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Solvent Extraction and Stripping of Silver Ions in Room-Temperature Ionic Liquids Containing Calixarenes

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We found that a calix[4]arene-bearing pyridine is soluble in a typical room-temperature ionic liquid (RTIL), 1-alkyl-3-methylimidazolium hexafluorophosphate. Pyridinocalix[4]arene showed a high extraction ability and selectivity for silver ions. The extraction performance of the calix[4]arene was greatly enhanced by dissolution in RTILs compared to in chloroform. In a competitive extraction test using five different metal ions (Ag^+, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}), only silver ions were transferred by the calix[4]arene from the aqueous feed phase into the RTILs, through a cation-exchange mechanism. The pyridinocalix[4]arene was found to form a stable 1:1 complex with silver ions, both by slope analysis and by Job's method. Since it is easy to strip silver ions from RTILs by controlling the aqueous-phase pH, the extraction performance of calix[4]arene in RTILs was maintained after five repeated uses.

Liquid−liquid extraction is an effective analytical separation method for various metal ions. The extractant has a crucial effect on the separation and extraction efficiency. Selection of an appropriate extractant often determines the success of an extraction process. To date, many extractants have been developed for the extraction of various metal ions. In particular, a cyclic ligand calixarene,[1] which consists of phenol rings connected by methylene bridges, has attracted much attention because the cyclic ligand can recognize the size of metal ions with its cavity.[2] This unique property often leads to an extremely high selectivity for a target metal ion. However, calixarene has an inherent problem in industrial applications: poor solubility in organic solvents other than toxic chloric organic solvents. This shortcoming is a barrier for the practical use of calixarene. In previous papers, we succeeded in dissolving calixarene in aliphatic organic solvents by the addition of reversed micellar solutions[3] or alcohols.[4] Calixarene dissolved in aliphatic diluents exhibited a high extraction efficiency for target molecules.

Room-temperature ionic liquids (RTILs), which are composed entirely of ions, are currently being investigated as alternative reaction media to replace conventional organic solvents in a variety of synthetic,[5] catalytic,[6] and electrochemical applications.[7] RTILs consisting of hydrophobic cations and anions are water immiscible, thus appearing to be available for liquid−liquid extraction. The unique properties of RTILs such as negligible volatility and nonflammability are important advantages over conventional organic diluents used in liquid−liquid extraction processes. Several investigators have focused on the application of RTILs to liquid−liquid extraction of metal ions. Dai et al.,[8] for example, first discovered that highly efficient extraction of strontium ions can be achieved when dicyclohexano-18-crown-6 (DC18C6) is combined with RTILs. Subsequently, Rogers et al.[9] and Bartsch et al.[10] reported the extraction of various alkali metal ions with crown ethers in RTILs. In a different extractant, our research group[11] and Visser and Rogers[12] demonstrated that octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) dissolved in RTILs enhances the extractability of lanthanides and actinides in comparison to when it is dissolved in a conventional organic solvent. In addition, the use of RTILs in liquid−liquid extraction of organic substances was also investigated.[13−15] Armstrong et al.[14] reported the partition coefficients of a large variety of organic compounds with different functionalities and mentioned the moderately effective extraction of aromatic amino acids in the presence of dibenzo-18-crown-6. Subsequently, Pletnev et al.[15]

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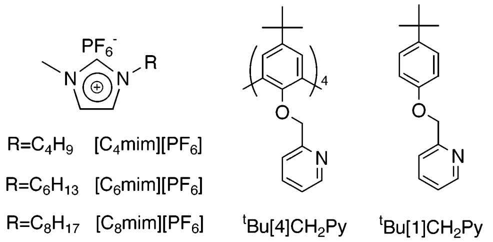

Figure 1. Molecular structures and abbreviations of RTILs and extractants.

reported that hydrophilic amino acids were quantitatively extracted into RTILs containing DC18C6 even though in the presence of crown ethers amino acids are typically not extracted into conventional solvents. RTILs can provide an appropriate environment that contributes to the performance of extractants and offer considerable potential as diluents in liquid−liquid extraction. The application of RTILs to liquid−liquid extraction is, however, problematic in that RTILs can dissolve only a few extractants. Thus, there has been much interest in the development of RTIL-soluble extractants.

Pyridine is miscible in RTILs, and it can also coordinate to soft metal ions. In a previous study,[16] we synthesized a calix[4]arene with pyridyl groups at the lower rim (^{t}Bu[4]CH_2Py, Figure 1) and reported the solubilities of various calixarenes in RTILs as well as their abilities to extract Ag^+. Nonsubstituted *tert*-butyl or *tert*-octylcalixarenes and their carboxylic acid derivatives were not dissolved in 3-methylimidazolium hexafluorophosphate-based RTILs ([$C_n$mim][PF_6], $n = 4, 6, 8$, Figure 1) at all; however, ^{t}Bu[4]CH_2Py was able to be dissolved in [$C_n$mim][PF_6] ($n = 4, 6, 8$), and this compound showed an unprecedentedly high ability to extract Ag^+.

