

## Extraction Mechanism of Metal Ion from Aqueous Solution to the Hydrophobic Ionic Liquid, 1-Butyl-3-methylimidazolium Nonafluorobutanesulfonate

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**Summary.** We studied the extraction behavior of metal ionic species in aqueous solutions into the hydrophobic ionic liquid, 1-butyl-3-methylimidazolium nonafluorobutanesulfonate ( $[bmi][NfO]$ ). The extraction ratios ( $E/\%$ ) of Li(I), Na(I), Cs(I), Ca(II), Sr(II), and La(III) species were found to be 39, 24, 5.0, 81, 79, and 98. This result is similar to the phenomena that the metal ions with larger charge are more easily adsorbed onto cation exchange resins. In order to examine the extraction mechanism, we studied the extraction behavior of La(III) species from the aqueous to the  $[bmi][NfO]$  phase. As a result, it was found that the  $E$  values of La(III) decrease remarkably with an increase in concentrations of  $HNO_3$  (0–1 M) in the aqueous phase and that the amount of La(III) transferred into  $[bmi][NfO]$  phase increases linearly with an increase in the amount of  $[bmi]$  transferred into the aqueous phase. Furthermore, we investigated the extraction behavior of La(III) species using 1-pentyl- and 1-hexyl-3-methylimidazolium nonafluorobutanesulfonate ( $[pmi][NfO]$ ,  $[hmi][NfO]$ ), which are more hydrophobic than  $[bmi][NfO]$ , and found out that the  $E$  values of La(III) decrease in order of  $[bmi][NfO] > [pmi][NfO] > [hmi][NfO]$ . From these results, it was proposed that the extraction of metal ionic species from the aqueous to the  $[bmi][NfO]$ ,  $[pmi][NfO]$ , or  $[hmi][NfO]$  phase is mainly ascribed to the cation exchanges between two phases.

**Keywords.** Ionic liquids; Extraction; Lanthanoid ions; Hydrophobicity; Cation exchange.

### Introduction

Room temperature ionic liquids (ILs) have been paid attention as environmentally benign alternatives to

conventional organic solvents, because of their attractive properties, such as thermal stability, non-flammability, high ionic conductivity, and wide electrochemical potential windows [1–3]. Therefore, ILs have been studied widely as media for various reactions, such as organic syntheses, catalysis, electrolysis, and liquid–liquid extractions [4–10].

In the research field for the liquid–liquid extraction using ILs, many groups have investigated the separation methods of metal ions since *Rogers et al.* reported the partitioning of substituted benzene derivatives between water and  $[bmi][PF_6]$  ( $bmi = 1$ -butyl-3-methylimidazolium) [11]. *Dai et al.* studied the extraction behavior of  $Sr^{2+}$  by using  $[Rmeim][Tf_2N]$  and  $[Rmeim][PF_6]$  ( $[Rmeim] = 1$ -alkyl-3-methylimidazolium,  $[Tf_2N] = bis[(trifluoromethyl)sulfonyl]amide$ ) and found that  $Sr^{2+}$  are more effectively extracted by the presence of 18-crown-6 crown ethers in these ILs [12]. On the basis of this report, the extraction of  $Na^+$ ,  $K^+$ ,  $Cs^+$ ,  $Sr^{2+}$ , and so on using ILs containing crown ethers has been studied extensively [13–18]. Investigations on the solvent extraction of heavy metal ions using ILs have also been carried out. *Wei et al.* reported that  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$  are effectively extracted from aqueous solutions containing dithizone to  $[bmi][PF_6]$  by controlling  $pH$ . The extraction behavior of f-elements using ILs containing extractants such as octyl(phenyl)- $N,N$ -diisobutylcarbamoylmethylphosphine oxide (*CMPO*) and Cyanex-272 has been also

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investigated from the viewpoint of treatment of radioactive waste [19–21].

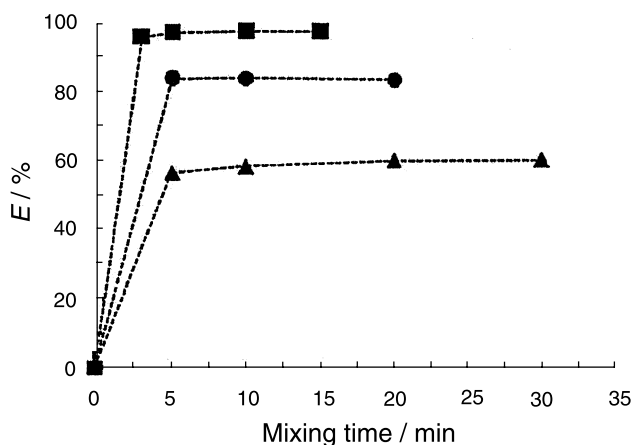
In spite of many studies on extraction of metal ions using ILs, however, little information is available concerning the extraction mechanism and the extractability of ILs [14, 22, 23]. Dietz *et al.* have proposed that the extraction of  $\text{Sr}^{2+}$  from the aqueous phase to  $[\text{Rmeim}][\text{Tf}_2\text{N}]$  containing 18-crown-6 proceeds through the cation exchange, and Jensen *et al.* reported that in the extraction of lanthanoides(III) ( $\text{Ln}(\text{III})$ ) in  $[\text{Rmeim}][\text{Tf}_2\text{N}]$  containing  $\beta$ -diketone the anion exchange plays an important role.

