First Application of Calixarenes as Extractants in Room-temperature Ionic Liquids

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We synthesized a calix[4]arene bearing pyridine, which has a similar molecular structure to the constitutional unit of 3-methylimidazolium hexafluorophosphate-based room-temperature ionic liquids. The pyridinocalix[4]arene was found to be soluble in ionic liquids, and this compound showed 230-fold extractability in ionic liquid over that in chloroform for silver ions.

Liquid–liquid extraction is well known as an effective technique for separating target molecules. The extractant plays a key role in the extraction efficiency and the separation operation. The discovery of the cyclic compound calixarene,[1] which consists of phenol rings connected by methylene bridges, has led to a new class of extractants for various metal ions.[2] They have found wide application in the design of novel solvent extraction systems that are selective for target metal ions based on the cavity sizes of the calixarene.[2] However, calixarene has an inherent problem in industrial applications: its poor solubility in organic solvents other than toxic chloric organic solvents. In a previous paper, we reported that the use of a reverse micellar solution[3] and the addition of alcohol[4] enabled calixarene to dissolve in aliphatic organic solvents. However, since organic solvents are sometimes toxic, flammable, and volatile, it has been recommended that their use as a diluent should be avoided.

Room-temperature ionic liquids (RTILs),[5] which are composed entirely of ions, have recently attracted much attention as novel environmentally friendly solvents. RTILs exhibit promising properties (e.g., water immiscibility, moisture stability, negligible volatility and non-flammability) as alternatives to conventional organic solvents in liquid–liquid extraction. Very recent efforts by several investigators[6,7] have focused on the application of RTILs in liquid–liquid extraction of metal ions. For example, crown ethers or octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) dissolved in RTILs enhance the extractability of various metal ions compared to that dissolved in conventional organic solvents. RTILs can provide a suitable environment which contributes to the performance of extractants in RTILs systems. However, the application of RTILs to solvent extraction can be problematic in that RTILs can dissolve only a few extractants, such as crown ethers[6] and CMPO.[7] Thus, there has been much interest in the development of RTILs-soluble extractants. To address this issue, we have attempted to apply calixarene, which is a highly effective extractant, to RTILs extraction systems.

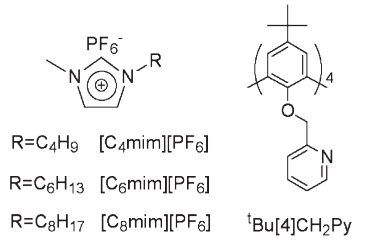

Figure 1. Molecular structures and abbreviations of RTILs and extractants.

In a preliminary study, the solubility of various calixarenes in 3-methylimidazolium hexafluorophosphate-based RTILs ([$C_n$mim][PF_6], $n = 4, 6, 8$, Figure 1), which possess rheological properties suitable for solvent extraction, was investigated. Nonsubstituted ^{t}butyl or ^{t}octylcalixarenes and their carboxylic acid derivatives were not dissolved in [$C_n$mim][PF_6] ($n = 4, 6, 8$) at all. We synthesized a calix[4]arene bearing pyridine[8] (^{t}Bu[4]CH_2Py, Figure 1), which has a similar molecular structure to the constitutional unit of RTILs, to enhance the affinity for RTILs. The ^{t}Bu[4]CH_2Py was found to be more soluble in [$C_n$mim][PF_6] with ultrasonic agitation under heating when the alkyl group in the RTILs was elongated, because RTILs with long alkyl chains can provide high hydrophobicity.

In the present study, the extraction behavior of silver ions into the RTILs phase was examined using ^{t}Bu[4]CH_2Py. To the best of our knowledge, no solvent extraction system based on the combination of RTILs and calixarenes has been reported in the literature.

An extracting phase was prepared by dissolving ^{t}Bu[4]CH_2Py in [C_8mim][PF_6], which provides the highest solubility for the calixarenes. For comparison with the performance of RTILs, chloroform containing the extractant was also prepared in the same manner. The organic phases were mixed and shaken on a vortex mixer with an equal volume of aqueous $AgNO_3$ (0.1 mM), at 298 K for 30 min, to attain equilibrium. These mixtures were then centrifuged for 3 min to promote phase separation. After each phase was separated, the concentration of Ag^+ in the aqueous phase was determined by using atomic absorption spectroscopy, which then allowed calculation of the distribution ratio ($D = [Ag^+]_{org.}/[Ag^+]_{aq.}$) and the degree of extraction ($E = [Ag^+]_{org.}/[Ag^+]_{ini.}$).

Figure 2 shows the dependence of the extraction behavior of the silver ion on the nitrate concentration for the systems with ^{t}Bu[4]CH_2Py in [C_8mim][PF_6] compared with the results in chloroform. Nitric acid was utilized as the source of counter ions for the Ag^+ transfer. In the absence of extractants, the partitioning of Ag^+ into [C_8mim][PF_6] or chloroform was negligibly small. In the case of chloroform, around 90% of Ag^+ was extracted with ^{t}Bu[4]CH_2Py at $[NO_3^-] = 10^{-1} - 10^{-2}$ mol dm^{-3} (pH 1–2), while at lower and higher pH conditions, the extraction percentage gradually reduced. The decrease in extractability at the high NO_3^- concentration could be attributed to the protonation of pyridyl nitrogens, and at the low NO_3^- concentration, the extraction efficiency decreased due to the lack of counter ions, which are required for ion pair extraction.