In the present study, we investigated the extraction performance of ^{t}Bu[4]CH_2Py with respect to the target ion Ag^+ and discuss the mechanism of Ag^+ extraction from an aqueous feed solution into RTILs by using ^{t}Bu[4]CH_2Py. The extraction mechanism using ionic liquids was compared to that using chloroform. Selectivity of calixarene in RTILs was also evaluated by a competitive extraction trial using transition metal ions. Further, since we succeeded in recovering Ag^+ that had been extracted by the calixarene in the RTILs, we here report the stripping behavior of Ag^+ with ^{t}Bu[4]CH_2Py.

EXPERIMENTAL SECTION

Reagents. 4-*tert*-Butylphenol (98.0%) and 2-(chloromethyl)pyridine hydrochloride were obtained from Tokyo Kasei Kogyo Co., Inc. (Tokyo, Japan). 1-Methylimidazole (99%) and hexafluorophosphoric acid (60 wt % solution in water) were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI). 1-Chlorobutane (98%), 1-chlorohexane (97%), and 1-chlorooctane (95%) were obtained from Wako Pure Chemical Industries (Osaka, Japan). Silver nitrate (99.8%), copper nitrate 3-hydrate (99.5%), zinc nitrate 6-hydrate (99%), cobalt nitrate 6-hydrate (98%), nickel nitrate 6-hydrate (98%), and chloroform (HPLC grade) were purchased from Kishida Chemical Co. Ltd. and used without further purification. All other reagents were of commercially available analytical grade and used as received.

Synthesis of Pyridinocalix[4]arene and Its Monomer Analogue. *tert*-Butylcalix[4]arene was prepared as described elsewhere.[17] Pyridinocalix[4]arene ^{t}Bu[4]CH_2Py was subsequently reacted with 2-(chloromethyl)pyridine in a Williamson ether synthesis, as described previously.[18] Briefly, the synthetic procedure was as follows: Under a nitrogen atmosphere, a slurry of *tert*-butylcalix[4]arene (5.0 g, 7.6 mmol) and sodium hydride (6.9 g, 173 mmol, 60% in oil) in anhydrous DMF (50 mL) was stirred for 2 h at room temperature. After the solution was cooled, 2-(chloromethyl)pyridine (25 g, 152 mmol, 20 mol equiv) was carefully added and the reaction was stirred for 30 h at 40 °C. The solvent was evaporated under reduced pressure, and the organic materials were extracted with chloroform. After the organic layer was dried with anhydrous magnesium sulfate, the solvent was removed in vacuo, and the residue was recrystallized from methanol; white powder 6.2 g (80.3%), cone conformation: ^{1}H NMR (250 MHz, $CDCl_3$, TMS, 25 °C) (s, 36H, *t*-Bu) δ 3.06 (d, 4H, $ArCH_AAr$), 4.41 (d, 4H, $ArCH_BAr$), 4.99 (s, 8H, OCH_2Py), 6.83 (s, 8H, Ar*H*), 7.05 (t, 4H, 5-Py*H*), 7.27 (t, 4H, 4-Py*H*), 7.68 (d, 4H, 3-Py*H*), 8.48 (d, 4H, 6-Py*H*); MS, m/e (% relative intensity) 1038 (MNa^+, 20), 1016 (MH^+, 100). Anal. Calcd for $C_{68}H_{76}N_4O_4$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.37; H, 7.57; N, 5.43.

tert-Butylphenoxymethyl-2-pyridine ^{t}Bu[1]CH_2Py was also prepared as a monomer analogue, by the same procedure. Thus, 2-(chloromethyl)pyridine was added to 4-*tert*-butylphenol. The final product, a golden liquid (yield 98%), was purified by column chromatography (SiO_2) using a gradient of methanol in chloroform as the eluent: ^{1}H NMR (250 MHz, $CDCl_3$, TMS, 25 °C) (s, 36H, *t*-Bu) δ 5.19 (s, 8H, OCH_2Py), 6.94 (s, 8H, ArH_A), 7.20 (t, 4H, 5-Py*H*), 7.29 (s, 8H, ArH_B), 7.54 (d, 4H, 3-Py*H*), 7.69 (t, 4H, 4-Py*H*), 8.58 (d, 4H, 6-Py*H*); MS, m/e (% relative intensity) 244 (MH^+, 100). Anal. Calcd for $C_{16}H_{19}N_1O_1$: C, 79.63; H, 7.94; N, 5.81. Found: C, 79.91; H, 7.97; N, 5.73.

