Recent Advances in Extraction and Separation of Rare-Earth Metals Using Ionic Liquids

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In the present review article, we summarize recent advances in extraction and separation of rare-earth metals using ionic liquids. Rare-earth metals have unique electronic and magnetic properties. In Japan, increasing amounts of rare-earth metals are being used every year in industries employing cutting-edge technology. Therefore, maintaining a stable supply of rare-earth metals is important. In recent times, extensive research has been carried out on the use of ionic liquids for the extraction of rare-earth metals; this is because the extraction ability and/or selectivity for rare-earth metals have been found to increase when using hydrophobic ionic liquids, which have potential applications in liquid–liquid extraction processes. In the octyl(phenyl)-*N,N*-diisobutyl carbamoylmethyl phosphine oxide (CMPO) extraction system using ionic liquids, the extraction ability was more than 10^3 times better than that when using *n*-dodecane; however, stripping of the extracted metal ions was difficult in the former case. In initial research on the extraction processes based on ionic liquids, industrial extractant PC-88A was employed as well as CMPO, but issues resulting from the low solubility of these extractants and their metal complexes remain to be addressed. To overcome this problem, a new extractant, *N,N*-dioctyldiglycol amic acid (DODGAA), which is highly soluble in the ionic liquids, has been synthesized. DODGAA shows better performance for the separation of rare-earth metals in ionic liquids than in *n*-dodecane. Furthermore, a liquid membrane system based on ionic liquids has been developed for the separation and recovery of rare-earth metals. The use of a liquid membrane system may help in reducing the amount of ionic liquids required for metal recovery.

Introduction

Rare-earth metals have important applications in cutting-edge technologies employed in the electronics, information technology, and automobile industries. As Japan does not have many natural metal resources, maintaining a steady supply of imported rare-earth metals is important. The total amount of rare-earth metals imported into Japan was 19,000 tons/year in 1996, and this amount increased to 40,000 tons/year over the following decade. Japan is now one of the world's major importers of rare-earth metals. However, more than 90% of the rare-earth metals imported into Japan come from China, the world's leading supplier of rare-earth metal resources, due to their low costs. This situation made us realize the importance of a second resource of rare-earth metals: "urban mines" or discarded electronic waste. Rare-earth metals are generally separated from their natural ores by solvent extraction. However, since urban mines have different metals and the concentrations of rare-earth metals are usually low, highly efficient separation and recovery methods are required for rare-earth metals.

Recently, ionic liquids (ILs), which are molten salts at room temperature, have attracted considerable attention since they are novel, environmentally friendly solvents (Kubota and Goto, 2006; Han and Armstrong, 2007). The use of ILs in liquid–liquid extraction of rare-earth metals has been reported; a comprehensive list of such studies is given in **Table 1**. In some cases, the IL-based systems showed better extraction ability and selectivity than those showed by the conventional organic solvent extraction systems. Therefore, more efficient solvent extraction processes by using ILs can be developed. In this review article, we summarize recent improvements made to solvent extraction processes in which ILs are employed and discuss the possibility of using ILs in the separation and recovery of rare-earth metals from electronic waste.

