Formation of Minimal Third Phase in Ionic Liquid Extraction System with Trioctylphosphine Oxide and Its Possible Application to Extraction Concentration

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The third-phase formation behavior in ionic liquid (IL) extraction system using trioctylphosphine oxide (TOPO) was investigated. In the use of a relatively less-lipophilic IL, such as 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C₄mimTf₂N), the third phase was formed between the aqueous phase and the IL phase. The third phase seems to have a relatively high lipophilicity compared to the IL phase. The main components of the third phase were suggested as being (H₃O)TOPO⁺, IL anion (Tf₂N⁻), IL cation (C₄mim⁺) and free TOPO. In addition, the third phase showed an extraction concentration ability for the Fe(III)-thiocyanato complex.

Keywords Ionic liquids, extraction, third phase, concentration

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Ionic liquids (ILs) have attracted attention as novel fluid media and hydrophobic ILs, including 1-alkyl-3-methylimidazolium hexafluorophosphates (C_nmimPF₆) and bis(trifluoromethanesulfonyl)imides (C_nmimTf₂N), have often been used as an extraction solvent in solvent extraction for metals.¹⁻⁶ Trioctylphosphine oxide (TOPO) is a well-known lipophilic monodentate Lewis base, and is often used in traditional metal extraction as an extractant or a synergistic agent. Also in the IL extraction, the possible use of TOPO has been energetically investigated.⁷⁻¹⁴ However, Liu *et al.* made mention in their literature¹⁵ that the use of TOPO on the IL extraction resulted in the formation of an “undesirable” third phase.

In the traditional metal extraction system using organic solvents, third-phase formation is a well-known problematic phenomenon.¹⁶ Generally, the co-use of a nonpolar organic solvent (ex. dodecane), a neutral Lewis base (ex. tributyl phosphate) and a relatively high concentration of a mineral acid (ex. nitric acid) often results in the formation, and the formed third phase is relatively less-lipophilic. On the contrary, ILs are relatively high-polar solvents and third-phase formation mechanism in the IL system seems to be different from that in the traditional one. In this communication, we discuss on the third-phase formation behavior on using TOPO in the IL (C_nmimTf₂N) extraction system, and possible use of the third-phase formation to extraction concentration.

Experimental

Chemicals were of reagent-grade and were used without further purification. Four ILs [1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C₂mimTf₂N), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C₄mimTf₂N), 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C₆mimTf₂N)]

and 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (C₈mimTf₂N)] were synthesized according to a reported procedure.^{17,18} High-purity water prepared with using a Direct-Q water purification system (Millipore) was used throughout.

A third-phase formation experiment was performed as follows. In a centrifuge tube, 1.0 cm³ of an IL phase containing 1.0 × 10⁻¹ mol dm⁻³ of TOPO and 5.0 cm³ of an aqueous phase containing 1.0 × 10⁻¹ mol dm⁻³ of (H, K)NO₃ were shaken mechanically at 25 ± 1 °C for 30 min. After centrifugation, the third-phase formation behavior was observed and the pH in the aqueous phase was measured. If needed, the volume of the third phase was measured after dissolving the phase into cyclohexane, putting the dissolved one into a calibrated glass tube and evaporating the cyclohexane under reduced pressure.

A metal extraction study was performed as follows. In a centrifuge tube, 1.0 cm³ of an IL phase containing 1.0 × 10⁻¹ mol dm⁻³ of TOPO and 5.0 cm³ of an aqueous phase containing 4.5 μg cm⁻³ of Fe(III), 1.0 × 10⁻¹ mol dm⁻³ of (H, K)NO₃ and 1.0 × 10⁻² mol dm⁻³ of KSCN were shaken mechanically at 25 ± 1 °C for 30 min. After phase separation by centrifugation, the pH in the aqueous phase was measured. The Fe concentration remaining in the aqueous phase was determined by flame atomic absorption spectrophotometry. That extracted into the IL phase was determined similarly after back-extraction into a 10-fold volume of 6 mol dm⁻³ HNO₃ and the extractability into the IL phase (%E_{IL}) was calculated. The extractability into the third phase (%E_{3rd}) was calculated based on the mass balance.

Results and Discussion

At first, we investigated whether the third phase is formed or not with using the four ILs. A small volume of the colorless third phase was formed with the use of less-lipophilic C₂mimTf₂N and C₄mimTf₂N, whereas the use of more-lipophilic C₆mimTf₂N and C₈mimTf₂N resulted in no third-phase formation. Figure 1 shows a typical photograph at aqueous phase pH 3.0, in which

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Fig. 1 Third-phase formation behavior upon adding TOPO in the IL extraction system. IL phase (1.0 cm³): A, C₂mimTf₂N; B, C₄mimTf₂N; C, C₆mimTf₂N; D, C₈mimTf₂N. Aqueous phase (5.0 cm³): 1.0 × 10⁻¹ mol dm⁻³ of KNO₃, pH 3.0. Initial TOPO concentration in the IL phase: 1.0 × 10⁻¹ mol dm⁻³. (Fe(III)-thiocyanato complex was added.)

Fig. 2 Relationship between the volume of the formed third phase and the aqueous phase pH in the C₄mimTf₂N-TOPO system. IL phase (1.0 cm³): 1.0 × 10⁻¹ mol dm⁻³ TOPO. Aqueous phase (1.0 cm³): 1.0 × 10⁻¹ mol dm⁻³ of (H, K)NO₃.

the Fe(III)-thiocyanato complex was added to the system with consideration for the visibility of the third phase. The result is in accordance with the previous report,¹⁵ and it was suggested that the third phase has a relatively high lipophilicity compared to the IL phase. In addition, it was confirmed that the density of the third phase is between water and the IL. In this study, further experiments were performed with using C₄mimTf₂N as an IL.