RTIL Synthesis. Syntheses of 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6], 1-hexyl-3-methylimidazolium hexafluorophosphate [C_6mim][PF_6], and 1-octyl-3-methylimidazolium hexafluorophosphate [C_8mim][PF_6] were conducted as described previously.[13] The analogous chloride salts [$C_n$mim][Cl] ($n = 4, 6, 8$) were prepared by adding equal amounts of 1-methylimidazole and a primary alkyl chloride and reacting for 72 h at 70 °C. The resulting viscous liquids were washed with ethyl acetate. After the last washing, the remaining ethyl acetate was removed by heating to 90 °C under vacuum and freeze-drying. The 1-alkyl-3-methylimidazolium hexafluorophosphate [$C_n$mim][PF_6] ($n = 4, 6, 8$) was prepared by slowly adding hexafluorophosphoric acid (1.3 mol equiv) to the corresponding chloride in 300 mL of water. After stirring for 12 h, the upper acidic aqueous layer was decanted and the lower ionic liquid portion was washed with water until the washings were no longer acidic. The remaining water was removed by heating to 90 °C under vacuum and freeze-drying.

1-Butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6]: 68% yield; ^{1}H NMR (250 MHz, acetone-d_6, TMS, 25 °C) δ 0.94 (t, 3H), 1.37 (m, 2H), 1.92 (m, 2H), 4.02 (s, 3H), 4.32 (t, 2H),

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7.64 (d, 2H), 8.86 (s, 1H). Anal. Calcd for $C_8H_{15}F_6N_2P_1$: C, 33.81; H, 5.32; N, 9.86. Found: C, 33.81; H, 5.33; N, 9.87.

1-Hexyl-3-methylimidazolium hexafluorophosphate [C$_6$mim]-[PF$_6$]: 72% yield; ^{1}H NMR (250 MHz, acetone-*d*$_6$, TMS, 25 °C) δ 0.87 (t, 3H), 1.33 (m, 6H), 1.90 (m, 2H), 4.02 (s, 3H), 4.33 (t, 2H), 7.65 (d, 2H), 8.89 (s, 1H). Anal. Calcd for $C_{10}H_{19}F_6N_2P_1$: C, 38.46; H, 6.13; N, 8.97. Found: C, 38.36; H, 6.11; N, 8.99.

1-Octyl-3-methylimidazolium hexafluorophosphate [C$_8$mim]-[PF$_6$]: 74% yield; ^{1}H NMR (250 MHz, acetone-*d*$_6$, TMS, 25 °C) δ 0.84 (t, 3H), 1.27 (m, 10H), 1.90 (m, 2H), 4.00 (s, 3H), 4.28 (t, 2H), 7.67 (d, 2H), 8.82 (s, 1H). Anal. Calcd for $C_{12}H_{23}F_6N_2P_1$: C, 42.35; H, 6.81; N, 8.23. Found: C, 42.39; H, 6.78; N, 8.24.

Liquid−Liquid Extraction of Metal Ions in RTILs or Chloroform. An extracting phase was prepared by dissolving ^{t}Bu[n]CH$_2$Py (n = 1, 4) in [C$_n$mim][PF$_6$] (n = 4, 6, 8). 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 25 °C 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 (Shimazu AA-6700), which then allowed calculation of the degree of extraction ($E = [\mathrm{Ag}^+]_{\mathrm{org.eq.}}/[\mathrm{Ag}^+]_{\mathrm{aq.ini.}}$) and the distribution ratio ($D = [\mathrm{Ag}^+]_{\mathrm{org.eq.}}/[\mathrm{Ag}^+]_{\mathrm{aq.eq.}}$). In the continuous variation method (Job's method), the total concentration of metal ion and extractant was kept constant at 0.2 mM. In the competitive solvent extraction, solutions containing various metal ions (AgNO$_3$, Cu(NO$_3$)$_2$, Zn(NO$_3$)$_2$, Ni(NO$_3$)$_2$, Co(NO$_3$)$_2$) were prepared at metal concentrations of 0.1 mM.

Solubility of RTILs in Water. A [C$_n$mim][PF$_6$] (n = 4, 6, 8) was mixed and shaken on a vortex mixer with an equal volume of deionized water at 25 °C for 30 min. These mixtures were then centrifuged for 3 min to promote phase separation. After each phase was separated, the aqueous phase was diluted with deionized water by 1/50-fold for [C$_8$mim][PF$_6$] and 1/200-fold for [C$_6$mim][PF$_6$] and [C$_4$mim][PF$_6$]. The absorbance of this solution at 211 nm was measured by a UV−visible spectrophotometer (Jasco U-best 570). The [C$_n$mim]$^+$ concentrations in aqueous phases were calculated with the Beer's law plots formed for [C$_n$mim][Cl] solutions.

