.73 ± 0.10 by a linear least-squares fitting of the plots, respectively. Electroneutrality is an essential principle, as only neutral complexes may enter the hydrophobic molecular layer. The coordination sphere of the trivalent ion is unsaturated in this six-coordinate chelate complex, so the Ln(III) ion can expand its coordination sphere by adduct formation, depending on the protocol, with water molecules for example $\text{LnL}_3(\text{H}_2\text{O})_x$, $x = 2$ or 3.

In the IL system, slope analysis of Ln extraction with HPBI was investigated as a function of the HPBI concentration in the IL phase at equilibrium (Fig. 4) in order to determine the stoichiometry of the Ln^{3+} -HPBI complexes in the $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ phase. The plots for the HPBI concentration were linear with a slope of 4 for La^{3+} , Eu^{3+} , and Lu^{3+} extraction, suggesting that four HPBI molecules were required to extract one Ln(III) ion into the IL, in that a 1:4 metal/ligand ratio complex was formed. The results clarify the difference in the extracted species between IL and organic solvent systems. The fourth ligand probably displaces the water molecules from the inner coordination sphere of the Ln(III) ion.³⁹ Two candidate forms, which are neutral self-adduct complexes ($\text{LnL}_3\cdot\text{HL}$) and anionic tetrakis complexes (LnL_4^-), can emerge as 1:4 complexes. To elucidate the convincing extraction mechanism, the slope analysis of Ln extraction with HPBI was investigated as a function of pH in the aqueous phase (Fig. 5). Here, $\log D - 4\log[\text{HPBI}]_{\text{IL}}$ vs. pH plots were collected because the concentration of HPBI in the IL phase at equilibrium varies depending on the pH condition due to its high acidity ($\text{pK}_a = 0.65 \pm 0.01$). The value of $[\text{HPBI}]_{\text{IL}}$ was calculated according to Eq. (10). As shown in Fig. 5, the slopes obtained for the pH dependency were around 4 for La^{3+} , Eu^{3+} , and Lu^{3+} . These results indicate that four protons from the HPBI molecules were released to extract all Ln(III) ions. Pioneering investigations of Ln^{3+} extraction conducted by Jensen *et al.*^{6,9} in $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ medium by HTTA notified the existence of anionic tetrakis complexes $\text{Ln}(\text{TTA})_4^-$ at high ligand concentration, while at low concentration of HTTA neutral complexes $\text{Ln}(\text{TTA})_3$ were extracted. In this study, the slope analysis of Ln^{3+} extraction

Fig. 5 $\log D - 4\log[\text{HPBI}]_{\text{IL}}$ vs. pH plots for Ln^{3+} extraction using 1 mM HPBI in $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$.

with HPBI demonstrates that anionic tetrakis complexes ($\text{Ln}(\text{PBI})_4^-$) were preferentially formed even at low HPBI concentration (1 mM) in the IL system, in contrast to the HTTA-IL systems, where a mixture of anionic tetrakis and neutral tris complexes was formed under the same condition.^{17,18} The extraction of anionic complexes is possible due to the exchange of $[\text{Tf}_2\text{N}^-]$ anions into the aqueous phase. The extraction of Ln^{3+} with HPBI in the IL system and the extraction constant of the anionic tetrakis complexes ($K_{\text{ex},4}$) can be expressed by the following equations:

$$K_{\text{ex},4} = \frac{[\text{Ln}(\text{PBI})_4^-]_{\text{IL}}[\text{H}^+]_{\text{aq}}^4[\text{Tf}_2\text{N}^-]_{\text{aq}}}{[\text{Ln}^{3+}]_{\text{aq}}[\text{HPBI}]_{\text{IL}}^4[\text{Tf}_2\text{N}^-]_{\text{IL}}}. \quad (14)$$

Given that $[\text{Tf}_2\text{N}^-]_{\text{aq}}$ and $[\text{Tf}_2\text{N}^-]_{\text{IL}}$ are constant under the stated conditions as described above, Eq. (14) can be rewritten as follows:

$$K'_{\text{ex},4} = \frac{[\text{Ln}(\text{PBI})_4^-]_{\text{IL}}[\text{H}^+]_{\text{aq}}^4}{[\text{Ln}^{3+}]_{\text{aq}}[\text{HPBI}]_{\text{IL}}^4}. \quad (15)$$

The values of $\log K'_{\text{ex},4}$ for La^{3+} , Eu^{3+} , and Lu^{3+} in the $[\text{C}_1\text{C}_4\text{im}][\text{Tf}_2\text{N}]$ system were determined to be 3.60 ± 0.02 , 5.12 ± 0.03 , and 5.07 ± 0.03 , respectively. As noted, the ionic character of ILs has important implications in coordination solution chemistry in the process of solvating charged metal complex (like $[\text{C}_1\text{C}_4\text{im}][\text{Ln}(\text{PBI})_4]$) as well as by the release of anionic components to the aqueous phase associating with ion-exchange mechanism in a rather satisfactory way. According to the reaction for each extracted Ln^{3+} ion into the IL, one anion $[\text{Tf}_2\text{N}^-]$ is lost by being transferred to the aqueous phase. Under this circumstances, not only the coordination power of ligand, but also the ion-exchange ability of IL would likely be important factors determining the extraction mechanism.

Conclusions

In the present study, the distribution behavior of HPBI between the IL and aqueous phases was investigated, and the distribution constants and the acid dissociation constant of HPBI were determined. The extraction behavior of lanthanoids with HPBI was compared between the IL and organic solvent systems. HPBI in IL provided a remarkably high extraction performance for lanthanoids compared with that in chloroform. The existence of anionic lanthanoid complexes ($\text{Ln}(\text{PBI})_4^-$) coordinated by PBI^- in ionic medium during solvent extraction process has been established hitherto. On the other hand, in the chloroform system, the neutral tris chelates ($\text{Ln}(\text{PBI})_3$) were usually formed with this ligand. We hope that the present findings will be contributory to the further development of separation chemistry for various metal ions.

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