Hence, we investigated the extraction behavior of metal ionic species in aqueous solutions into the hydrophobic IL,  $[\text{bmi}][\text{NfO}]$  ( $\text{NfO}$  = nonafluorobutanesulfonate), to examine the extractability of hydrophobic IL itself and to consider the extraction mechanism.

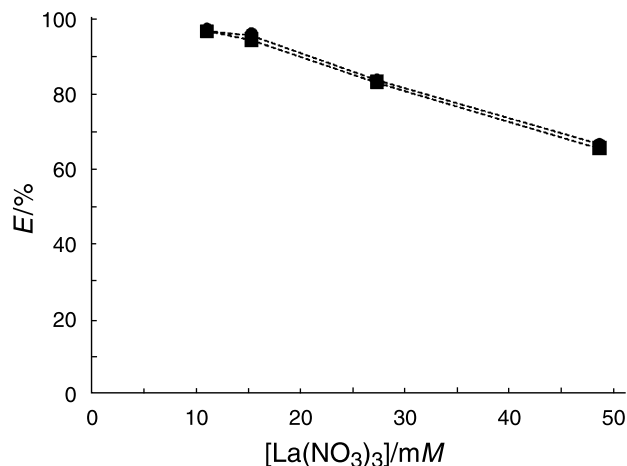
## Results and Discussion

### Extraction Behavior of Metal Ions

In order to examine the time for attaining extraction equilibrium, we measured the  $E$  values of metal ionic species [Li(I), Na(I), Cs(I), Ca(II), Sr(II), and  $\text{Ln}(\text{III})$ ] at various mixing time. Typical results for extraction of La(III) species from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , or  $[\text{hmi}][\text{NfO}]$  ( $\text{pmi}$  = 1-pentyl-3-methylimidazolium,  $\text{hmi}$  = 1-hexyl-3-methylimidazolium) phase are shown in Fig. 1. From



**Fig. 1.** Plots of  $E$  values vs. the mixing time for the extraction of La(III) species from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , or  $[\text{hmi}][\text{NfO}]$  phase. ■:  $[\text{bmi}][\text{NfO}]$ , ●:  $[\text{pmi}][\text{NfO}]$ , ▲:  $[\text{hmi}][\text{NfO}]$ . Initial concentration of  $\text{La}(\text{NO}_3)_3$  in aqueous solution:  $5.0 \times 10^{-3} \text{ M}$



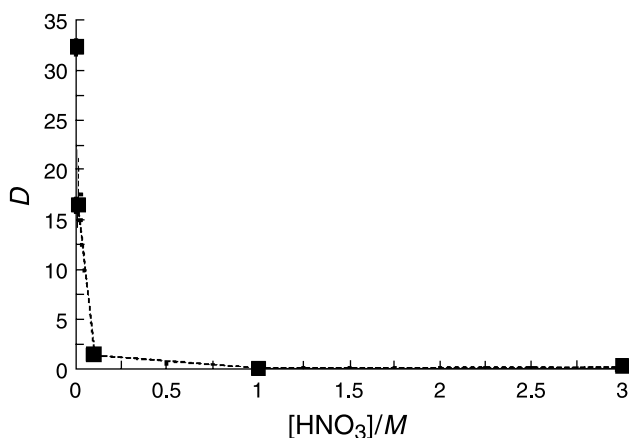
**Fig. 2.** Plots of  $E$  values for the extraction of La(III) species from the aqueous to the dried  $[\text{bmi}][\text{NfO}]$  phase (●) or the  $[\text{bmi}][\text{NfO}]$  phase saturated by water (■: water content 15 wt%)

Fig. 1, the extraction equilibrium is reached at around 10 min for  $[\text{bmi}][\text{NfO}]$  and  $[\text{pmi}][\text{NfO}]$  systems and at 20 min for  $[\text{hmi}][\text{NfO}]$  one. Thus, all extraction experiments in the present study were carried out at the mixing time of 20 min. Furthermore, to examine the effect of water on the extraction behavior of metal ions, we measured the  $E$  values of La(III) species from the aqueous to the dried  $[\text{bmi}][\text{NfO}]$  phase and the  $[\text{bmi}][\text{NfO}]$  phase saturated by water, in which water content is 15.8 wt%. The results are shown in Fig. 2. The  $E$  values are found to be almost consistent with each other in the two extraction systems. This means that water does not affect the extraction behavior of La(III) species from the aqueous to the  $[\text{bmi}][\text{NfO}]$  phase and suggests that the La(III) species are extracted to IL phase without accompanying water. On the basis of this result, all extraction experiments of metal ions were performed using the ILs saturated by water.