Stripping Test. Forward extraction of Ag$^+$ (0.1 mM) with ^{t}Bu-[4]CH$_2$Py (0.5 mM) was performed following the same procedure. After equal volumes (15 mL) of the aqueous and RTIL solutions were mixed and shaken on the vortex mixer, Ag$^+$ was quantitatively transferred to the RTIL phase. The RTIL phase was divided into 2.5-mL aliquots, and a fresh aqueous solution (2.5 mL) containing nitric acid was added to each aliquot. Both phases were mixed and shaken on the vortex mixer at 25 °C for 30 min. These mixtures were then centrifuged for 3 min to promote phase separation. The stripping solution was separated from the RTIL phase and the Ag$^+$ concentration was quantified in order to evaluate the stripping ratio ($= 100 \times [\mathrm{Ag}^+]_{\mathrm{aq.eq.}}/[\mathrm{Ag}^+]_{\mathrm{org.ini.}}$)

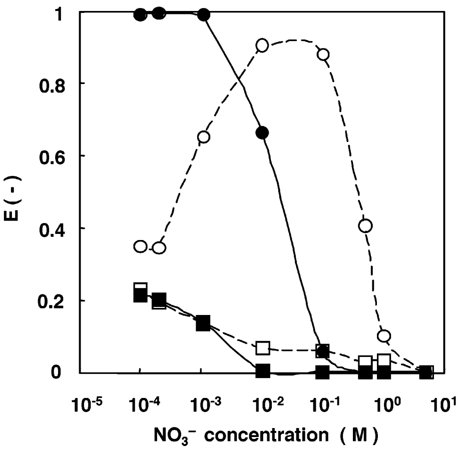

Figure 2. Extraction behavior of Ag$^+$ in [C$_8$mim][PF$_6$]/aqueous (closed symbols) or chloroform/aqueous (open symbols) systems. Extracting phase: 0.5 mM ^{t}Bu[4]CH$_2$Py (circles) or 2 mM ^{t}Bu[1]CH$_2$-Py (squares). Aqueous phase: 0.1 mM AgNO$_3$.

RESULTS AND DISCUSSION

Extraction Equilibria of Silver Ions in RTILs or Chloroform. The monomer analogue ^{t}Bu[1]CH$_2$Py was synthesized in order to compare its ability to extract Ag$^+$ with that of the cyclic ligand ^{t}Bu[4]CH$_2$Py. Both extractants are soluble in [C$_n$mim][PF$_6$] (n = 4, 6, 8). The silver ion, which exhibits a high affinity for ligands containing a soft donor, was employed as the target metal ion. Figure 2 shows the extraction behavior of Ag$^+$ in the systems with ^{t}Bu[4]CH$_2$Py or ^{t}Bu[1]CH$_2$Py in [C$_8$mim][PF$_6$] in comparison to the systems with ^{t}Bu[4]CH$_2$Py or ^{t}Bu[1]CH$_2$Py in chloroform. Nitric acid was used as the source of counterions for the Ag$^+$ transfer, because Ag$^+$ forms a water-insoluble complex with chloride. The concentration of ^{t}Bu[1]CH$_2$Py was 4-fold greater than that of ^{t}Bu[4]CH$_2$Py, to provide the same number of functional pyridyl groups. In the absence of these extractants, the partitioning of Ag$^+$ into [C$_8$mim][PF$_6$] or chloroform was confirmed to be negligibly small. The monomer analogue ^{t}Bu[1]CH$_2$-Py did not extract Ag$^+$ very well, whereas the cyclic ligand ^{t}Bu[4]CH$_2$Py efficiently extracted Ag$^+$ from the aqueous to the organic phase, which indicates that the inclusion and chelating effects are predominant factors in the exceptionally high Ag$^+$ extraction. The cavity size of ^{t}Bu[4]CH$_2$Py fits the Ag$^+$ ion size (ionic radius, 1.02 Å), which is also similar to that of Na$^+$ (ionic radius, 1.02 Å).

The extraction behavior of Ag$^+$ with ^{t}Bu[4]CH$_2$Py in [C$_8$mim]-[PF$_6$] is quite different from that with ^{t}Bu[4]CH$_2$Py in chloroform. In the case with chloroform, ~90% of Ag$^+$ was extracted by ^{t}Bu-[4]CH$_2$Py at relatively high nitric acid concentrations (10^{-1}−10^{-2} M; pH 1−2). The decrease in extractability at low NO$_3^-$ concentrations could be attributed to the lack of counterions, and at the high NO$_3^-$ concentrations, the extraction efficiency was reduced due to the protonation of pyridyl nitrogens in the cyclic ligand. In contrast, in the ionic liquids, ^{t}Bu[4]CH$_2$Py exhibited high extraction affinity for Ag$^+$ at a low NO$_3^-$ concentration. In particular, even when no HNO$_3$ was present, Ag$^+$ was efficiently transferred into [C$_8$mim][PF$_6$]. These results suggest that metal complexation in [C$_8$mim][PF$_6$] proceeds via a different mechanism from that in a conventional organic solvent.

