Introduction

Liquid–liquid extraction is now widely used in industrial and analytical fields for the separation and purification of metal ions. However, in conventional solvent extraction, toxic and/or volatile diluents are commonly employed. In recent years, industrial wastes and scrap such as spent TV displays, fluorescent lamps, batteries, and cellular phones have been highlighted as valuable secondary resources of rare metals. Therefore a highly efficient separation technique for the recovery of these metals from such potentially complex mixtures is required (Nakamura et al., 2007; Kubota et al., 2009; Li et al., 2009; Pranolo et al., 2010).

Growing attention has recently focused on room temperature ionic liquids (ILs) as alternatives to conventional organic solvents (Huddleston et al., 2001; Anderson et al., 2002; Rogers and Seddon, 2002; Zhao et al., 2005; Kubota and Goto, 2006; Plechko and Seddon, 2008; Liu et al., 2009; Sun and Armstrong, 2010). ILs, which are molten salts generally composed of organic cations and various anions, have unique properties such as high thermal stability, negligible vapor pressure, and nonflammability, and are thus regarded as eco-friendly solvents. Their greatest appeal is that their physicochemical properties such as polarity, viscosity, density, and affinity with other solvents are extensively tunable by varying the combination of cationic and anionic partners (Huddleston et al., 2001; Anderson et al., 2002). Water immiscible ILs have a variety of potential applications in separation science as well as in metal ion separation (Zhao et al., 2005; Kubota and Goto, 2006; Liu et al., 2009; Sun and Armstrong, 2010). Since Dai et al. (1999) first reported that the use of ILs as extraction diluents for metal ions offered significant improvements in extraction efficiency, IL-based extraction systems for metal ions have been intensively investigated using several conventional commercial extractants. The use of dicyclohexano-18-crown-6 (DC18C6) as an extractant in imidazolium-based ILs significantly improves the extraction efficiency for Sr2+ compared to that in a traditional organic solvent system. Enhancement
of the extractability of lanthanides and selectivity among the metal ions with octyl(phenyl)-N,N-diisobutylcarbamoylethyl phosphate oxide (CMPO) has also been demonstrated in IL systems (Nakashima et al., 2003, 2005; Visser and Rogers, 2003). Although ILs have a number of advantages as extracting solvents, there have been limitations to their practical use, imposed by the difficulty in finding a suitable soluble extractant. While neutral extractants such as DC18C6 and CMPO are readily soluble in ILs, their behavior in IL systems is different from that in organic solvents. This change causes the loss of ILs to the aqueous phase and also complicates the recovery of the metal ions from the IL phase (Dietz and Dzielawa, 2001; Visser and Rogers, 2003; Nakashima et al., 2005). Extraction of metal ions with a typical chelating β-diketone such as thenoyltrifluoroacetone (HTTA) has also been associated with the release of IL constituents to the aqueous phase (Jensen et al., 2003; Kidani et al., 2008), although such proton-exchange-type extractants enable effective stripping of the metal ions from the ILs by controlling the pH value of the aqueous phase. The proton exchange-type organophosphorus extractants, bis(2-ethylhexyl)phosphoric acid (DEHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88 A), show similar proton-exchange equilibria for metal ions such as UO$_2^{2+}$, Am$^{3+}$, and the rare earth metals in ILs as in conventional organic solvents (Cocalia et al., 2005; Kubota et al., 2008); however, previous researchers did not achieve high recovery of the metal ions due to their poor solubility in the ILs. Significant efforts have been devoted to develop a novel extractant suitable for ILs, enabling ILs to be exploited for metal recovery (Luo et al., 2004; Shimojo and Goto, 2004; Shimojo et al., 2009).

Recently, we reported that an advanced liquid membrane extraction system for rare earth metals using ILs could be developed by employing the newly synthesized imidazolium-based ILs (Shimojo, 2007; Kubota et al., 2008). The commercial extractant Versatic 10, a tertiary-branched carboxylic acid, was kindly supplied by Japan Epoxy Resin Co., Ltd. (now Mitsubishi Chemical Co.). All other chemicals were of reagent grade.

1. Experimental

1.1 Reagents

The extractant DODGAA shown in Figure 1 was synthesized from diglycolic anhydride and dioctylamine as described previously (Naganawa et al., 2007; Shimojo et al., 2007). ILs—1-ethyl-, 1-butyl-, 1-octyl-, and 1-dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (abbreviated as [C$_n$ mim][Tf$_2$ N], $n = 2, 4, 8, 12$)—were synthesized as described previously (Kubota et al., 2008). The commercial extractant Versatic 10, a tertiary-branched carboxylic acid, was kindly supplied by Japan Epoxy Resin Co., Ltd. (now Mitsubishi Chemical Co.). All other chemicals were of reagent grade.