The  $E$  values for the extraction of various metal ionic species from the aqueous to the  $[\text{bmi}][\text{NfO}]$  phase are summarized in Table 1. In this experiment,

**Table 1.**  $E$  values for the extraction of various metal ionic species from the aqueous solutions to the  $[\text{bmi}][\text{NfO}]$  phase

	$E/\%$					
	Li(I)	Na(I)	Cs(I)	Ca(II)	Sr(II)	La(III)
Nitrate	38.7	23.8	4.8	81.3	79.1	95.5
Chloride	39.7	25.3	3.8	80.6	79.8	97.3



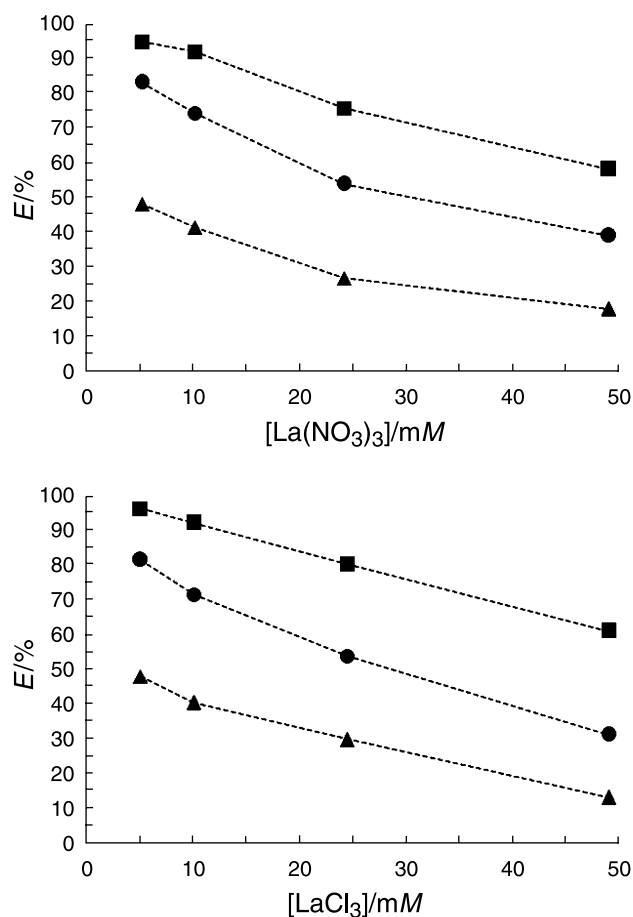
**Fig. 3.** A plot of  $D$  values vs.  $\text{HNO}_3$  concentrations in aqueous solutions for the extraction of  $\text{La(III)}$  species from the aqueous to the  $[\text{bmi}][\text{NfO}]$  phase. Initial concentration of  $\text{La}(\text{NO}_3)_3$  in aqueous solution:  $5.0 \times 10^{-3} \text{ M}$

two kinds of metal salts, nitrates and chlorides, were used. The  $E$  values for both systems are found to be consistent with each other. This means that the extraction of metal ionic species under the present conditions is controlled by properties of the cations themselves. Furthermore, the distribution ratios of  $\text{La(III)}$  species decrease remarkably with an increase in  $[\text{HNO}_3]$  as shown in Fig. 3. These results are different from the common phenomena that the distribution ratios of  $\text{La(III)}$  species increase with an increase in  $[\text{HNO}_3]$ , and are similar to the phenomena that are normally observed in the adsorption of metal ions onto cation exchange resins [24, 25], *i.e.*, the metal ions with larger charge are easily adsorbed onto the cation exchange resins and the distribution ratios decrease with an increase in the acid concentrations. Hence, it is suggested that the extraction of metal ionic species from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , or  $[\text{hmi}][\text{NfO}]$  phase proceeds through cation exchange reactions.

#### Effect of Hydrophobicities of ILs on the Extraction of Metal Ions

If the extraction of metal ionic species mentioned above are performed by the cation exchange reactions between imidazole ( $[\text{bmi}]$ ,  $[\text{pmi}]$ , or  $[\text{hmi}]$ ) and metal cations, the  $E$  values should be affected by the hydrophobicities of imidazolium cations, because the transfer of the hydrophobic cation from the IL to the aqueous phase must be diminished.