Table 1 Application of ionic liquids to solvent extraction of rare earth metals

Year	Author	Ionic liquids	Extractants	Targets
2003	Nakashima *et al.*	$[C_4mim][PF_6]$	CMPO	Lanthanides, Y
2003	Jensen *et al.*	$[C_4mim][Tf_2N]$	Htta	Nd, Eu
2005	Cocalia *et al.*	$[C_{10}mim][Tf_2N]$	D2EHPA, Cyanex 272	U, Am, Nd, Eu
2005	Nakashima *et al.*	$[C_4mim][PF_6]$, $[C_4mim][Tf_2N]$	CMPO	Lanthanides, Y
2006	Mekki *et al.*	$[C_4mim][Tf_2N]$	Htta	Eu, La
2006	Shimojo *et al.*	$[C_6mim][Tf_2N]$	TPEN	Eu
2007	Kozonoi and Ikeda	$[C_4mim][NfO]$	—	La, Sr, Ca, Li, Na, Cs
2007	Sun *et al.*	$[C_8mim][PF_6]$	Cyanex 925	Sc, Y, La, Yb
2008	Turanov *et al.*	$[C_4mim][PF_6]$, $[C_4mim][Tf_2N]$	TPMDPO, Ph_2Et_2, Bu_2Et_2	Lanthanides, Y
2008	Kubota *et al.*	$[C_nmim][Tf_2N]$ ($n = 8, 12$)	PC-88A	Y, Eu, Ce, La
2008	Hirayama *et al.*	$[C_4mim][Tf_2N]$	Htta-18C6 (synergistic extraction)	La, Eu, Lu
2008	Shimojo *et al.*	$[C_nmim][Tf_2N]$ ($n = 2, 4, 6$)	TODGA	Lanthanides
2008a	Zuo *et al.*	$[C_8mim][PF_6]$	—	Ce, Th, Gd, Yb
2008b	Zuo *et al.*	$[C_8mim][PF_6]$	primary amine N1923	Th/Rare earths
2009	Zuo *et al.*	$[C_8mim][PF_6]$	D2EHPA	Lanthanides, Sc, Y, Th
2009	Mallah *et al.*	$[C_nmim][Tf_2N]$ ($n = 4, 6$)	HYD	Sm, Eu, Gd, Dy
2009	Sun *et al.*	[A336][CA-100] (TSIL)	[A336][CA-100] (TSIL)	Sc, Y, Eu, Ce
2009	Liu *et al.*	$[C_nmim][PF6]$ ($n = 4, 8$), Cyphos IL 104 (TSIL)	Cyphos IL 104 (TSIL)	Y, Dy, Ho, Er, Yb
2010	Mallah *et al.*	$[C_6mim][Tf_2N]$	PAN-HYD (synergistic extraction)	Sm, Eu, Gd, Dy
2010	Kubota *et al.*	$[C_nmim][Tf_2N]$ ($n = 4, 8, 12$)	DODGAA	Y, Eu
2010	Odinets *et al.*	CMPO-modified IL (TSIL)	CMPO-modified IL (TSIL)	U, Pu, Eu, Am
2010	Yoon *et al.*	$[C_nmim][PF6]$ ($n = 2, 4$), $[C_4mpy][PF_6]$	D2EHPA	Ce, Nd, Sm, Dy, Yb
2010	Okamura *et al.*	$[C_4mim][Tf_2N]$	Htta, Htta-18C6, Htta-DC18C6, Htta-DB18C6, Htta-15C5 (synergistic extraction)	Lanthanides

CMPO: octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide, Htta: 2-thenoyltrifluoroacetone, D2EHPA: bis(2-ethylhexyl)phosphoric acid, Cyanex 272: bis(2,4,4-trimethylpentyl)phosphinic acid, TPEN: *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)ethylenediamine, NfO: Nonafluorobutanesulfonate, Cyanex 925: bis(2,4,4-trimethylpentyl)octylphosphine oxide, TPMDPO: tetraphenylmethylenediphosphine dioxide, Ph_2Et_2: diphenyl(diethylcarbamoylmethyl)phosphine oxide, Bu_2Et_2: dibutyl(diethylcarbamoylmethyl)phosphine oxide, PC-88A: 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester, 18C6: 18-crown-6, TODGA: *N*,*N*,*N'*,*N'*-tetra(*n*-octyl)diglycolamide, HYD: (1-hydroxy-2,5-pyrrolidinedione), [A336][CA-100]: [trialkylmethylammonium][sec-nonylphenoxyacetate], Cyphos IL 104: trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, PAN: 1-(2-pyridylazo)-2-naphthol, DODGAA: *N*,*N*-dioctyldiglycol amic acid, mpy: 4-methylpyridinium, TSIL: Task-specific ionic liquids, DC18C6: *cis*-dicyclohexano-18-crown-6, DB18C6: dibenzo-18-crown-6, 15C5: 15-crown-5