1.2 Extraction procedure

Extraction equilibrium studies were performed by the conventional extraction method. Extracting phases were prepared by dissolving the extractant DODGAA in the ILs, or in n-dodecane containing 5 vol% 1-octanol as a solubilizer (Shimojo et al., 2007). Aqueous solutions containing 0.1 mol/m$^3$ metal ions were prepared by dissolving nitrate salts of Y$^{3+}$, Eu$^{3+}$ and Zn$^{2+}$ in 100 mol/m$^3$ nitric acid and 100 mol/m$^3$ sodium acetate solutions. The pH values of the aqueous solutions were adjusted by mixing these aqueous solutions in appropriate ratios. Equal volumes (2 cm$^3$) of the aqueous and organic solutions were mixed in a sealed glass tube and gently shaken at 298 K to attain equilibrium. After phase separation, the concentrations of the metal ions in the aqueous phase were measured with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima 5300, Perkin Elmer Co.). Stripping of the metal ions from the extracting phase using nitric acid solution was also examined. The extraction and stripping degrees of the metal ions, $E$ [—] and $E'$ [—] were calculated by the following equations:

$$E = \frac{[M]_{aq,0} - [M]_{aq}}{[M]_{aq,0}} \quad (1)$$

$$E' = \frac{[M]_{aq,strip}}{[M]_{IL,0}} \quad (2)$$

2. Results and Discussion

2.1 Extraction behavior of metal ions in ionic liquid systems

The extraction behavior of metal ions (Y$^{3+}$, Eu$^{3+}$, and Zn$^{2+}$) in ILs with DODGAA is shown in Figure 2.
as a function of the equilibrium pH in the feed aqueous phases. A control n-dodecane system is also shown. The degree of extraction, $E$, for $Y^{3+}$ and $Eu^{3+}$ increased with increasing pH in the IL systems as well as the n-dodecane system. The results suggest that the metal extraction into ILs proceeds via proton exchange from the extractants for the metal ions, similar to the n-dodecane system. For the three ILs with different alkyl chain lengths in the imidazolium cation, the extraction efficiency for $Y^{3+}$ and $Eu^{3+}$ increased in the $[C_4\text{mim}][\text{Tf}_2\text{N}] > [C_8\text{mim}][\text{Tf}_2\text{N}] > [C_{12}\text{mim}][\text{Tf}_2\text{N}]$ and was greatly enhanced in the $[C_4\text{mim}][\text{Tf}_2\text{N}]$ compared to that in the n-dodecane system. Although DODGAA is a proton-dissociation-type extractant with a carboxyl group, it was readily soluble in all the ILs tested, even in $[C_4\text{mim}][\text{Tf}_2\text{N}]$. This solubility was not observed for the proton-dissociation-type extractants PC-88A and D2EHPA. Moreover, the metal ions were effectively stripped in a manner identical to that in the case of the organic solvent system. The high solubility of DODGAA in polar ILs was assumed to be due to the polar nature of the oxygen-containing core of the molecule. The related alkyl monocarboxylic acid, Versatic 10, was less soluble in ILs. The solubility of DODGAA was higher in ILs with longer imidazolium cation alkyl substituents, similar to what has been observed for PC-88A (Kubota et al., 2008) and Versatic 10.

A precipitate, perhaps the insoluble DODGAA-metal complex, appeared at the water-IL interface at equilibrium in the $[C_2\text{mim}][\text{Tf}_2\text{N}]$ system. The extraction ability of the solvents mentioned above was considered to depend on the partitioning property of the extractant in the aqueous and organic phases and the solubility of the extracted metal complex. The extraction ability may also be to the result of a peculiar solvent effect of the ionic liquids. Further detailed investigations are required.

Whereas quantitative extraction was achieved for $Y^{3+}$ and $Eu^{3+}$ with DODGAA (as shown in Figure 2), no $Zn^{2+}$ was extracted into any extraction phases under the present experimental conditions. The high extractability and selectivity for the rare earth metal ions against $Zn^{2+}$ can be attributed to the putative tridentate diglycol amic acid frame because as shown in Figure 3, the extractabilities of $Y^{3+}$ and $Eu^{3+}$ were as low as that of $Zn^{2+}$ when Versatic 10 was used. It was demonstrated that the extractant DODGAA was useful for the recovery of rare earth metals from the leaching solution of electronic wastes such as fluorescent materials, even in the presence of a large amount of base metal such as $Zn^{2+}$.