On the basis of this expectation, we examined the extraction behavior of  $\text{La(III)}$  from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , or  $[\text{hmi}][\text{NfO}]$  phase by using aqueous solutions of  $\text{La}(\text{NO}_3)_3$  and  $\text{LaCl}_3$ . Since the hydrophobicities of imidazolium cations should increase in the order of  $[\text{bmi}] < [\text{pmi}] < [\text{hmi}]$ , the  $E$  values for the extraction of  $\text{La(III)}$  into  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , and  $[\text{hmi}][\text{NfO}]$  phases are expected to decrease in this order. The results are shown in Fig. 4. As expected, the  $E$  values are found to decrease with an increase in hydrophobicities of imidazolium cations. This result supports that the extraction of metal ionic species from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , and  $[\text{hmi}][\text{NfO}]$  phases proceeds through the cation exchange reactions.

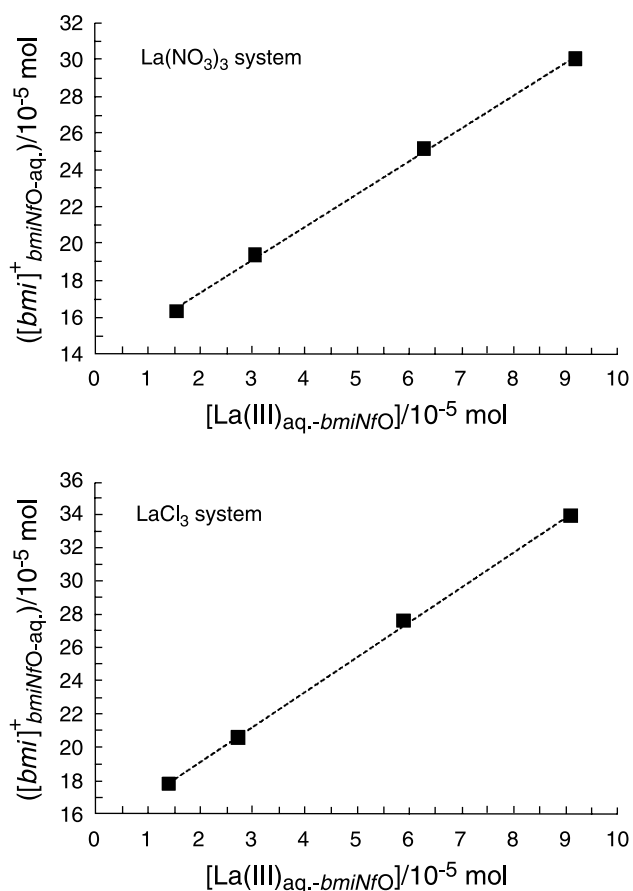


**Fig. 4.** Plots of  $E$  values vs. the concentrations of  $\text{La}(\text{NO}_3)_3$  in aqueous solution for the extraction of  $\text{La(III)}$  species from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , or  $[\text{hmi}][\text{NfO}]$  phase. The upper and lower parts correspond to the results in  $\text{La}(\text{NO}_3)_3$  and  $\text{LaCl}_3$  systems. ■:  $[\text{bmi}][\text{NfO}]$  ●:  $[\text{pmi}][\text{NfO}]$  ▲:  $[\text{hmi}][\text{NfO}]$

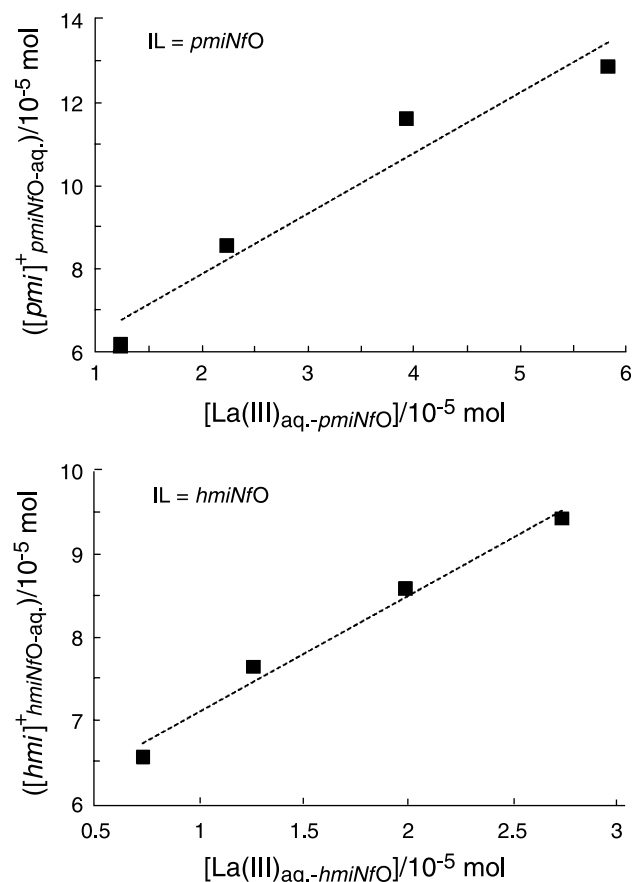
### Distribution Behavior of Cations between ILs and Aqueous Phases