It is assumed that the properties of the extracting solvent affect the ability of ^{t}Bu[4]CH$_2$Py to act as an extractant. The extraction behavior of Ag$^+$ with increasing ^{t}Bu[4]CH$_2$Py concentrations in

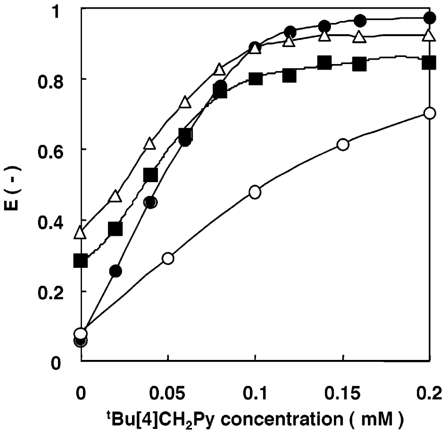

Figure 3. Degree of Ag^+ extraction with increasing ^{t}Bu[4]CH$_2$Py concentration in [C$_n$mim][PF$_6$] ($n = 4$ (closed squares), $n = 6$ (open triangles), $n = 8$ (closed circles)) and chloroform (open circles). Aqueous phase: 0.1 mM $AgNO_3$ in deionized water when using [C$_n$mim][PF$_6$] or 0.1 mM $AgNO_3$ in 0.1 M HNO_3 when using chloroform.

various RTILs and in chloroform was investigated (Figure 3). This trial was carried out under optimal conditions for the RTILs or chloroform systems, based on the results presented in Figure 2: The aqueous solution for the RTILs system was prepared by dissolving 0.1 mM $AgNO_3$ in deionized water, while in the chloroform system, 0.1 mM $AgNO_3$ in 0.1 M HNO_3 was used as the aqueous phase. The solubility of RTILs in deionized water was measure to be 7.48 ± 0.07 ([C$_8$mim][PF$_6$]), 24.66 ± 0.23 ([C$_6$mim][PF$_6$]), and 73.17 ± 0.10 mM ([C$_4$mim][PF$_6$]). In [C$_4$mim][PF$_6$] and [C$_6$mim][PF$_6$], Ag^+ distributed into the organic phase to some extent without any extractant. The efficiency of Ag^+ extraction by ^{t}Bu[4]CH$_2$Py increased slightly as the 1-alkyl group in the RTILs was elongated. The solubility of ^{t}Bu[4]CH$_2$Py in [C$_n$mim][PF$_6$] also increased as the 1-alkyl group in the RTILs was elongated, because RTILs with a long alkyl chain result in high hydrophobicity. Thus, it was suggested that ^{t}Bu[4]CH$_2$Py in [C$_8$mim][PF$_6$] can form a more stable complex with Ag^+ than it can when in the other RTILs tested in this study.

The extraction ability of ^{t}Bu[4]CH$_2$Py was remarkably higher in the RTILs than in chloroform. For example, Ag^+ can be quantitatively extracted into [C$_8$mim][PF$_6$] at a concentration of only 0.2 mM ^{t}Bu[4]CH$_2$Py, which is only twice the concentration of Ag^+. In chloroform, however, a 10-fold higher concentration, 2 mM ^{t}Bu[4]CH$_2$Py, is required to obtain equivalent Ag^+ extraction.

Determination of the Extraction Equilibrium Equation. In recent studies of metal extraction in RTILs, it has been demonstrated that the partitioning mechanism with crown ethers[19] or CMPO[20] changes from an ion pair extraction mechanism (eq 1) in conventional organic solvents to a cation-exchange extraction mechanism (eq 2) in which the metal ion is exchanged for the cationic constituent of the RTILs.

