Solvent Extraction of Lanthanides into an Ionic Liquid Containing *N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)ethylenediamine

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The extraction behavior of lanthanides from aqueous solutions into an ionic liquid (IL) was investigated with *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) as a ligand. The extraction performance of TPEN for lanthanides is greatly enhanced by dissolution in IL compared to in chloroform. Furthermore, the stripping of lanthanides from IL into a receiving phase is successfully achieved under acidic conditions.

Ionic liquids (ILs), which are composed of an organic cation and either an organic or an inorganic anion, have attracted much attention as a new class of solvents. They possess unique properties, e.g., negligible volatility, nonflammability, and high thermal stability. Furthermore, the physicochemical properties such as the water immiscibility and polarity are able to effectively be tuned, depending on the structure of cations and anions.[1] Because of their unusual properties, ILs have been extensively investigated as replacements for conventional molecular solvents in numerous synthetic,[2] catalytic,[3] and biochemical[4] applications.

ILs can also be applied to solvent extraction processes.[5] Conventional liquid–liquid extraction using organic solvents, which are flammable, volatile, and usually toxic, is widely utilized as an effective analytical separation technique. However, from the viewpoint of environmental protection, the use of such hazardous solvents is unfavorable. To address this issue, ILs are receiving much interest as alternative media of extracting phases in liquid–liquid extraction systems of a variety of substances, including metal ions,[6] organic molecules,[7] and proteins.[8] However, the application of ILs to solvent extraction can be problematic in that the solubility of typical extractants in ILs is very poor.[9] Actually, ILs-based extraction systems using only a few extractants such as crown ethers and β-diketones, which show the high solubility in ILs, have become mainstream. In addition, these systems have difficulties in back extraction of extracted metal ions, which is possible only in limited conditions.[10]

In a previous study, we found that the introduction of pyridyl groups to an extractant enables the extractant to be solubilized into ILs and allows extracted metal ions to be stripped under acidic conditions, because pyridyl group provides a high affinity for imidazolium-based ILs and is easily protonated to lose its coordination ability under acidic conditions.[9,10a] In the present study, we employed *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine[11] (TPEN, Figure 1), which is a neutral hexadentate ligand effectively coordinating with lanthanides. TPEN with four pyridyl groups is able to be dissolved in ILs and to be protonated in itself. Therefore, TPEN is expected to exhibit a high extraction ability for lanthanides in ILs and to release the extracted metal ions into an aqueous acid solution.

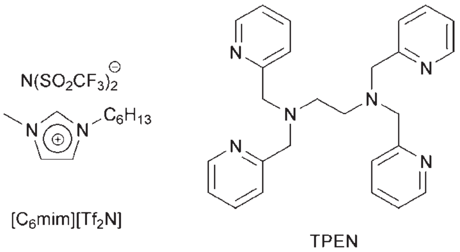

Figure 1. Molecular structures and abbreviations of IL and ligand.

An extracting phase was prepared by dissolving TPEN in 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_6mim][Tf_2N]$, Figure 1), which provides the high solubility for TPEN. For comparison with the performance of ILs, chloroform containing the ligand was also prepared in the same manner. An aqueous phase was prepared by dissolving 0.01 mM $Eu(NO_3)_3$ in deionized water or NH_4NO_3 solution. Equal volumes of the IL and aqueous solutions were mixed and shaken on a vortex mixer at 298 K for 15 min to attain equilibrium. These mixtures were then centrifuged for 3 min to promote phase separation. After each phase was separated, the concentration of Eu^{3+} in the aqueous phase was determined by using inductively coupled plasma mass spectrometry (Hewlett Packard HP 4500) to obtain the extractability ($E = [Eu^{3+}]_{org.}/[Eu^{3+}]_{ini.}$; org. and ini. denote the organic phase and the initial condition.).

Figure 2 shows the dependence of the extractability of Eu^{3+} on the concentration of NH_4NO_3 for the $[C_6mim][Tf_2N]$ system compared with that in the chloroform system. NH_4NO_3 was utilized as the source of counter ions for the Eu^{3+} transfer. In the absence of TPEN, the partitioning of Eu^{3+} into $[C_6mim][Tf_2N]$ or chloroform was negligibly small. In the case of chloroform, the extractability of Eu^{3+} was enhanced with increasing NH_4NO_3 concentration. This result indicates that NO_3^- is indispensable for the metal extraction into chloroform, which proceeds through the formation of an ion pair between Eu^{3+}–TPEN complex cation and NO_3^-. In the case of $[C_6mim][Tf_2N]$, the degree of Eu^{3+} extraction was independent of NO_3^- concentration. In particular, even in the absence of NH_4NO_3, Eu^{3+} was quantitatively extracted into $[C_6mim][Tf_2N]$. This result suggests that the partitioning of Eu^{3+} proceeds through a different mechanism from that in conventional organic solvents: The metal transfer into ILs does not involve anion coextraction. Previously, it was reported that the transfer of metal ions with neutral extractants in ILs proceeds by a cation-exchange mechanism.