In order to confirm whether our proposed mechanism is reasonable, we carried out extraction experiments by mixing the aqueous solutions of  $\text{La}(\text{NO}_3)_3$  ( $[\text{La}(\text{III})] = 5\text{--}50\text{ mM}$ ) with  $[\text{bmi}][\text{NfO}]$  solution, and measured the mole numbers ( $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{bmiNfO}}$ ) of  $\text{La}(\text{III})$  species transferred from the aqueous to the IL phase and those ( $[\text{bmi}]_{\text{bmiNfO} \rightarrow \text{aq.}}^+$ ) of  $[\text{bmi}]^+$  cations transferred from the  $[\text{bmi}][\text{NfO}]$  to the aqueous phase. If our proposal is reasonable, the  $[\text{bmi}]^+$  cations corresponding to three times as much as  $\text{La}^{3+}$  ions transferred from the aqueous to IL phase should be transferred inversely, and hence the plot of  $[\text{bmi}]_{\text{bmiNfO} \rightarrow \text{aq.}}^+$  against  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{bmiNfO}}$  should give a straight line with a slope of 3. Such a plot is shown in Fig. 5 (upper). As expected, the plot showed the linear relationship, whereas the slope is not 3 but approximately 1.8. This result suggests that

$\text{La}(\text{III})$  species are transferred from the aqueous to IL phase as the species with charges less than  $+3$ , *i.e.*,  $\text{LaNO}_3^{2+}$ ,  $\text{La}(\text{NO}_3)_2^+$ . Similar phenomena were also observed in the mixtures of the aqueous solution of  $\text{LaCl}_3$  and  $[\text{bmi}][\text{NfO}]$  as shown in Fig. 5 (lower). In this case, the slope is almost 2, which suggests that  $\text{La}(\text{III})$  species are extracted from the aqueous to IL phase as  $\text{LaCl}_2^+$ . These results are reasonable, because  $\text{La}(\text{III})$  is well known to form ion-pairs such as  $\text{La}^{3+} - \text{NO}_3^-$  or  $-\text{Cl}^-$  [26, 27], whose equilibrium constants are  $0.45$  and  $0.15\text{ M}^{-1}$  at  $300\text{ K}$ . These data suggest that the slope in the plot of  $[\text{bmi}]_{\text{bmiNfO} \rightarrow \text{aq.}}^+$  against  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{bmiNfO}}$  for the  $\text{La}(\text{NO}_3)_3$  system is smaller than that for the  $\text{LaCl}_3$  system. This is consistent with the experimental results (see Fig. 5). However, from the equilibrium constants, the mole fraction of  $\text{LaNO}_3^{2+}$  or  $\text{LaCl}_2^+$  species are evaluated to be very small compared with that of  $\text{La}^{3+}$ . Hence, the plot of  $[\text{bmi}]_{\text{bmiNfO} \rightarrow \text{aq.}}^+$  against  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{bmiNfO}}$



**Fig. 5.** A plot of  $[\text{bmi}]_{\text{bmiNfO} \rightarrow \text{aq.}}^+$  vs.  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{bmiNfO}}$  for the extraction of  $\text{La}(\text{III})$  species from the aqueous to the  $[\text{bmi}][\text{NfO}]$  phase



**Fig. 6.** A plot of  $[\text{pmi}]_{\text{pmiNfO} \rightarrow \text{aq.}}^+$  or  $[\text{hmi}]_{\text{hmiNfO} \rightarrow \text{aq.}}^+$  vs.  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{IL}}$  for the extraction of  $\text{La}(\text{III})$  species from the aqueous to the  $[\text{pmi}][\text{NfO}]$  or  $[\text{hmi}][\text{NfO}]$  phase

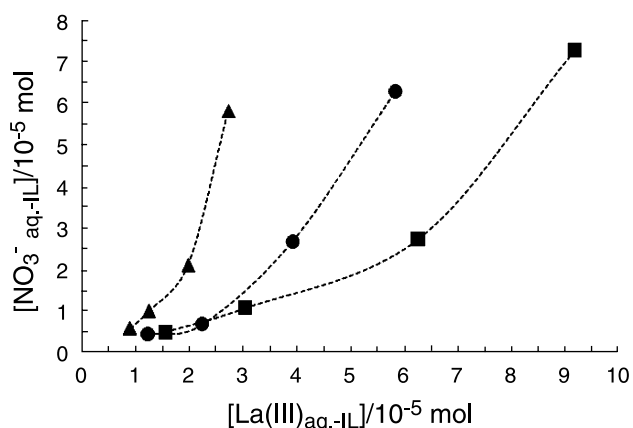
for  $\text{La}(\text{NO}_3)_3$  and  $\text{LaCl}_3$  systems should give the straight line with slope of nearly 3. This difference from the experimental results is considered to be due to the fact that the transfer of the  $[\text{bmi}]^+$  cation from IL to the aqueous phase is diminished by its hydrophobicity.