1. Recycling of Rare-Earth Metals

Rare-earth metals are used in many advanced materials. In particular, the use of Nd and Dy is rapidly increasing because of the increasing demand for magnetic materials in the automobile industry (electric and hybrid automobiles). La and Ce are used as additives in glasses and novel catalysts. Y, Eu, La, Ce, and Tb are used as fluorescent materials for lamps and TV displays. However, in these applications, rare-earth metals are used in extremely low concentrations and are dispersed in a wide variety of materials. As a result, the recovery of rare-earth metals from urban mines is difficult. The bulk of the total amount of Y and Eu consumed in Japan is used in electronic materials, for example, more than 800 tons of rare-earth metals are estimated to be used every year in fluorescent materials. With the shift to digital TV in July 2011, a large number of CRT TVs may be discarded as waste. Then, TV tubes will be important sources of rare-earth metals that can be recycled. X-ray fluorescence analysis revealed that rare-earth metals comprise more than 30% of the fluorescent sample in the tube (**Figure 1**). The rare-earth metals, if leached from
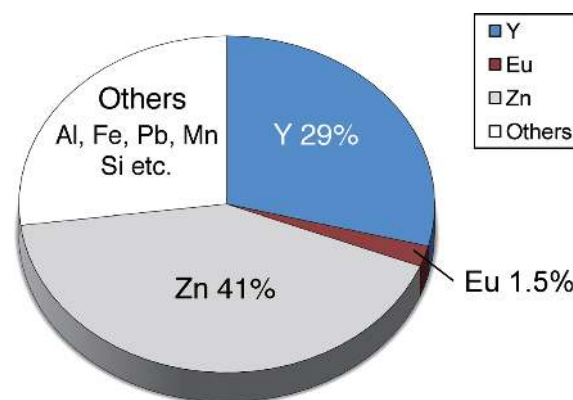

Fig. 1 Composition of fluorescent materials in CRT: Results of X-ray fluorescence analysis (XRF)

the wastes with an acidic aqueous solution, could be recovered by conventional solvent extraction from the aqueous solution. However, a large amount of base metals such as Zn also dissolve in the aqueous feed solution. Therefore, the selective separation of rare-earth metals from such metal impurities is required. In the present re-
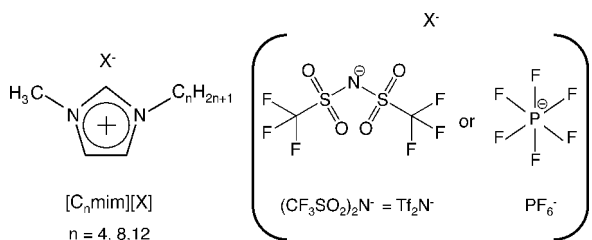
Fig. 2 Molecular structures of imidazolium-based ionic liquids

Fig. 3 Molecular structures of commercial extractants

view, we introduce an efficient process developed for selective recovery of Y and Eu from waste electronic materials.

2. ILs as Extracting Solvents

We carried out the extraction and separation of rare-earth metals using imidazolium-based ILs, as shown in **Figure 2**. ILs usually comprise heterocyclic organic cations and various anions and have unique properties such as negligible vapor pressure and high thermal stability. One of the most attractive features of ILs is that their physicochemical properties are extensively tunable by the combination of cationic and anionic partners. Water-immiscible ILs can be obtained by extending the alkyl-chain length in the cation part and/or by introducing hydrophobic anions such as $(CF_3SO_2)_2N^-$ (abbreviated as Tf_2N^-) or PF_6^- shown in Figure 2. Therefore, such hydrophobic ILs can be used in separation techniques based on the biphasic system, such as liquid–liquid extraction. ILs when used as solvent have a high potential to enhance the efficiency of the extraction process, but it is crucial to choose a suitable extractant and IL combination.

