Application of Ionic Liquids to Extraction Separation of Rare Earth Metals with an Effective Diglycol Amic Acid Extractant

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The application of ionic liquids as alternatives to conventional organic solvents in extraction processes has been actively investigated. A crucial step towards the practical use of ionic liquids is the development of extractants that work effectively within these new media. In the present study, the extraction separation of rare earth metals into ionic liquids, 1-butyl, 1-octyl, and 1-dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_n\text{mim}][Tf_2N]$, $n = 4, 8, 12$), was performed using a novel extractant, *N,N*-dioctyldiglycol amic acid (DODGAA). Quantitative extraction of metal ions such as Y^{3+} and Eu^{3+} was selectively achieved in the presence of the base metal ion Zn^{2+}, which was not extracted at all under the present experimental conditions. The extraction efficiency was enhanced for the shorter-alkyl-chain imidazolium ionic liquid $[C_4\text{mim}][Tf_2N]$ compared to that for a conventional organic solvent system. Extraction mechanism studies elucidated that the metal extraction proceeds via proton exchange reactions between DODGAA and the metal ions in the ionic liquid (the same mechanism as in the conventional organic solvent). The stripping reaction, or recovery, of the metal ions from the extracting phase was readily accomplished with an acid solution such as nitric acid.

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; Plechkova 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 and analytical chemistry as separation media (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 Sr^{2+} compared to that the use in a traditional organic solvent system. Enhancement

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of the extractability of lanthanides and selectivity among the metal ions with octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine 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 (D2EHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88 A), show similar proton-exchange equilibria for metal ions such as UO^{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 *N*,*N*-dioctyldiglycol amic acid (DODGAA) as an extractant (Kubota *et al.*, 2010). The liquid membrane system is the most feasible technology for the application of expensive ILs as extraction media because only a small amount of solvent is used within the membrane. DODGAA, which is an anionic ligand having a carbamoyl and a carboxyl group connected by an ether chain, can be prepared with relative ease from a commercially available starting reagent (Naganawa *et al.*, 2007; Shimojo *et al.*, 2007). In the present study, we investigated the extraction behavior of rare earth metals with DODGAA in imidazolium-based ILs and elucidated the extraction mechanism. The application of ILs to the separation and recovery of rare earth metals (yttrium (Y) and europium (Eu)) from base metals such as zinc (Zn) was examined as a model case for the recovery of valuable metals. These metals are the main components of the waste fluorescent materials in used TV tubes (Kubota *et al.*, 2001).

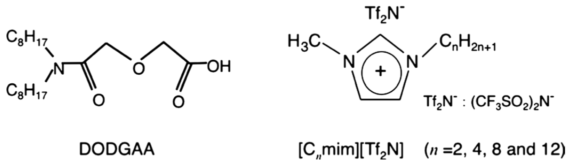


Fig. 1 Molecular structures of extractant DODGAA and imidazolium-based ILs (Shimojo *et al.*, 2007; Kubota *et al.*, 2010)

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 $[C_n\text{mim}][Tf_2N]$, $n = 2, 4, 8, 12$)—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:

$$E = ([\mathrm{M}]_{\mathrm{aq},0} - [\mathrm{M}]_{\mathrm{aq}}) / [\mathrm{M}]_{\mathrm{aq},0} \tag{1}$$

$$E' = [\mathrm{M}]_{\mathrm{aq,strip}} / [\mathrm{M}]_{\mathrm{IL},0} \tag{2}$$

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**

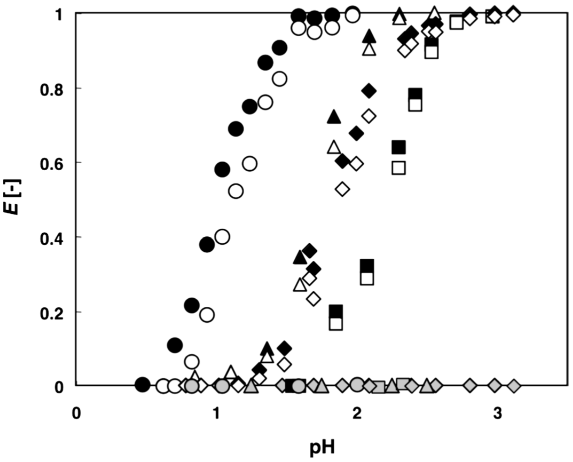


Fig. 2 Extraction behavior of metal ions with DODGAA in IL and *n*-dodecane systems. $[M]_i = 0.1\ \mathrm{mol/m^3}$, $[\mathrm{DODGAA}] = 10\ \mathrm{mol/m^3}$; metal ions: Y^{3+} (filled symbols), Eu^{3+} (open symbols), Zn^{2+} (gray symbols); solvents: $[C_4mim]$ (circle), $[C_8mim]$ (diamond), $[C_{12}mim]$ (square), *n*-dodecane (triangle)

