

Ionic Liquids as a Novel Solvent for Lanthanide Extraction

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Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) dissolved in an ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate, greatly enhances extractability and selectivity of lanthanide cations compared to that dissolved in conventional organic solvents; further, the recovery of lanthanides extracted into ionic liquids can be accomplished using several stripping solutions containing complexing agents. The possibility of utilizing ionic liquids as novel separation media in an industrial liquid-liquid extraction process was demonstrated.

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Ionic liquids (ILs) show unique properties such as a wide temperature range in the liquid phase, an absence of vapor pressure, and high solubility of a great variety of compounds. Recently, a number of studies have reported the utilization of ILs in many fields as alternatives to conventional organic solvents.¹⁻³ ILs incorporating hydrophobic cations and anions are water immiscible,⁴ thus appearing to be available for liquid-liquid extraction processes. Several reports have detailed results of the extraction of organic compounds or metal ions from water into various phases of ILs.⁵⁻⁸ Dai *et al.*⁵ examined the extraction behavior of strontium into imidazolium cation-based ILs, and obtained a high distribution coefficient compared to that of ordinary organic diluents such as chloroform or toluene.

The purpose of this communication is to demonstrate the possibility of utilizing ILs as novel separation media in industrial liquid-liquid extraction processes. With the increasing dependence on the nuclear energy, the recovery of fission products from spent nuclear fuels has a high priority. Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) can extract trivalent actinides and was employed in ILs.⁹ However, the difficulty in stripping metal ions from the IL phase has not been solved. In this study, we also selected CMPO as an extractant for the extraction of trivalent lanthanides (Ln³⁺) from water into ILs.

The extracting phase was prepared by dissolving CMPO in ILs; 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]), applying an ultrasonic agitation. For comparison with the performance of ILs, the organic solvent of *n*-dodecane (industrial solvent for CMPO) containing the extractant was prepared in the same manner. Since CMPO is a neutral extractant, an anion such as NO₃⁻ is required to extract cationic metal ions into nonpolar organic solvents; thus, an effective extraction needs to be accomplished under high acidic conditions. In the ILs-based extraction system, however, we discovered in a preliminary investigation that highly efficient extraction of lanthanides can be achieved without an anionic species (*i.e.*, deionized water). Based on these results, an aqueous solution in the ILs system was prepared by dissolving

0.1 mM lanthanide nitrates in deionized water, while in the dodecane system 1 M HNO₃ was used as the aqueous phase. Equal volumes (3 ml) of the aqueous and ILs solutions were mixed in a stoppered test tube and vigorously shaken by a vortex mixer for 15 min and then allowed to stand for 30 min to achieve phase separation. After each phase was separated, the concentrations of lanthanide ions in the aqueous phase were measured by an ICP-AES.

Figure 1 shows the extraction behavior of Ce³⁺, Eu³⁺ and Y³⁺ with increasing CMPO concentrations in [Bmim][PF₆] or in *n*-dodecane. In the ILs system (filled symbols), the extractability of CMPO for the three metals is extremely high compared to that in the dodecane system (open symbols). This result indicates that the use of ILs as the extracting phase can reduce extractant consumption. For example, in dodecane, if about 50 mM of CMPO is necessary to extract 90% of Ce³⁺, then with ILs only 3 mM of CMPO is enough to obtain the equivalent extraction. This result should be of great benefit for industrial extraction processes, considering the high cost of the extractant CMPO. Further, in both the ILs and the dodecane systems, a linear relationship between log[CMPO] and log *D* was obtained

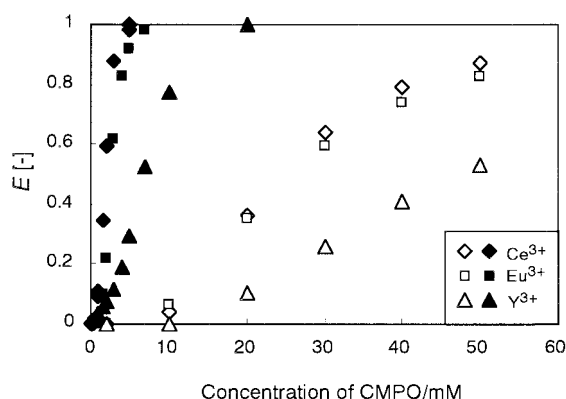


Fig. 1 Percentage extraction (%E) of cerium, europium and yttrium ions with increasing CMPO concentration in [Bmim][PF₆] (filled symbols) and *n*-dodecane (open symbols).