3. Development of a New Extraction System for Rare-Earth Metals by Using ILs

3.1 Extraction using industrial extractants

CMPO (**Figure 3**), which is an effective extractant used for the separation and recovery of actinides in the nuclear-fuel cycle, has been found to be useful for the extraction of rare-earth metals. CMPO is a neutral extractant that easily dissolves in hydrophobic ILs such as [C$_4$mim][Tf$_2$N] and [C$_4$mim][PF$_6$]. Nakashima *et al.* (2003) examined the extraction behavior of lanthanide ions by using CMPO dissolved in such hydrophobic ILs and compared the results with those obtained when using *n*-dodecane, which is used as the model solvent for kerosene in the industry. All the lanthanide ions were quantitatively extracted into [C$_4$mim][PF$_6$] containing 5 mol m^{-3} CMPO, whereas no metal ions were extracted into *n*-dodecane under the same experimental conditions (**Figure 4**). The extraction performance in the [C$_4$mim][PF$_6$] system was 10^3 times better than that in
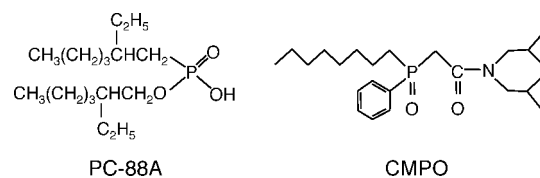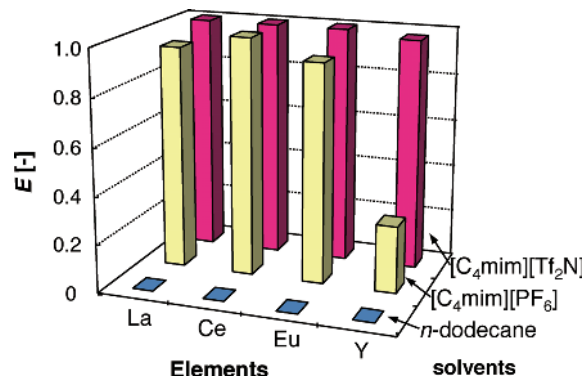

Fig. 4 Extraction of rare earth metals using CMPO. $C_{Mi0} = 0.1$ mol m^{-3}, $C_{CMPO} = 5$ mol m^{-3}. $C_{HNO_3} = 0.1$ mol dm^{-3} (in ILs), 1 mol dm^{-3} (in *n*-dodecane)

the *n*-dodecane system, and the extraction ability was shown in the [C$_4$mim][Tf$_2$N] system better than the [C$_4$mim][PF$_6$] system. Successful stripping of the metal ions from the extraction phase is also an essential part of an efficient solvent extraction process used for metal recovery. Nakashima *et al.* (2003, 2005) were the first to carry out quantitative stripping of metal ions by using a mixture of complexing agents: 0.1 mol dm^{-3} citric acid + 0.4 mol dm^{-3} formic acid + 0.4 mol dm^{-3} hydrazine hydrate (**Figure 5**). In general, stripping is very difficult in IL extraction systems based on neutral extractants. Therefore, the successful stripping in Nakashima *et al.*'s experiment indicated that ILs can be useful alternatives to organic solvents for use as the separation media for metal ions. However, the high cost of the reagents required for IL-based systems limits the practical applications of such systems.

Much of the difficulty associated with the stripping process in IL systems can be attributed to the unique extraction mechanism (Nakashima *et al.*, 2005). It is known that in the organic system, the metal cations are co-extracted with nitrate counterions into the organic solvent containing CMPO, as described in Eq. (1):