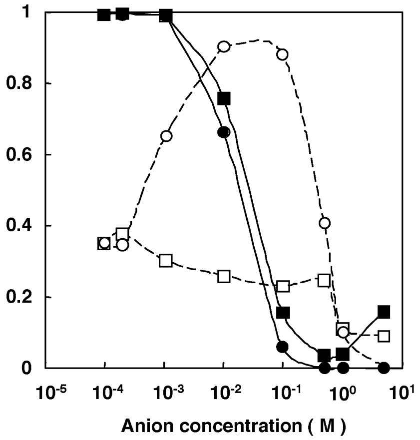

Figure 4. Effect of the anionic species (NO_3^- (circles) or SO_4^{2-} (squares)) on the extraction of Ag^+ by ^{t}Bu[4]CH$_2$Py. Extracting phase: 0.5 mM ^{t}Bu[4]CH$_2$Py in [C$_8$mim][PF$_6$] (closed symbols) or chloroform (open symbols). Aqueous phase: 0.1 mM $AgNO_3$.

$$\mathrm{M}^{m+} + x\mathrm{L}_{\mathrm{org}} + m\mathrm{NO_3}^- \leftrightarrow \mathrm{ML}_x(\mathrm{NO_3})_{m,\mathrm{org}} \qquad (1)$$

$$\mathrm{M}^{m+} + x\mathrm{L}_{\mathrm{org}} + m\mathrm{C}_n\mathrm{mim}^+{}_{\mathrm{org}} \leftrightarrow \mathrm{ML}_{x,\mathrm{org}}{}^{m+} + m\mathrm{C}_n\mathrm{mim}^+ \qquad (2)$$

In the above equations, species present in the organic phase are indicated by the subscript org.

In contrast, Dietz et al.[21] argued that, as in conventional organic solvents, Sr^{2+} transfer with a crown ether (DC18C8) in highly hydrophobic RTILs proceeds through ion pair extraction. In the present study, ^{t}Bu[4]CH$_2$Py dissolved in RTILs greatly enhanced the extractability of Ag^+ compared with that of ^{t}Bu[4]CH$_2$Py dissolved in chloroform, which prompted us to investigate the difference in the extraction mechanism between [C$_8$mim][PF$_6$] and the chloroform system. Figure 4 shows the effect of the anionic species on the extraction of Ag^+ by ^{t}Bu[4]CH$_2$Py. Nitric acid or sulfuric acid was employed as counterion. In chloroform, the degree of extraction was reduced drastically when SO_4^{2-} was used as the anion. This result indicates that the anionic species greatly affects Ag^+ transfer by ^{t}Bu[4]CH$_2$Py. In fact, ^{t}Bu[4]CH$_2$Py in chloroform extracts Ag^+ through ion pair extraction accompanied by counterions. In [C$_8$mim][PF$_6$], the extraction behavior of Ag^+ with SO_4^{2-} was similar to that with NO_3^-, which demonstrates that the Ag^+ transfer into [C$_8$mim][PF$_6$] does not involve anion coextraction.

The influence of the aqueous-phase C$_8$mim$^+$ concentration on Ag^+ extraction by ^{t}Bu[4]CH$_2$Py is shown in Figure 5. The C$_8$mim$^+$ concentration in the aqueous phase was adjusted using [C$_8$mim][Cl], which is soluble in water. We carefully verified that the initial concentration of Ag^+ shows a steady value in all samples for a long period. This result means that Ag^+ does not form a precipitate with Cl^- under the present experimental conditions. The transfer of Ag^+ into chloroform was independent of the aqueous-phase C$_8$mim$^+$ concentration. In contrast, in the system with [C$_8$mim][PF$_6$], the degree of extraction decreased gradually with increases in the aqueous-phase C$_8$mim$^+$ concentration. This means that exchange of Ag^+ for C$_8$mim$^+$ in the organic phase becomes difficult when the concentration of C$_8$mim$^+$ in the aqueous phase

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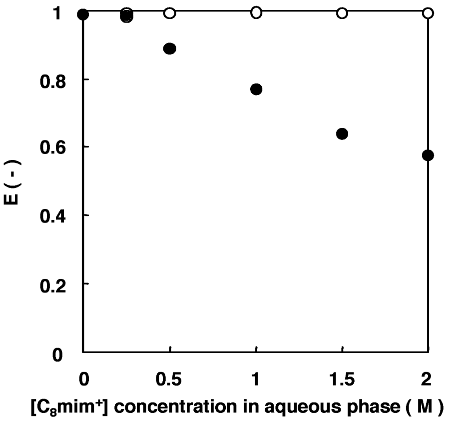

Figure 5. Effect of aqueous-phase C_8mim^+ concentration on the extraction of Ag^+ by $^tBu[4]CH_2Py$. Extracting phase: 0.5 mM $^tBu[4]CH_2Py$ in $[C_8mim][PF_6]$ (closed symbols) or chloroform (open symbols). Aqueous phase: 0.1 mM $AgNO_3$.