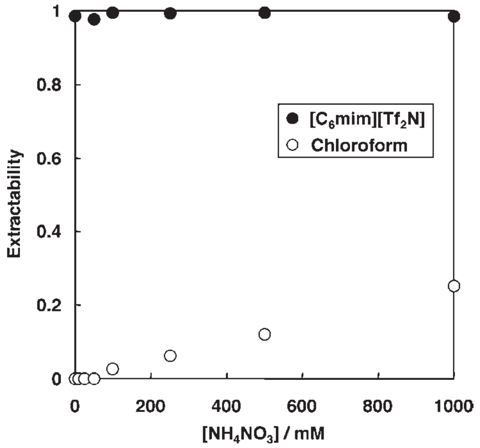

Figure 2. Dependence of extractability of Eu^{3+} on NH_4NO_3 concentration with TPEN in $[C_6mim][Tf_2N]$ (closed symbols) or in chloroform (open symbols). Extracting phase: 5 mM TPEN. Aqueous phase: 0.01 mM $Eu(NO_3)_3$.

That is, the exchange of metal ion for the cationic constituent of the ILs ($[C_nmim^+]$).[10,12] The difference in the extraction behavior of Eu^{3+} between $[C_6mim][Tf_2N]$ and chloroform in this study also supports their discussions.

The influence of TPEN concentration in $[C_6mim][Tf_2N]$ and in chloroform on Eu^{3+}extraction was compared (Figure 3). This trial was carried out under optimal conditions for the IL or chloroform systems, on the basis of the results in Figure 2: The aqueous solution in the $[C_6mim][Tf_2N]$ system was prepared by dissolving 0.01 mM $Eu(NO_3)_3$ in deionized water containing no NH_4NO_3, while in the chloroform system, 0.01 mM $Eu(NO_3)_3$ in 1 M NH_4NO_3 was used as the aqueous phase. The efficiency of Eu^{3+} extraction with TPEN was remarkably higher in $[C_6mim][Tf_2N]$ than in chloroform. For example, 95% of Eu^{3+} was extracted into $[C_6mim][Tf_2N]$ at a concentration of 1 mM TPEN. In chloroform, however, only 5% of Eu^{3+} was transferred at the same TPEN concentration. Even when the TPEN concentration was 100 mM, the degree of Eu^{3+} extraction was 70%. In addition, by analyzing these data, the stoichiometry of Eu^{3+}–TPEN complex was found to be 1:2 in $[C_6mim][Tf_2N]$ and 1:1 in chloroform. Details will be described in a forthcoming full paper.

Furthermore, the back extraction of Eu^{3+} in the $[C_6mim]$-$[Tf_2N]$ system was examined. It is well known that the recover of metal ions extracted into ILs with neutral extractants is very difficult, since they are able to extract metal ions, independently of the salt or acid concentrations. We found that Eu^{3+} was able to be efficiently stripped from $[C_6mim][Tf_2N]$ into a receiving phase at low pH conditions ($pH \leq 0.5$) because TPEN was protonated under acidic conditions. A recycling test was also carried out.[13] During five cycles of forward and backward extraction, the TPEN–IL extraction system maintained its high extraction performance. That is, the degree of extraction was more than 97%. The IL solution with TPEN found to be reused as the extracting phase.

In conclusion, we have demonstrated that IL system with TPEN shows extremely high extraction efficiency for Eu^{3+} compared to chloroform system. Furthermore, the stripping of Eu^{3+} from IL found to be successfully achieved under acidic conditions. These results encourage the utilization of ILs as alternative solvents in industrial liquid–liquid extraction processes, e.g., the recovery of harmful and/or valuable metals from industrial wastes.

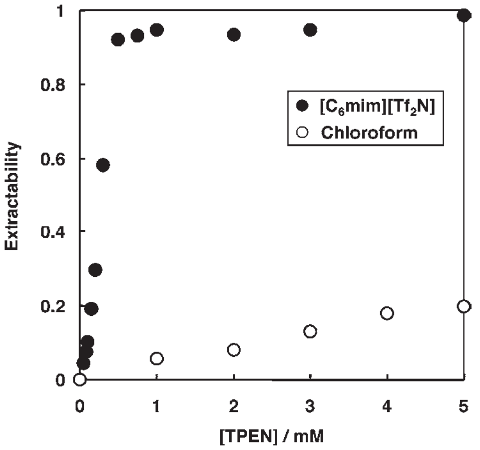

Figure 3. Degree of Eu^{3+} extraction with increasing TPEN concentration in $[C_6mim][Tf_2N]$ (closed symbols) or in chloroform (open symbols). Aqueous phase: 0.01 mM $Eu(NO_3)_3$ in deionized water when using $[C_6mim][Tf_2N]$ or 0.01 mM $Eu(NO_3)_3$ in 1 M NH_4NO_3 when using chloroform.

References and Notes

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13 A procedure of recycling test: Forward extraction of Eu^{3+} (0.01 mM) into $[C_6mim][Tf_2N]$ with TPEN (5 mM) was performed following the same procedure. After the extraction, the IL phase was mixed with 0.5 M HNO_3 to strip Eu^{3+} from the IL. Then, the IL was recycled for reuse. This forward and backward extraction was repeated five cycles. Provided that 50 mM Tris was used as a buffer in an aqueous solution in the forward extraction in order to deprotonate the recycled TPEN.