$$M^{3+} + 3CMPO_{org} + 3NO_3^- \rightleftarrows M(NO_3)_3 \cdot 3CMPO_{org}$$
(1)
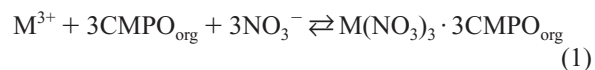
However, the extraction of the metal ions takes place by a cation-exchange mechanism as described in Eq. (2). That is, a metal cation coordinated with CMPO is exchanged for a cationic component of the IL, [C$_n$mim]$^+$, and accordingly, the anionic components in the IL play a
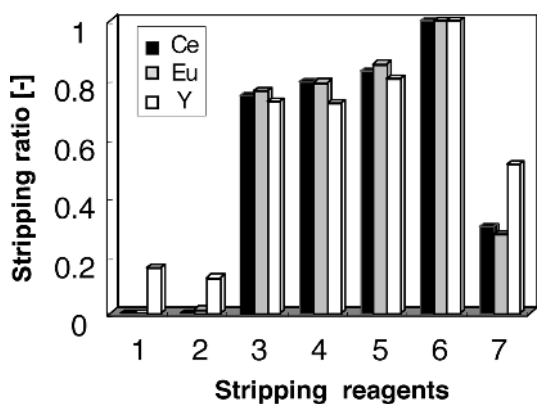
1: 0.05 mol dm^{-3} HNO$_3$
2: 7.0 g dm^{-3} AHA + 0.5 mol dm^{-3} HNO$_3$
3: 7.0 g dm^{-3} AHA + 1.0 mol dm^{-3} guanidine carbonate
4: 0.05 mol dm^{-3} DTPA + 1.0 mol dm^{-3} guanidine carbonate
5: 0.05 mol dm^{-3} EDTA + 1.0 mol dm^{-3} guanidine carbonate
6: 0.1 mol dm^{-3} citric acid + 0.4 mol dm^{-3} formic acid
   + 0.4 mol dm^{-3} hydrazine hydrate
7: 0.5 mol m^{-3} [C$_4$mim][Cl]

Fig. 5 Stripping behavior of rare earth metals from IL phases containing CMPO (AHA: acetohydroxamic acid, DTPA: diethylenetriamine pentaacetic acid, EDTA: ethylenediamine tetraacetic acid) (Nakashima *et al.*, 2005)

role as counterions of the extracted metal species.

$$M^{3+} + 3CMPO_{IL} + 3C_n mim^+{}_{IL}$$
$$\rightleftarrows M \cdot 3CMPO^{3+}{}_{IL} + 3C_n mim^+ \qquad (2)$$
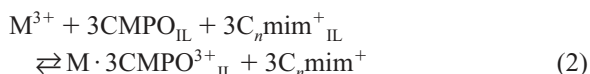
The extraction equilibrium reveals that stripping of the metal ions from ILs will be difficult when the extraction species involve the constituents of ILs, as described in Eq. (2).

We thought that it was necessary to develop an IL extraction system in which the extraction mechanism is the same as that in an organic solvent and the extractability can be controlled by changing the acid concentration in the aqueous feed solution.

To fulfill these requirements, we used acidic extractants such as PC-88A. **Figure 6** shows the extraction behavior of the metal ions in the ILs. In the IL system, the extractability increased with pH, as shown in Figure 6. It has been reported that the extraction mechanism in the IL-based system in which PC-88A is used is the same as that in an organic solvent system (Kubota *et al.*, 2008):

$$M^{3+} + 3(HR)_{2\,org} \rightleftarrows MR_3 \cdot 3HR + 3H^+ \quad HR: PC\text{-}88A \qquad (3)$$
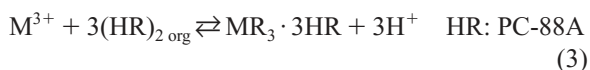
However, the extraction performance was low when using ILs because PC-88A, which has bulky hydrophobic groups, has poor solubility in the ILs, and the solubility of metal complexes of PC-88A is even poorer.