Based on these results, it is supposed that the plots of  $[\text{pmi}]_{\text{pmiNfO} \rightarrow \text{aq.}}^+$  or  $[\text{hmi}]_{\text{hmiNfO} \rightarrow \text{aq.}}^+$  vs.  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{pmiNfO}}$  or  $\text{hmiNfO}$  for the extraction of  $\text{La}(\text{III})$  species from the aqueous to  $[\text{pmi}][\text{NfO}]$  or  $[\text{hmi}][\text{NfO}]$  phase give smaller slopes than that for the  $[\text{bmi}][\text{NfO}]$  system. Figure 6 shows such plots for the extraction experiments using the aqueous solution of  $\text{La}(\text{NO}_3)_3$  and  $[\text{pmi}][\text{NfO}]$  or  $[\text{hmi}][\text{NfO}]$ . As expected, the slopes are 1.45 for  $[\text{pmi}][\text{NfO}]$  system and 1.39 for  $[\text{hmi}][\text{NfO}]$  one.

These results also support that the extraction mechanism of metal ions from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , or  $[\text{hmi}][\text{NfO}]$  phase is a cation exchange.

#### Distribution Behavior of $\text{NO}_3^-$ between IL and Aqueous Phases

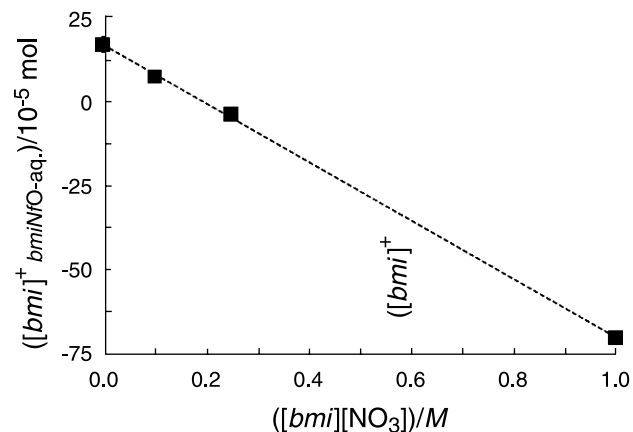
We also examined the distribution behavior of  $\text{NO}_3^-$  in the extraction of  $\text{La}(\text{III})$  species from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , or  $[\text{hmi}][\text{NfO}]$  phase. Figure 7 shows the plot of the mole number ( $\text{NO}_3^-_{\text{aq.} \rightarrow \text{IL}}$ ) of  $\text{NO}_3^-$  transferred from the aqueous to the IL phase against  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{IL}}$  for  $\text{La}(\text{NO}_3)_3$  system. As seen from this figure, the  $\text{NO}_3^-_{\text{aq.} \rightarrow \text{IL}}$  values increase with an increase in  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{IL}}$



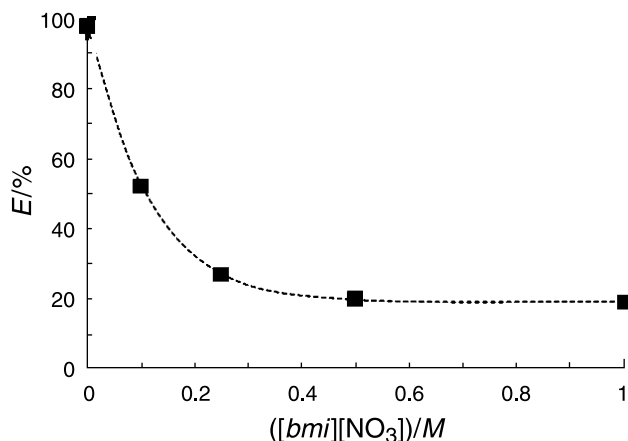
**Fig. 7.** Plots of  $\text{NO}_3^-_{\text{aq.} \rightarrow \text{IL}}$  vs.  $\text{La}(\text{III})_{\text{aq.} \rightarrow \text{IL}}$  for the extraction of  $\text{La}(\text{III})$  species from the aqueous to the IL phase. ■: IL =  $[\text{bmi}][\text{NfO}]$ ; ●: IL =  $[\text{pmi}][\text{NfO}]$ ; ▲: IL =  $[\text{hmi}][\text{NfO}]$

and the slopes become steeper in the order of  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , and  $[\text{hmi}][\text{NfO}]$ . This means that  $\text{NO}_3^-$  species are transferred from the aqueous to the IL phase accompanied by the extraction of  $\text{La}(\text{III})$  and that the  $\text{La}(\text{III})$  species with +2 or +3 charge are not easily extracted to hydrophobic IL,  $[\text{hmi}][\text{NfO}]$ . This tendency is consistent with the phenomenon that the  $E$  values decrease with an increase in hydrophobicities of imidazolium cations as mentioned above.