A compound having a structure similar to DODGAA, $N,N,N',N'$-tetra(n-octyl)-diglycolamide (TODGA) (which is a neutral tridentate ligand with two carbamoyl groups connected by an ether chain), has also been reported to exhibit a high affinity for rare earth metals (Shimojo et al., 2008). Since the proton of DODGAA cannot dissociate in highly acidic conditions, DODGAA may react as a neutral tridentate extractant like TODGA for metal ions in the aqueous phase at high acid concentrations. Thus, the extraction behavior of DODGAA was also examined for a high nitric acid concentration range in the aqueous phase. At nitric acid concentrations between 0.5 mol/dm$^3$ and 5 mol/dm$^3$, $Y^{3+}$ and $Eu^{3+}$ were not extracted as well as $Zn^{2+}$ into either the organic solvent or the IL systems.

Figure 4 shows the stripping behavior of $Y^{3+}$ and $Eu^{3+}$ from $[C_4\text{mim}][\text{Tf}_2\text{N}]$ to nitric acid solutions. The metal ions were readily stripped with nitric acid and quantitative recovery was achieved at concentrations of nitric acid above 0.5 mol/dm$^3$. On the basis of the results of extraction and stripping experiments, it was confirmed that DODGAA was an acidic extractant and that it extracted the metal ions exclusively via a proton ex-
change mechanism, maintaining the mass balance of metal ions between the aqueous and IL phases.

### 2.2 Extraction mechanism of rare earth metal ions with DODGAA

In the IL system, neutral extractants such as CMPO, DC18C6, and also TODGA are known to extract metal ions by a mechanism different from that occurring in organic solvents (Dietz and Dzielawa, 2001; Nakashima et al., 2005; Shimojo et al., 2008). That is, metal ions are extracted into ILs without the co-extraction of counterions such as nitrate, from the aqueous phase. Instead, the imidazolium cations are released to the aqueous phase, as demonstrated by a decrease in the extractability of metal ions with increasing concentration of C4mim+/H11001 doped into the aqueous phase (Nakashima et al., 2005). In the present study with DODGAA, the extraction performance for Y3+/H11001 and Eu3+/H11001 was not affected by the addition of C4mim+/H11001 to the aqueous feed phase, indicating that metal transfer with DODGAA into ILs does not involve C4mim+/H11001 exchange.

Slope analysis of the distribution ratio \( D (= [M]_{\text{ext}}/[M]_{\text{aq}}) \) was performed as a function of the equilibrium pH and concentration of DODGAA. As shown in Figure 5(a), straight lines with slope 3 were obtained from the plots of \( \log D \) against pH for the IL system as well as for the n-dodecane system. Therefore, three protons were released to the aqueous phase for the extraction of one metal ion. The plots of \( \log D \) versus \( \log [\text{DODGAA}] \) also gave straight lines with a slope of 3 for both systems, as shown in Figure 5(b). These results suggest that the extraction equilibrium equation for Y3+ and Eu3+ with DODGAA (HR) is as follows:

\[
M^{3+} + 3HR_{\text{ext}} = MR_{3,\text{ext}} + 3H^+ \quad (3)
\]

Some alkyl monocarboxylic acids such as Versatic 10 exist as dimers in organic solvents; the rare earth metals are extracted with such dimers \((HR)_{2}\) as follows (Dupreez and Preston, 1992):

\[
M^{3+} + 3(HR)_{2,\text{org}} = MR_{3,\text{org}} + 3H^+ \quad (4)
\]

A linear dependency of slope 3 should also be obtained for the log plots of \( D \) versus the concentration of the extractant dimer when the metal ion forms a 1 : 3 complex with the dimers. It seems to be difficult for DODGAA to dimerize in polar diluents such as ILs. However, in order to confirm the extraction stoichiometry in ILs, a loading test was conducted for Y3+. Equal volumes of the IL phase containing 6 mol/m³ DODGAA and aqueous phases with varying Y3+ concentrations were equilibrated. The results, shown in Figure 6, demonstrated
that the molar ratio of the initial DODGAA concentration to the loaded Y$_3$/H$_{11001}$ concentration approached a constant value of 3 with increasing Y$_3$/H$_{11001}$ concentration in the aqueous phase. This result supports the idea that Y$_3$/H$_{11001}$ and Eu$_3$/H$_{11001}$ were extracted to the organic phase as 1 : 3 complexes with monomer DODGAA as described in Eq. (3). The equilibrium constant of Eq. (3), $K_{ex}$, is defined as follows:

$$K_{ex} = \frac{[M]_{eq}[HR]^3}{[M]_{aq}[H]^3}$$  \hspace{1cm} (5)