Though the use of a conventional commercial extractant would be economically advantageous for metal recycling by solvent extraction, a new extractant de-
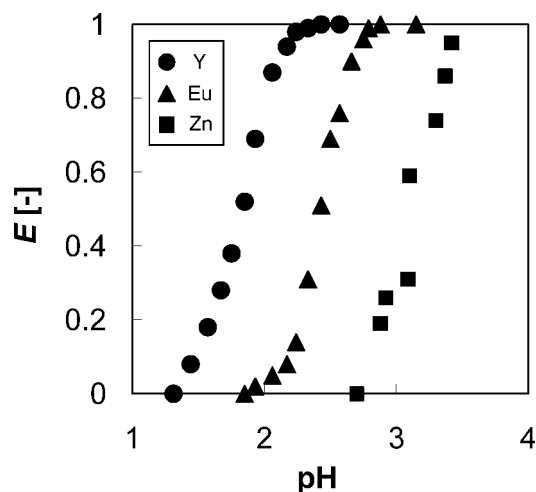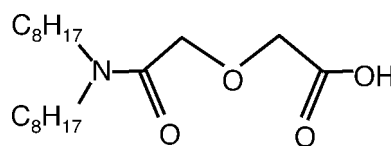

Fig. 6 Extraction behavior of metal ions with PC-88A in [C$_{12}$mim][Tf$_2$N], $C_{Mi0} = 0.1$ mol m^{-3}, $C_{PC\text{-}88A} = 10$ mol m^{-3}

Fig. 7 A novel extractant, DODGAA (Naganawa *et al.*, 2007; Shimojo *et al.*, 2007)

signed specifically for ILs is required to develop a more efficient IL-based separation system.

3.2 Development of an IL-based liquid–liquid extraction system using a novel extractant

It was found that neutral extractants such as CMPO were readily soluble in ILs and provide high extractivities (*E*) for the metal ions. In the IL system employing acidic extractants such as PC-88A, the extability of the metal ions could be controlled by changing the pH in the aqueous feed phase. These findings suggested that an extractant having properties of both neutral and acidic extractants would be suitable for the IL-based extraction system. Then, a new extractant that would fulfill these requirements, *N,N*-dioctyldiglycol amic acid (DODGAA), was synthesized. DODGAA is analogous to *N,N,N′,N′*-tetra(*n*-octyl)-diglycolamide (TODGA), which has high affinity for rare-earth metals (Shimojo *et al.*, 2008). DODGAA has a molecular structure replaced one of the two carbamoyl groups at TODGA by carboxy group, as shown in **Figure 7**. DODGAA has no hazardous elements, and it can be synthesized by a simple one-step reaction from diglycolic anhydride and dioctylamine, which are inexpensive (Naganawa *et al.*, 2007; Shimojo *et al.*, 2007). DODGAA is readily soluble in [C$_4$mim][Tf$_2$N], but 5 vol% of 1-octanol was required to solubilize DODGAA in the organic solvent *n*-dodecane.
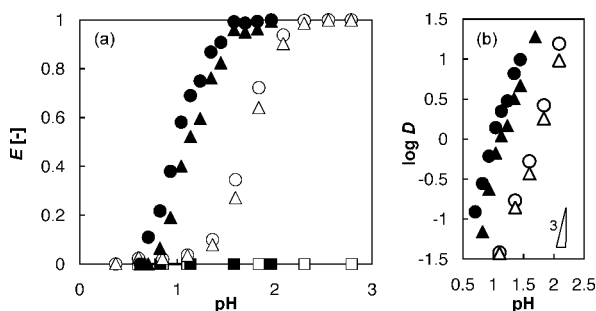
Fig. 8 Extraction behavior of metal ions with DODGAA in IL and *n*-dodecane systems (Kubota *et al.*, 2010). (a) extraction equilibria (b) plots of $\log D$ versus pH. $C_{Mi0} = 0.1\,mol\,m^{-3}$, $C_{DODGAA} = 10\,mol\,m^{-3}$, ● Y, ▲ Eu, ■ Zn: [C$_4$mim][Tf$_2$N], ○ Y, △ Eu, □ Zn: *n*-dodecane