These results suggest that the metal ions from the aqueous to the  $[\text{bmi}][\text{NfO}]$ ,  $[\text{pmi}][\text{NfO}]$ , or  $[\text{hmi}][\text{NfO}]$  phase are not extracted only by the cation exchange mechanism, that is, even non-charged species can be extracted into the IL phases. In order to confirm the validity of this speculation, we examined the extraction behavior of  $\text{La}(\text{III})$  species under the condition, where the  $[\text{bmi}]^+$  cations exist in equilibrium between aqueous and  $[\text{bmi}][\text{NfO}]$  phases. Such a condition was found by examining the distribution behavior of  $[\text{bmi}]^+$  between the  $[\text{bmi}][\text{NfO}]$  phase and the aqueous solutions containing appropriate amounts of  $[\text{bmi}][\text{NO}_3]$ . Figure 8 shows the plot of the  $[\text{bmi}]_{\text{bmiNfO} \rightarrow \text{aq.}}^+$  values against the concentration of  $[\text{bmi}][\text{NO}_3]$  in aqueous solutions. The  $[\text{bmi}]_{\text{bmiNfO} \rightarrow \text{aq.}}^+$  value is found to be zero at around  $([\text{bmi}][\text{NO}_3]) = 0.2 M$ . This means that at around  $([\text{bmi}][\text{NO}_3]) = 0.2 M$  the distribution of  $[\text{bmi}]^+$  cations is in equilibrium and that the transfer of  $[\text{bmi}]^+$  cations between the two phases does not occur. Hence, we examined the extraction behavior of  $\text{La}(\text{III})$  species from the aqueous solution contain-



**Fig. 8.** A plot of  $[\text{bmi}]_{\text{bmiNfO} \rightarrow \text{aq.}}^+$  vs.  $([\text{bmi}][\text{NO}_3])$  for the extraction of  $[\text{bmi}]^+$  from the aqueous solution containing  $[\text{bmi}][\text{NO}_3]$  to the  $[\text{bmi}][\text{NfO}]$  phase



**Fig. 9.** A plot of  $E$  values vs.  $([bmi][NO_3])$  for the extraction of La(III) species from the aqueous solution containing  $[bmi][NO_3]$  of various concentrations to the  $[bmi][NfO]$  phase.  $[La(III)] = 5.0 \times 10^{-3} M$

ing  $[bmi][NO_3]$  of various concentrations to the  $[bmi][NfO]$  phase. If the extraction of La(III) species proceeds only by the cation exchange mechanism, the  $E$  value should be zero in the aqueous solution containing  $[bmi][NO_3]$  of 0.2 M. Figure 9 shows the plot of  $E$  values vs.  $([bmi][NO_3])$ . The  $E$  values are found to be approximately 30% even at  $([bmi][NO_3]) = 0.2 M$ . This indicates that the even non-charged La(III) species are extracted from the aqueous to the  $[bmi][NfO]$  phase and that the extraction of metal ions from the aqueous to the  $[bmi][NfO]$ ,  $[pmi][NfO]$ , or  $[hmi][NfO]$  phase is not ascribed to only the cation exchange mechanism.

## Conclusion

We studied the extraction behavior of various metal ionic species [Li(I), Na(I), Cs(I), Ca(II), Sr(II), Ln(III)] from the aqueous solution to the hydrophobic ILs,  $[bmi][NfO]$ ,  $[pmi][NfO]$ , or  $[hmi][NfO]$ . As a result, the following phenomena were observed.

- Cations are extracted into  $[bmi][NfO]$  phase without using extractants.
- Cations with large hydrated radii are more effectively extracted into the  $[bmi][NfO]$ ,  $[pmi][NfO]$ , or  $[hmi][NfO]$  phase.
- The  $E$  values of La(III) decrease remarkably from 97% to 38% with an increase in  $[HNO_3]$  in aqueous solutions, and also decrease with an increase in hydrophobicities of ILs, *i.e.*,  $[bmi][NfO] > [pmi][NfO] > [hmi][NfO]$ .

- The amount of La(III) transferred into  $[bmi][NfO]$  phase increases linearly with an increase in that of  $[bmi]^+$  transferred into aqueous phase, and the slope of such a linear plot is almost 2.
- The  $E$  values are approximately 30% even at  $([bmi][NO_3]) = 0.2 M$ , where the  $[bmi]^+$  cations exist in equilibrium between aqueous and  $[bmi][NfO]$  phases and hence do not transfer between two phases.

From these results, it is proposed that the extraction of metal ionic species from the aqueous to the  $[bmi][NfO]$ ,  $[pmi][NfO]$ , or  $[hmi][NfO]$  phase proceeds through mainly the cation exchange between two phases with the partial transfer of non-charged species.