Rewriting Eq. (5) using the definition of $D$ gives:

$$\log D = \log K_{ex} + 3 \log [HR] + 3 \log H$$

As shown in Figure 7, the plots of log $D$ versus log ([DODGAA]/[H]) give straight lines with slope 3 for Y$^{3+}$ and Eu$^{3+}$ in the organic and IL systems. The values of $K_{ex}$ determined from the data in Figure 7 are listed in Table 1. The extraction performance of DODGAA for rare earth metals was enhanced by a factor of 80 in the [C$_4$ mim][Tf$_2$N] system relative to the conventional organic solvent, n-dodecane. The metal extraction was found to proceed via a proton exchange mechanism in both the ILs and in the organic solvent. Metal stripping from the IL phase was easily accomplished with an acid solution such as 1 mol/dm$^3$ HNO$_3$, Y$^{3+}$ (Black), Eu$^{3+}$ (gray).

Table 1 Equilibrium constants for rare earth metals with DODGAA in ionic liquids and n-dodecane systems (298 K)

<table>
<thead>
<tr>
<th>Solvents</th>
<th>[C$_4$ mim][Tf$_2$N]</th>
<th>[C$_8$ mim][Tf$_2$N]</th>
<th>[C$_{12}$ mim][Tf$_2$N]</th>
<th>n-dodecane, 5 vol% octanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{ex}$</td>
<td>Y</td>
<td>9.48 × 10$^2$</td>
<td>2.79</td>
<td>2.86 × 10$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Eu</td>
<td>4.06 × 10$^2$</td>
<td>1.78</td>
<td>2.45 × 10$^{-1}$</td>
</tr>
</tbody>
</table>

Fig. 7 Plots of log $D$ versus log ([DODGAA]/[H]). Metal ions: Y$^{3+}$ (filled symbols), Eu$^{3+}$ (open symbols); solvents: [C$_4$ mim] (circle), [C$_8$ mim] (diamond), [C$_{12}$ mim] (square), n-dodecane (triangle); [M]$_{aq}$ = 0.1 mol/m$^3$

2.3 Recyclability of ionic liquid and the recovery of rare earth metals

The reuse of the ILs for recycling the extracting phase was examined. After the extraction of rare earth metal ions of 0.1 mol/m$^3$ each into [C$_4$ mim][Tf$_2$N] with 15 mol/m$^3$ DODGAA, the metal ions were quantitatively stripped from the extracting phase into 1 mol/dm$^3$ nitric acid solution. The IL phase that was separated from the stripping aqueous phase was reused as the extracting phase for the next fresh feed aqueous solution. The extraction and stripping processes were repeated three times. As shown in Figure 8, no decline in the extraction efficiency of the extracting phase was observed, and quantitative recovery was achieved after the third stage. These results demonstrate that ILs can be reused as the extracting phase in aqueous/IL extraction.

Conclusion

For the application of ILs to the extraction separation of rare earth metal ions, alkyl monocarboxylic acid DODGAA was employed as an extractant. DODGAA was readily dissolved in imidazolium-based ILs, and quantitative transfer of Y$^{3+}$ and Eu$^{3+}$ to [C$_n$ mim][Tf$_2$N] ($n = 4, 8, 12$) was achieved. High extraction performance was observed for the metal ions when ILs having shorter alkyl chains in the imidazolium cation were used, and the extraction performance in [C$_4$ mim][Tf$_2$N] was far superior to that in the conventional organic solvent, n-dodecane. The metal extraction was found to proceed via a proton exchange mechanism in both the ILs and in the organic solvent. Metal stripping from the IL phase was easily accomplished with an acid solution such as
nitric acid, and the reusability of the IL phase was demonstrated. DODGAA displayed selective behavior, with high affinity for rare earth metal ions and no extraction of the base metal Zn\(^{2+}\) under the experimental conditions used. These results suggest that the IL-based extraction system should be applicable to the recovery of rare earth metals from waste solutions derived from industrial or post-consumer refuse.

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Literature Cited