Then, we examined the extraction behavior of rare-earth metals (Y^{3+} and Eu^{3+}) and selectivity in the presence of Zn^{2+} as a metal impurity, in order to study the feasibility of using IL-based extraction with DODGAA for recovering rare-earth metals from waste CRT fluorescent materials. As shown in **Figure 8(a)**, the extractability for Y^{3+} and Eu^{3+} increased with increasing the pH in the IL-based systems; this trend is similar to that in the *n*-dodecane system. This result suggests that the extraction of the metal ions was proceeded by a proton exchange mechanism in the IL-based system as well as in the organic solvent system. The extractability of the metal ions into [C$_4$mim][Tf$_2$N] is considerably higher than that of the metal ions into the *n*-dodecane system (Kubota *et al.*, 2010). The increase in the extractability may be due to the increase in the diffusivity of the extractant to the aqueous phase or a peculiar solvent effect caused by the ILs. At present, the details of this consideration are under examination. In conventional extraction systems, PC-88A is known to be an excellent extractant for rare-earth metals; however, its extraction performance is relatively low in ILs, and Zn^{2+} ions are extracted along with the target ions, as shown in Figure 6. Consequently, the selective separation of rare-earth metals from an aqueous feed solution containing a large amount of Zn^{2+} is difficult when using PC-88A. On the other hand, Y^{3+} and Eu^{3+} can be quantitatively extracted into ILs and organic phases when using DODGAA; moreover, the Zn^{2+} ions are not extracted into either of the extracting phases under the present experimental conditions. The high extractability and selectivity for rare-earth metals are probably because of the presence of three oxygen donors in DODGAA, which might take part in complex formation with metal ions. Another advantage of using DODGAA is that the complete stripping of the metal ions from the IL phase can be achieved by using an acidic solution such as nitric acid solution. Straight lines with a slope of 3 were obtained in the plots of logarithmic distribution ratio, $\log D$, ($D = [M^{3+}]_{org}/([M^{3+}]_{aq})$ versus pH (**Figure 8(b)**) and the logarithmic concentration of extractant
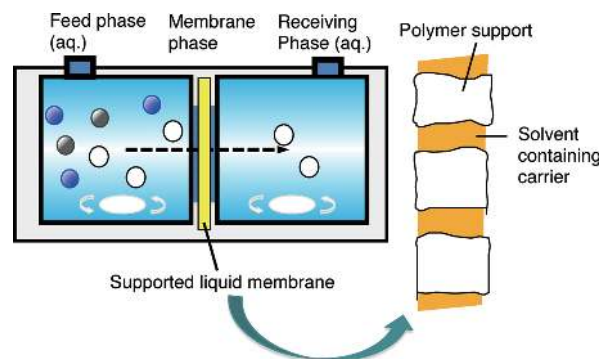

Fig. 9 Schematic of liquid membrane system

(data not shown) for the rare-earth metals in the IL system as well as in the *n*-dodecane system. This implies that one metal ion is extracted with three DODGAA molecules, that is, the extracted species was a 1 : 3 metal complex with DODGAA.

In addition, we showed that Y^{3+} and Eu^{3+} could be recovered from an acidic leaching solution from a fluorescent material in the waste CRT.

4. Development of an IL-Based Liquid Membrane System

As mentioned above, solvent extraction using ILs can be a useful technique for recovering rare-earth metals. However, if an IL is used as the solvent, the amount of IL used should be as small as possible, because ILs are expensive. The liquid membrane method is the most feasible for the use of ILs, since a small amount of the solvent is required as the membrane phase.

As shown in **Figure 9**, in a liquid membrane system, the feed and receiving phases are separated by an immiscible membrane phase. This type of system, which allows for simultaneous extraction and stripping on both sides of the membrane, is one of the most efficient separation systems (Kubota and Goto, 2005). In supported liquid membranes (SLMs), the liquid membrane phase containing a carrier that binds selectively to a target metal ion is impregnated into the pores of a microporous thin polymer film, and this liquid membrane is sandwiched between the feed and receiving phases. The key requirements for using SLMs as successful separation systems for metal ions are not only a good carrier but also a stable liquid membrane that can survive long-term operation. However, in SLM systems in which a conventional organic solvent is used as the liquid membrane phase, the solvent leaks from the membrane phase into the aqueous phase, and water penetrates the membrane, thereby leading to destabilization of the membrane. ILs, owing to their unique properties, can be used as the membrane phase so that the liquid membrane remains stable.