Next, the volume of the formed third phase in the C₄mimTf₂N-TOPO system was evaluated. At pH > 3, the phase decreased in size and disappeared based on visual observation, suggesting that an acidic condition is needed to form the third phase. Using the fact that the third phase is soluble into cyclohexane, the volume of the third phase was measured at pH 0.9–3.5. (The third phase is so viscous that its volume cannot be directly measured by pipetting it.) The determined volume is summarized in Fig. 2. Although the volume decreased slightly with the increase in the aqueous phase pH, the volume was estimated as being ca. 40 mm³ at 1 < pH < 3. In addition, a decrease in the TOPO concentration resulted in a noticeable decrease in the third-phase volume, and the phase disappeared almost completely on 1.0 × 10⁻² mol dm⁻³ TOPO. From these results, it was suggested that the (H₃O)TOPO⁺ complex is an important component for the third phase.

Fig. 3 Transition of phase separation behavior. A: 5.0 cm³ of aqueous phase (1.0 × 10⁻¹ mol dm⁻³ of KNO₃, pH 3.0) + 20 mm³ of (H₃O)TOPO⁺Tf₂N⁻; B: A + 40 mm³ of C₄mimTf₂N; C: A + 1.0 cm³ of C₄mimTf₂N. (Fe(III)-thiocyanato complex was added.)

Fig. 4 Aqueous phase pH dependency of %E_{IL} (○) and %E_{3rd} (●) in the C₄mimTf₂N-TOPO system (A) and the C₆mimTf₂N-TOPO system (B). IL phase (1.0 cm³): 1.0 × 10⁻¹ mol dm⁻³ TOPO. Aqueous phase (1.0 cm³): 1.0 × 10⁻¹ mol dm⁻³ of (H, K)NO₃ and 1.0 × 10⁻² mol dm⁻³ of KSCN.

To evaluate other components in the third phase, the following phase separation experiment was performed. The addition of TOPO to a 0.1 mol dm⁻³ HTf₂N aqueous solution resulted in forming a water-immiscible colorless liquid phase upon the solution. It was estimated that this liquid phase consisted mainly of (H₃O)TOPO⁺Tf₂N⁻, and the density of the phase was less than water. After pipetting 20 mm³ of the liquid phase and adding it to 5.0 cm³ of an aqueous solution (pH 3.0) (Fig. 3A), 40 mm³ of C₄mimTf₂N was added. The liquid phase became unified with the IL phase and sank under the aqueous phase (Fig. 3B). A further addition of C₄mimTf₂N resulted in re-forming a new phase between the aqueous phase and the IL phase (Fig. 3C). From the result, it was suggested that not only Tf₂N⁻ (IL anion) but also C₄mim⁺ (IL cation) are important components for the third phase formed in the C₄mimTf₂N-TOPO extraction system.

Because of the relatively lipophilic nature, it was expected that the third phase contains a significant amount of TOPO not

only as $(\text{H}_3\text{O})\text{TOPO}^+$ but also as free TOPO. This hypothesis can be verified by studying metal extraction into the third phase. Thus, the extraction behavior of the Fe(III)-thiocyanato complex into the third phase was investigated. Figure 4 shows $\%E_{\text{IL}}$ and $\%E_{3\text{rd}}$ for Fe(III) in the $\text{C}_4\text{mimTf}_2\text{N}$ -TOPO system coexisting $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ of thiocyanate in the aqueous phase as a function of the aqueous phase pH. For a comparison, $\%E_{\text{IL}}$ for Fe(III) in the $\text{C}_6\text{mimTf}_2\text{N}$ -TOPO system is also shown in the figure. In the $\text{C}_4\text{mimTf}_2\text{N}$ -TOPO system, Fe(III) was quantitatively extracted into the third phase with a reddish coloration, whereas the use of the $\text{C}_6\text{mimTf}_2\text{N}$ -TOPO system resulted in the extraction of Fe(III) into the IL ($\text{C}_6\text{mimTf}_2\text{N}$) phase. Moreover, the absence of TOPO resulted in scarce Fe(III) extraction in both of the systems, which is in agreement with a previous study using the C_4mimPF_6 system.¹⁹ From these results, it was suggested that the formed third phase in the $\text{C}_4\text{mimTf}_2\text{N}$ -TOPO has a certain content of free TOPO, and that the extracted Fe(III) species is the Fe(III)-SCN-TOPO ternary (and probably neutral) complex. In addition, Fe(III) in the aqueous phase was calculationaly *ca.* 100-fold concentrated by extraction into the third phase.

In conclusion, it was confirmed that third phase is formed in the $\text{C}_2\text{mimTf}_2\text{N}$ -TOPO and $\text{C}_4\text{mimTf}_2\text{N}$ -TOPO extraction systems under an acidic condition. In the latter system, *ca.* 40 mm³ of the third phase was formed from 1.0 cm³ of the $\text{C}_4\text{mimTf}_2\text{N}$ containing $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ of TOPO and 5.0 cm³ of the aqueous phase at $1 < \text{pH} < 3$. The main components of the third phase were suggested as being $(\text{H}_3\text{O})\text{TOPO}^+$, IL anion (Tf_2N^-), IL cation and free TOPO. Since its extraction ability for the Fe(III)-thiocyanato complex, furthermore, it was found that the third-phase formation is not always unfavorable for extraction separation but that the third phase can be used as an extraction concentration medium.

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