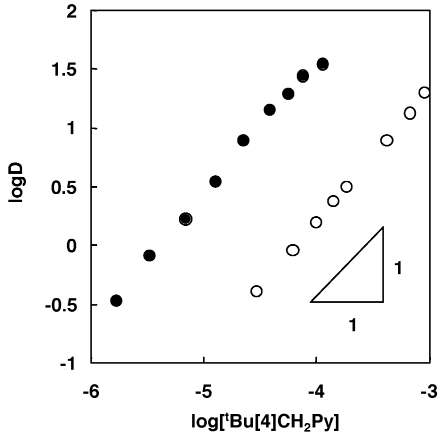

Figure 6. Slope analysis of Ag^+ extraction as a function of $^tBu[4]CH_2Py$ concentration in $[C_8mim][PF_6]$ (closed symbols) or chloroform (open symbols). Aqueous phase: 0.1 mM $AgNO_3$ in deionized water when using $[C_n mim][PF_6]$ or 0.1 mM $AgNO_3$ in 0.1 M HNO_3 when using chloroform.

is high, because metal ion transfer by $^tBu[4]CH_2Py$ into $[C_8mim][PF_6]$ proceeds via a cation-exchange mechanism, as expressed by eq 2.

To determine the fundamental stoichiometry of the Ag^+–$^tBu[4]CH_2Py$ complex, slope analysis was conducted as a function of the equilibrium concentration of $^tBu[4]CH_2Py$ in the organic phase. As shown in Figure 6, linear relationships between log *D* and log[$^tBu[4]CH_2Py$] with a slope of 1 were obtained for both the RTIL and the chloroform systems. Furthermore, the stoichiometry of the extraction complex was confirmed by Job's method. As illustrated in Figure 7, the concentration of Ag^+ in $[C_8mim][PF_6]$ reached a maximum value when the ratio of the $^tBu[4]CH_2Py$ concentration to the total concentration was 0.5. These results suggest that one $^tBu[4]CH_2Py$ is required to extract one Ag^+, indicating that a 1:1 complex is formed. On the basis of these results, the extraction mechanisms in RTILs and in chloroform were determined to be as follows:

$$Ag^+ + {}^tBu[4]CH_2Py_{org} + NO_3^- \Leftrightarrow Ag\cdot{}^tBu[4]CH_2Py\cdot NO_{3,org} \text{ in chloroform} \quad (3)$$

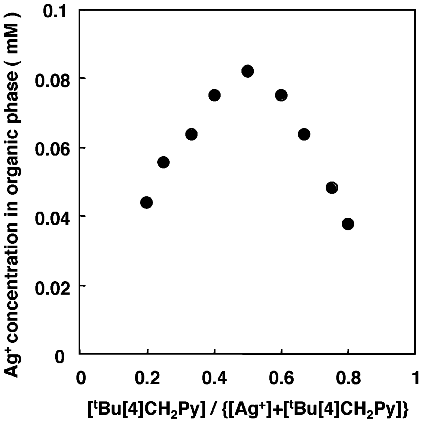

Figure 7. Job's plots of the complexation between Ag^+ and $^tBu[4]CH_2Py$ in $[C_8mim][PF_6]$. Total concentration of Ag^+ and $^tBu[4]CH_2Py$ was kept constant at 0.2 mM.

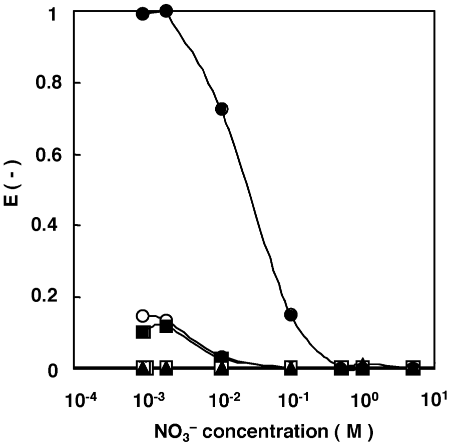

Figure 8. Competitive extraction of transition metal ions by $^tBu[4]CH_2Py$ in $[C_8mim][PF_6]$. Extracting phase: 0.5 mM $^tBu[4]CH_2Py$ in $[C_8mim][PF_6]$. Aqueous phase: 0.1 mM $AgNO_3$ (closed circles), 0.1 mM $Cu(NO_3)_2$ (open circles), 0.1 mM $Zn(NO_3)_2$ (closed squares), 0.1 mM $Co(NO_3)_2$ (open squares), and 0.1 mM $Ni(NO_3)_2$ (closed triangles).

$$Ag^+ + {}^tBu[4]CH_2Py_{org} + C_8mim^+{}_{org} \Leftrightarrow Ag\cdot{}^tBu[4]CH_2Py_{,org}{}^+ + C_8mim^+ \text{ in } [C_8mim][PF_6] \quad (4)$$