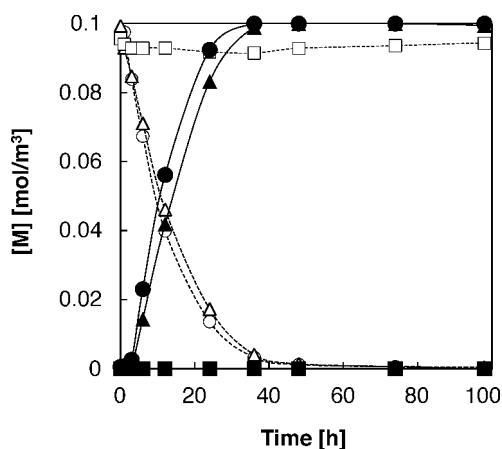An SLM was prepared by immersing a hydropho-

Fig. 10 Time courses of metal ion concentrations in the feed (open symbols) and receiving (closed symbols) phases during IL-based SLM operation (Kubota *et al.*, 2010). Feed phase: $0.1 \, mol \, m^{-3}$ each of Y^{3+} (circles), Eu^{3+} (triangles) and Zn^{2+} (squares), pH 4. Receiving phase: $1 \, mol \, dm^{-3}$ HNO_3. Membrane phase: $[C_8mim][Tf_2N]$ containing $10 \, mol \, m^{-3}$ DODGAA, 298 K

bic porous polyvinylidene fluoride film (Millipore Corp., pore size = 0.45 μm; thickness = 125 μm) in $[C_nmim][Tf_2N]$ or *n*-dodecane containing DODGAA under the same conditions as those used for the liquid–liquid extraction processes. A transport experiment was performed using a glass cell unit shown in Figure 9, in which the membrane (effective area = $5 \, cm^2$) was sandwiched between two independent 55-cm^3 compartments acting as the feed and receiving phases. Samples were periodically withdrawn from the two phases, and the metal concentration was measured. In the SLM system in which an organic solvent such as *n*-dodecane was used, the metal concentration in the receiving phase increased, with a corresponding decrease in the metal concentration in the feed phase; finally, the metal concentration in both the glass cells became uniform. Here, Zn^{2+}, which cannot be extracted normally with DODGAA, was transported along with Y^{3+} and Eu^{3+}. This indicated that the membrane was ruptured during the process.

In contrast, uphill transport of Y^{3+} and Eu^{3+} through an SLM was observed when using $[C_8mim][Tf_2N]$ or $[C_{12}mim][Tf_2N]$ as the membrane solvent, as shown in **Figure 10** (Kubota *et al.*, 2010). Zn^{2+} were not transported and only the rare-earth metals were transferred to the receiving phase. The membrane was stable even after 140 h. The membrane stability was poor when using $[C_4mim][Tf_2N]$ as in the *n*-dodecane system. This suggested that $[C_8mim][Tf_2N]$ or $[C_{12}mim][Tf_2N]$, since they are nonvolatile and have suitable viscosity, were firmly lodged in the micropores of the membrane support. Thus, we could conclude that a highly stable and efficient liquid membrane system can be developed by choosing a suit-

able IL and a well-designed carrier for the IL and the target metal ions.

Conclusions

Ionic liquids can contribute greatly to the development of novel and highly efficient separation processes for rare-earth metals. We found that the success of the separation process depends on the use of an extractant that is suitable for ionic liquids. In some cases in which ionic liquids were used, the extraction ability and selectivity for the target rare-earth metals were better than those observed when using a conventional organic solvent, *n*-dodecane. The use of liquid membrane processes can help in reducing the overall cost of the systems based on ionic liquids, which are expensive. The use of a well-designed carrier and ionic liquids will also help in the development of better liquid membrane separation systems for metal ions.

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