In the case of [C_8mim][PF_6], ^{t}Bu[4]CH_2Py could quantitatively extract Ag^+ at the low NO_3^- concentration. However, the degree of extraction gradually reduced, when the nitric acid concentration increased, This result suggests that metal com-

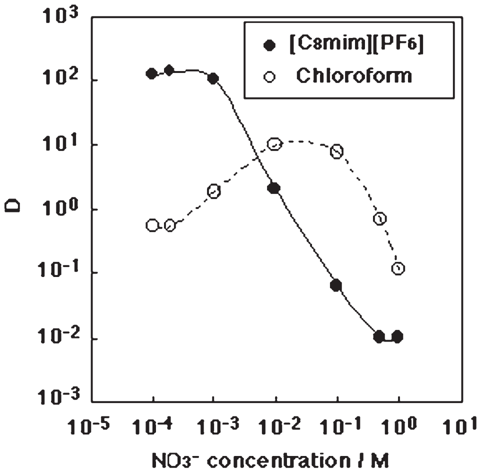

Figure 2. Dependence of extraction behavior of silver ion with ^{t}Bu[4]CH$_2$Py on nitrate ion concentration: filled symbols show the [C$_8$mim][PF$_6$] results, open symbols show the chloroform results, [^{t}Bu[4]CH$_2$Py] $= 0.5$ mM, [AgNO$_3$] $= 0.1$ mM.

plexation proceeds via a different mechanism from that in conventional organic solvents; Ag$^+$ transfer into the RTILs does not involve anion coextraction. In particular, even when HNO$_3$ was absent, Ag$^+$ was efficiently extracted into [C$_8$mim][PF$_6$], and the distribution ratio for [C$_8$mim][PF$_6$] is around 230-fold higher than that for chloroform. Dietz et al.[9] and Rogers et al.[10] reported that the transfer of metal ions with crown ethers or CMPO in RTILs proceeds by a cation-exchange mechanism: the exchange of metal ion for the cationic constituent of the RTILs ([C$_n$mim$^+$]), in contrast to that in conventional organic solvents. The difference in Ag$^+$ extraction behavior between [C$_8$mim][PF$_6$] and chloroform in this study also supports their discussions and indicates that the phase-transfer mechanism of Ag$^+$ with ^{t}Bu[4]CH$_2$Py changes from ion pair extraction in chloroform to cation-exchange extraction in [C$_8$mim][PF$_6$]. As is well known, extraction of metal ions from an aqueous solution into an organic solvent using a neutral extractant requires that electroneutrality should be maintained. The charge balance of the Ag$^+$–^{t}Bu[4]CH$_2$Py complex is compensated by PF$_6^-$ anions in [C$_8$mim][PF$_6$].

Furthermore, we found that Ag$^+$ could be completely stripped from [C$_8$mim][PF$_6$] into a fresh aqueous phase, when the extracting phase was contacted with an acidic solution.

The influence of ^{t}Bu[4]CH$_2$Py concentration in [C$_8$mim][PF$_6$] and in chloroform on Ag$^+$ extraction was compared (Figure 3). Based on the result in Figure 2, an aqueous solution in the [C$_8$mim][PF$_6$] system was prepared by dissolving 0.1 mM AgNO$_3$ in deionized water, while in the chloroform system, 0.1 M HNO$_3$ was used as the aqueous phase. ^{t}Bu[4]CH$_2$Py had a much higher affinity for Ag$^+$ in the RTILs system than in chloroform. This result means that the use of RTILs as the extracting phase can reduce extractant consumption. For example, in chloroform, if 2 mM of ^{t}Bu[4]CH$_2$Py is necessary to extract around 97% of 0.1 mM Ag$^+$, then in [C$_8$mim][PF$_6$], only 0.2 mM of ^{t}Bu[4]CH$_2$Py is required to obtain equivalent Ag$^+$ extraction. This RTILs system, which provides efficient extraction with such a low concentration of ^{t}Bu[4]CH$_2$Py (i.e. only twice the concentration of Ag$^+$), is unprecedented.

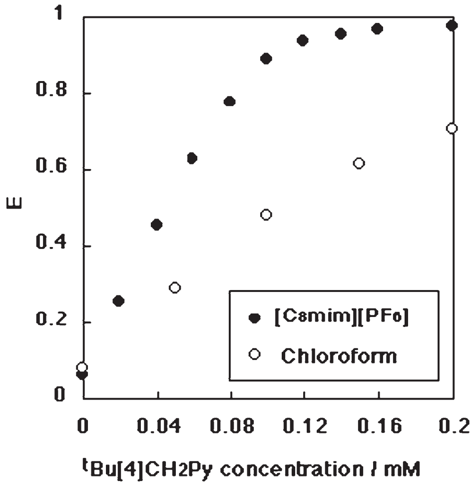

Figure 3. Dependence of extaction behavior of silver ion on ^{t}Bu[4]CH$_2$Py concentration: filled symbols show the results for [C$_8$mim][PF$_6$], open symbols show the results for chloroform, [AgNO$_3$] $= 0.1$ mM, [HNO$_3$] $= 0$ M in [C$_8$mim][PF$_6$] or [HNO$_3$] $= 0.1$ M in chloroform.

In conclusion, ^{t}Bu[4]CH$_2$Py dissolved in an ionic liquid, [C$_8$mim][PF$_6$], provides enormously high extractability for silver ions. This result might highlight the vast opportunities that exist for the use of calixarenes as extractants, and promote the utilization of ionic liquids as alternative solvents for industrial liquid–liquid extraction processes. Ionic liquids have potential for enhancing the principles of "green" chemistry in various chemical processes. Based on this report, we envision future uses of ionic liquids containing calixarenes for not only metal ion extraction, but also extraction of bioproducts such as amino acids.

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