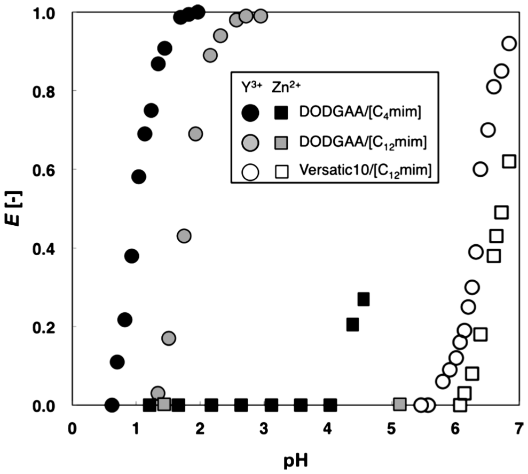


Fig. 3 Comparison of extractability and selectivity for metal ions between DODGAA and Versatic 10. $[M]_i = 0.1\ \mathrm{mol/m^3}$, $[\mathrm{Extractant}] = 10\ \mathrm{mol/m^3}$

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 $[C_4mim] > [C_8mim] > [C_{12}mim]$ and was greatly enhanced in the $[C_4mim][Tf_2N]$ 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 $[C_2mim][Tf_2N]$. This solubility was not observed for the proton-dissociation-type extractants PC-88 A 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 $[C_2mim][Tf_2N]$ 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 $0.5\ \mathrm{mol/dm^3}$ and $5\ \mathrm{mol/dm^3}$, 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 $[C_4mim][Tf_2N]$ to nitric acid solutions. The metal ions were readily stripped with nitric acid and quantitative recovery was achieved at concentrations of nitric acid above $0.5\ \mathrm{mol/dm^3}$. 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-

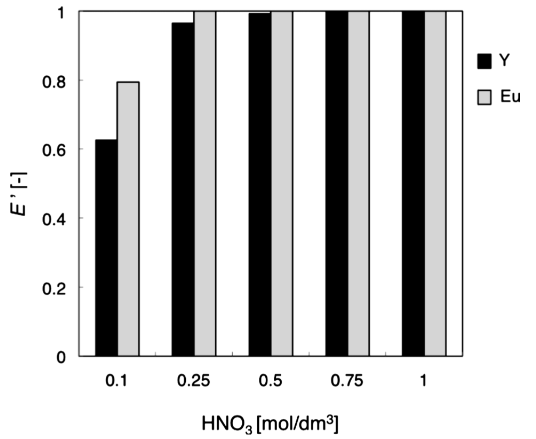


Fig. 4 Stripping behavior of metal ions from IL phase ([C$_4$mim][Tf$_2$N]) with nitric acid. $[M]_{IL,0} = 0.1$ mol/m^3, $[DODGAA]_{IL} = 10$ mol/m^3

change mechanism, maintaining the mass balance of metal ions between the aqueous and IL phases.

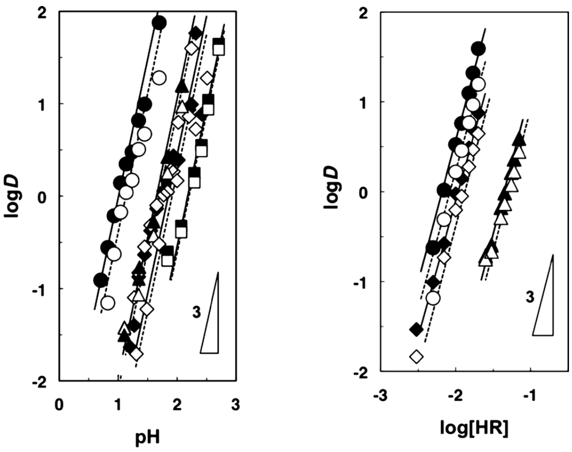
2.2 Extraction mechanism of rare earth metal ions with DODGAA

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 C$_4$mim$^+$ doped into the aqueous phase (Nakashima *et al.*, 2005). In the present study with DODGAA, the extraction performance for Y^{3+} and Eu^{3+} was not affected by the addition of C$_4$mim$^+$ to the aqueous feed phase, indicating that metal transfer with DODGAA into ILs does not involve C$_4$mim$^+$ exchange.

Slope analysis of the distribution ratio D ($= [M]_{ext} / [M]_{aq}$) 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 [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 Y^{3+} and Eu^{3+} with DODGAA (HR) is as follows:

$$M^{3+} + 3HR_{ext} = MR_{3,ext} + 3H^+ \tag{3}$$

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):



(a) (b)

Fig. 5 Slope analysis for extraction of rare earth metals. (a) log D versus pH. (b) log D versus DODGAA concentration [HR]. 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); $[M]_i = 0.1$ mol/m^3. (a) [DODGAA] = 10 mol/m^3, (b) pH: 1.2 ([C$_4$mim]), 1.8 ([C$_8$mim]), 1 (*n*-dodecane)