## Experimental

### Synthesis of Ionic Liquids

Ionic liquids (ILs) used in the present study,  $[bmi][NfO]$ ,  $[pmi][NfO]$ , and  $[hmi][NfO]$ , were synthesized by a conventional method. As a typical example,  $[bmi][NfO]$  was synthesized as follows: 1-Butyl-3-methylimidazole (41.05 g, 0.5 mol) was dissolved in 150 cm<sup>3</sup> tetrahydrofuran (THF) and stirred vigorously. Then, 82.2 g 1-bromobutane (0.6 mol) were dropwise added during 1 h and the resulting solution was refluxed for 3 h. After refluxing, the THF phase was separated and stirred with 100 cm<sup>3</sup> ethyl acetate (EA). Crude  $[bmi][Br]$  was obtained by removing THF and EA *in vacuo*. The crude  $[bmi][Br]$  (92 g, 0.4 mol) was dissolved into distilled water and stirred vigorously. To this solution 135.2 g KNfO (0.4 mol) were added. The resulting solution was refluxed for 7 h at 70°C with stirring. The  $[bmi][NfO]$  phase was separated from the aqueous phase, and mixed with activated carbon for removing organic impurities. After filtration, the filtrate was mixed with distilled water for stripping inorganic impurities. This washing procedure was repeated 10–16 times. The more hydrophobic ILs,  $[pmi][NfO]$  and  $[hmi][NfO]$ , were also synthesized in a similar manner as mentioned above.

The hydrophilic IL,  $[bmi][NO_3]$ , was prepared by adding AgNO<sub>3</sub> to the  $[bmi][Br]$  aqueous solution, followed by removing AgBr precipitates.

### Extraction Experiments

Extraction experiments were carried out by using the conventional batchwise extraction method. Aqueous solutions were prepared by dissolving an appropriate amount of metal nitrate or chloride into the distilled water. Aqueous solution (3 cm<sup>3</sup>) and IL ( $[bmi][NfO]$ ,  $[pmi][NfO]$ , or  $[hmi][NfO]$ , 3 cm<sup>3</sup>) saturated with water were charged into a 10 cm<sup>3</sup> bottle with a screw cap. The two phases were mixed by using a vortex mixer at constant temperature (295 or 298 K). After mixing for an appropriate time, the aqueous and IL phases were centrifuged and each phase was with-

drawn carefully. Then, concentrations of the metal ionic species in the aqueous phase were measured, and the extraction ratio ( $E/\%$ ) and the distribution ratio ( $D$ ) were evaluated using following equations:

$$E = C_i V_i / (C_w V_w + C_i V_i) \times 100, \quad D = E / (100 - E) (V_w / V_i)$$

where  $V_w$  and  $V_i$  are the volume of aqueous and IL phases, and  $C_w$  and  $C_i$  are the concentrations of metal ionic species in aqueous and IL phases. The error in  $E$  values is typically  $\pm 2\%$  in our experiments.

#### Analysis of Chemical Species

The concentrations of Ca(II), Sr(II), and Ln(III) species in aqueous phases were measured by using ICP-AES (Perkin Elmer Optima3000), and those of Li(I), Na(I), and Cs(I) species were analyzed with Atomic absorption spectrophotometer (Shimadzu AA-6650).

The amounts of  $\text{NO}_3^-$  and  $\text{Cl}^-$  distributed from the aqueous to the IL phase were evaluated by measuring the concentrations of these anions in the aqueous phases before and after extraction by means of an ion chromatographic method (Toso IC-2001). In this analysis, the solution prepared by mixing  $\text{H}_3\text{BO}_4$  (9.28 g),  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (2.29 g), and  $\text{NaHCO}_3$  (17 mg) with ion exchanged water ( $1000 \text{ cm}^3$ ) was used as an eluent.

The concentrations of  $[\text{bmi}]^+$ ,  $[\text{pmi}]^+$ ,  $[\text{hmi}]^+$ , and  $[\text{NfO}]^-$  distributed into the aqueous phases were measured by using  $^1\text{H}$  and  $^{19}\text{F}$  NMR (JEOL JNM-L300WB) as follows. The separated aqueous phase ( $0.5 \text{ cm}^3$ ) was mixed with sodium acetate solution (50 mM,  $0.3 \text{ cm}^3$ ) and used for  $^1\text{H}$  NMR measurements. The concentrations of  $[\text{bmi}]^+$ ,  $[\text{pmi}]^+$ , and  $[\text{hmi}]^+$  were evaluated from the area ratios of  $^1\text{H}$  NMR signals of these cations to the  $-\text{CH}_3$  signal of acetate. The sample solutions for measuring concentrations of  $[\text{NfO}]^-$  were prepared by mixing the aqueous phase with sodium trifluoroacetate. The concentrations of  $[\text{NfO}]^-$  were obtained from the area ratio of  $^{19}\text{F}$  NMR signal of  $[\text{NfO}]^-$  to the  $-\text{CF}_3$  peak of trifluoroacetate.

The content of water in ILs was measured using Karl Fisher method (Mitsubishi Moisturemeter Model CA-02).

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