Competitive Extraction of Transition Metal Ions. The unique property of calixarene is its high selectivity for a target metal ion. To assess the selectivity of $^tBu[4]CH_2Py$, competitive extraction of five different transition metal ions (Ag^+, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}) by $^tBu[4]CH_2Py$ in $[C_8mim][PF_6]$ was conducted. As summarized in Figure 8, $^tBu[4]CH_2Py$ could separate only Ag^+ from the aqueous phase containing the transition metal ions. Two possible reasons for this selectivity could be that Ag^+ fits the cavity of $^tBu[4]CH_2Py$ much better than the other metal ions tested in this study (ionic radii: Ag^+, 1.02 Å; Cu^{2+}, 0.73 Å; Zn^{2+}, 0.74 Å; Co^{2+}, 0.75 Å' Ni^{2+}, 0.69 Å), and is a monovalent cation, which is favorable for exchange with C_8mim^+.

Stripping and Recycling Test. The back-transfer of metal ions into a receiving phase is also important for separation and concentration of a target metal ion. Recently, Wei et al.[22] reported that metal ions extracted with the acidic chelator dithizone in

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[22] Wei, G. T.; Yang, Z.; Chen, C. J. *Anal. Chim. Acta* **2003**, *488*, 183.

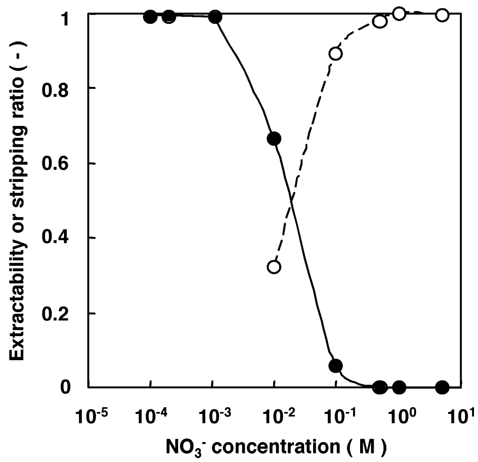

Figure 9. Extraction and stripping profile of Ag^+ in $[C_8mim][PF_6]$. Extraction (closed symbols); stripping (open symbols). Extracting phase: 0.5 mM $^tBu[4]CH_2Py$ in $[C_8mim][PF_6]$. Aqueous phase: 0.1 mM $AgNO_3$.

RTILs can be stripped into an acidic solution. However, since neutral extractants such as crown ethers or CMPO are able to extract metal ions under acidic conditions, researchers have experienced difficulties in recovering cations extracted by neutral extractants, despite the positive results for RTILs extraction systems. Fortunately, the efficiency of Ag^+ extraction by $^tBu[4]CH_2Py$ in RTILs is reduced with increasing nitric acid concentration, even though $^tBu[4]CH_2Py$ is a neutral extractant. The stripping test for Ag^+ extracted by $^tBu[4]CH_2Py$ in $[C_8mim][PF_6]$ was performed using pH control of the receiving phase (Figure 9). The stripping efficiency of Ag^+ was dependent on the concentration of HNO_3, and the profile of the stripping ratio was the inverse of the profile for the degree of extraction. As a result, Ag^+ was efficiently transferred into the receiving phase at low-pH conditions because $^tBu[4]CH_2Py$ was protonated under acidic conditions. In comparison to the results in chloroform, a 0.1 M HNO_3 solution ensures the recovery of 90% of the Ag^+ in $[C_8mim][PF_6]$, whereas in chloroform, only 10% of the Ag^+ is recovered under the same conditions, and a 5 M HNO_3 solution is required to completely recover Ag^+. In addition, it was found that Ag^+ recovery could be achieved using a stripping solution containing 1 M thiourea. A recycling test for the RTILs phase was also carried out, following the same procedure. A 0.5 M HNO_3 solution was employed as the receiving phase, and the RTIL phase was then recycled. Even though five cycles of forward and back extraction were carried out, the $^tBu[4]CH_2Py$-RTILs extraction system maintained its high extraction ability (the average degree of extraction was 99.5%). This extraction system was found to be very reproducible.

CONCLUSION

A solvent extraction system based on combining RTILs and calixarene was investigated. Pyridinocalix[4]arene dissolved in $[C_8mim][PF_6]$ is able to extract silver ions much more effectively than when it is dissolved in chloroform, and high selectivity for silver ions from among five different transition metal ions (Ag^+, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}) was demonstrated. This compound transfers silver ions into RTIL phases via a cation-exchange mechanism and forms a stable 1:1 complex with silver ions. Furthermore, recovery of silver ions from $[C_8mim][PF_6]$ into a receiving phase can be achieved under acidic conditions, which are mild in comparison to those required for the chloroform system. These results highlight the great potential of calixarenes as extractants in RTILs systems. In the future, modification of appropriate functional groups at the lower and/or upper rims will enable expansion of the frontiers of RTILs system applications.

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