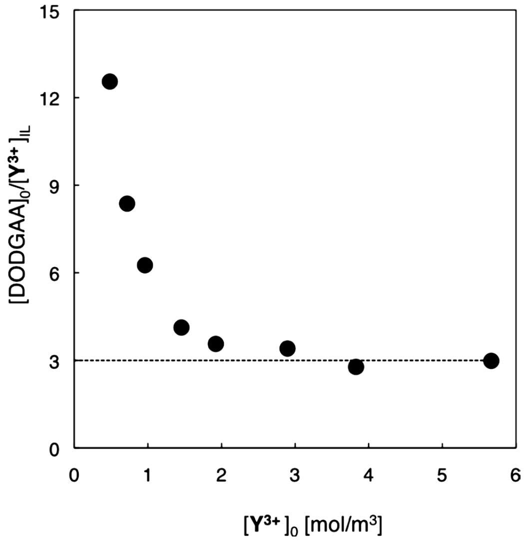


Fig. 6 Loading test for Y^{3+} on DODGAA in [C$_8$mim][Tf$_2$N]. [DODGAA] = 6 mol/m^3, pH = 5.2

$$M^{3+} + 3(HR)_{2,org} = MR_3 3HR_{org} + 3H^+ \tag{4}$$

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 Y^{3+}. Equal volumes of the IL phase containing 6 mol/m^3 DODGAA and aqueous phases with varying Y^{3+} concentrations were equilibrated. The results, shown in **Figure 6**, demonstrated

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

Solvents		$[C_4mim][Tf_2N]$	$[C_8mim][Tf_2N]$	$[C_{12}mim][Tf_2N]$	*n*-dodecane, 5 vol% octanol
K_{ex}	Y	9.48×10^2	2.79	2.86×10^{-1}	1.12×10^1
	Eu	4.06×10^2	1.78	2.45×10^{-1}	8.15

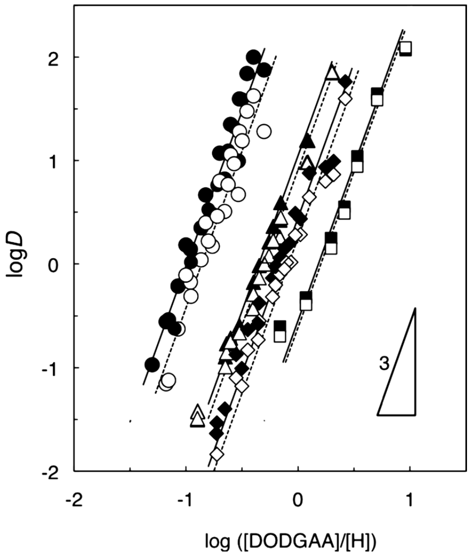


Fig. 7 Plots of log *D* versus log([DODGAA] / [H]). Metal ions: Y^{3+} (filled symbols), Eu^{3+} (open symbols); solvents: $[C_4mim]$ (circle), $[C_8mim]$ (diamond), $[C_{12}mim]$ (square), *n*-dodecane (triangle); $[M]_i = 0.1\ mol/m^3$

that the molar ratio of the initial DODGAA concentration to the loaded Y^{3+} concentration approached a constant value of 3 with increasing Y^{3+} concentration in the aqueous phase. This result supports the idea that Y^{3+} and Eu^{3+} 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:

$$K_{ex} = [M]_{ext}[H]^3 / [M]_{aq}[HR]^3 \qquad (5)$$

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

$$\begin{aligned} \log D &= \log K_{ex} + 3\log[HR] + 3pH \\ &= \log K_{ex} + 3\log([HR]/[H]) \qquad (6) \end{aligned}$$

As shown in **Figure 7**, the plots of log *D* versus log([HR] / [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 $[C_4mim][Tf_2N]$ system relative to the *n*-dodecane system.

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 $[C_4mim][Tf_2N]$ 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.

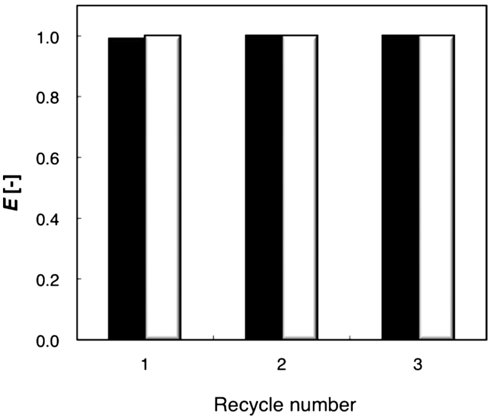


Fig. 8 Extracting phase recycling. Initial extraction phase: $[DODGAA]_{IL,0} = 15\ mol/m^3$, $[C_4mim][Tf_2N]$; Aqueous feed phase: $[M]_{i,0} = 0.1\ mol/m^3$; Stripping phase: $1\ mol/dm^3\ HNO_3$, Y^{3+} (Black), Eu^{3+} (gray)

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 $[C_nmim][Tf_2N]$ ($n = 4, 8, 12$) 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 $[C_4mim][Tf_2N]$ 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.

Acknowledgment

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