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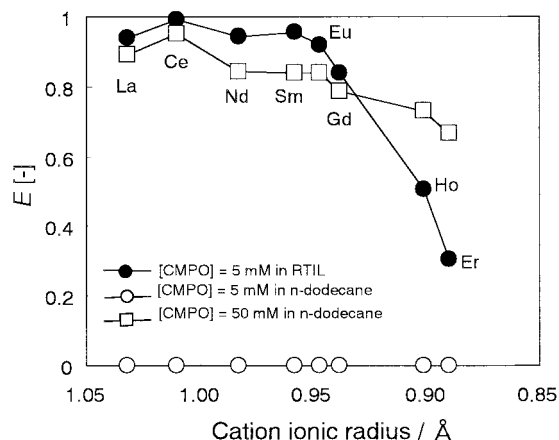


Fig. 2 Extraction of lanthanides into [Bmim][PF₆] containing 5 mM of CMPO (filled symbols) and *n*-dodecane containing 5 mM or 50 mM of CMPO (open symbols).

with a slope of 3 for the lanthanides examined (data not shown), indicating that a 1:3 Ln-CMPO complex (Ln³⁺·3CMPO) is formed.

In general, CMPO has high extractability under high acidic conditions. It has been noted that lanthanide cations can be quantitatively extracted from deionized water into the ILs phase without adding acids (*i.e.* no anionic species). This result suggests that the PF₆⁻ anion in ILs relates to the complexation, that is, the PF₆⁻ anion plays a key role in the electrically neutralization of the Ln³⁺·3CMPO complex. Thus, a number of anions in the ILs system appear to promote the extraction of lanthanide ions with CMPO. In addition, the dielectric constant of ionic liquids might affect extraction efficiency; that is the ion-pair complex, the complexing of which is based on the Coulomb interaction should distribute readily to the ferroelectric ILs phase, resulting in the excellent extraction.

The effects of the extracting phases on selectivity for eight lanthanide ions are depicted in Fig. 2. Although 5 mM of CMPO in dodecane extracts none of lanthanides, 5 mM of CMPO in ILs shows high extractability of all the lanthanides tested, particularly for the light lanthanides. Selectivity among the trivalent lanthanides in the ILs system (CMPO = 5 mM) is higher than that in the dodecane system (CMPO = 50 mM), especially among gadolinium, holmium and erbium. By utilizing ILs as the extracting phase, not only extractability but also selectivity of lanthanides extraction with CMPO is enhanced.

Recently, several studies reported the extraction of metal ions using ILs, however, to our knowledge none have succeeded in the stripping of metal ions extracted in the ILs. Thus, we have sought to recover metals (Ce, Eu, Y) using several buffer solutions containing a complexing agent (Fig. 3). These complexing agents: acetohydroxamic acid (AHA), diethylenetriamine pentaacetic acid (DTPA), ethylenediamine tetraacetic acid (EDTA) and citric acid are known to form water-soluble complexes with many metal ions. As shown in Fig. 3, it was difficult to strip the metals using solution 1, which contained no complexing agents. While solutions 2, 3¹⁰ and 4 that contained a complexing agent facilitated stripping of all the metals. The optimum solution 5¹¹ could completely strip the metal ions.

In conclusion, CMPO dissolved in an ionic liquid, [Bmim][PF₆], shows enormously high extractability and selectivity for lanthanides. These results might promote the

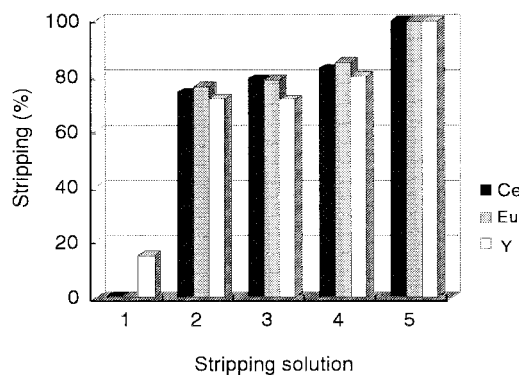


Fig. 3 Stripping of lanthanides from ILs phase using various stripping solutions. 1, 0.05 M HNO₃; 2, 7 g/l AHA + 1.0 M guanidine carbonate; 3, 50 mM DTPA + 1.0 M guanidine carbonate; 4, 50 mM EDTA + 1.0 M guanidine carbonate; 5, 100 mM citric acid + 0.4 M formic acid + 0.4 M hydrazine hydrate.

utilization of ionic liquids as alternative solvents for industrial liquid-liquid extraction processes. However, the extraction mechanism in the ILs system is deduced to be different from those of conventional extraction systems; indicating that studies will be required to elucidate the extraction mechanism and why the ILs enhances extractability and selectivity of lanthanides. This is the first report to successfully demonstrate the stripping of metal cations by extraction into ionic liquids.

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