Rapid Communications

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

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Abstract

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 (H₂O)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 \((C_n\text{mimPF}_6)\) and bis(trifluoromethanesulfonyl)imides \((C_n\text{mimTf}_2\text{N})\), have often been used as an extraction solvent in solvent extraction for metals.\(^{1,6}\) Triocytlyphosphine 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 literature\(^{15}\) 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 \((C_n\text{mimTf}_2\text{N})\) 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 \((C_2\text{mimTf}_2\text{N})\), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide \((C_4\text{mimTf}_2\text{N})\), 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide \((C_6\text{mimTf}_2\text{N})\) and 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide \((C_8\text{mimTf}_2\text{N})\)] were
synthesized according to a reported procedure. 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 cm$^3$ of an IL phase containing 1.0×10$^{-1}$ mol dm$^{-3}$ of TOPO and 5.0 cm$^3$ of an aqueous phase containing 1.0×10$^{-1}$ mol dm$^{-3}$ of (H, K)NO$_3$ were shaken mechanically at 25±1 ºC 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 cm$^3$ of an IL phase containing 1.0×10$^{-1}$ mol dm$^{-3}$ of TOPO and 5.0 cm$^3$ of an aqueous phase containing 4.5 µg cm$^{-3}$ of Fe(III), 1.0×10$^{-1}$ mol dm$^{-3}$ of (H, K)NO$_3$ and 1.0×10$^{-2}$ mol dm$^{-3}$ of KSCN were shaken mechanically at 25±1 ºC 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$^{-3}$ HNO$_3$ 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 C$_2$ mimTf$_2$N and C$_4$ mimTf$_2$N, whereas the use of more-lipophilic C$_6$ mimTf$_2$N and C$_8$ mimTf$_2$N resulted in no third-phase formation. Figure 1 shows a typical photograph at aqueous phase pH 3.0, in which
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,\textsuperscript{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 C\textsubscript{4}mimTf\textsubscript{2}N as an IL.

Next, the volume of the formed third phase in the C\textsubscript{4}mimTf\textsubscript{2}N–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 mm\textsuperscript{3} at 1 <
\textit{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\times10\textsuperscript{-2} mol dm\textsuperscript{-3}
TOPO. From these results, it was suggested that the (H\textsubscript{3}O)TOPO\textsuperscript{+} complex is an important
component for the third phase.

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\textsuperscript{-3} HTf\textsubscript{2}N aqueous solution
resulted in forming a water-immiscible colorless liquid phase upon the solution. It was
estimated that this liquid phase consisted mainly of (H\textsubscript{3}O)TOPO\textsuperscript{+}·Tf\textsubscript{2}N\textsuperscript{−}, and the density of the
phase was less than water. After pipetting 20 mm\textsuperscript{3} of the liquid phase and adding it to 5.0 cm\textsuperscript{3} of
an aqueous solution (pH 3.0) (Fig. 3A), 40 mm\textsuperscript{3} of C\textsubscript{4}mimTf\textsubscript{2}N was added. The liquid phase
became unified with the IL phase and sank under the aqueous phase (Fig. 3B). A further
addition of C\textsubscript{4}mimTf\textsubscript{2}N 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 Tf\textsubscript{2}N\textsuperscript{−} (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 (H₃O)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_IL and %E_3rd for Fe(III) in the C₄mimTf₂N–TOPO system coexisting 1.0×10⁻² mol dm⁻³ of thiocyanate in the aqueous phase as a function of the aqueous phase pH. For a comparison, %E_IL for Fe(III) in the C₆mimTf₂N–TOPO system is also shown in the figure. In the C₄mimTf₂N–TOPO system, Fe(III) was quantitatively extracted into the third phase with a reddish coloration, whereas the use of the C₆mimTf₂N–TOPO system resulted in the extraction of Fe(III) into the IL (C₆mimTf₂N) 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 C₄mimPF₆ system.¹⁹ From these results, it was suggested that the formed third phase in the C₄mimTf₂N–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 calculationally ca. 100-fold concentrated by extraction into the third phase.

In conclusion, it was confirmed that third phase is formed in the C₂mimTf₂N–TOPO and C₄mimTf₂N–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 C₄mimTf₂N containing 1.0×10⁻¹ mol dm⁻³ of TOPO and 5.0 cm³ of the aqueous phase at 1 < pH < 3. The main components of the third phase were suggested as being (H₂O)TOPO⁺, IL anion (Tf₂N⁻), 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.
Acknowledgements

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References


Figure Captions

Fig. 1  Third-phase formation behavior upon adding TOPO in the IL extraction system. IL phase (1.0 cm$^3$): A, C$_2$mimTf$_2$N; B, C$_4$mimTf$_2$N; C, C$_6$mimTf$_2$N; D, C$_8$mimTf$_2$N. Aqueous phase (5.0 cm$^3$): 1.0×10$^{-1}$ mol dm$^{-3}$ of KNO$_3$, 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 C$_4$mimTf$_2$N–TOPO system. IL phase (1.0 cm$^3$): 1.0×10$^{-1}$ mol dm$^{-3}$ TOPO. Aqueous phase (1.0 cm$^3$): 1.0×10$^{-1}$ mol dm$^{-3}$ of (H, K)NO$_3$.

Fig. 3  Transition of phase separation behavior. A: 5.0 cm$^3$ of aqueous phase (1.0×10$^{-1}$ mol dm$^{-3}$ of KNO$_3$, pH 3.0) + 20 mm$^3$ of (H$_3$O)TOPO$^+$$\cdot$Tf$_2$N$^-$, B: A + 40 mm$^3$ of C$_4$mimTf$_2$N, C: A + 1.0 cm$^3$ of C$_4$mimTf$_2$N. (Fe(III)–thiocyanato complex was added.)

Fig. 4  Aqueous phase pH dependency of $\%E_{\text{IL}}$ (□) and $\%E_{\text{3rd}}$ (●) in the C$_4$mimTf$_2$N–TOPO system (A) and the C$_6$mimTf$_2$N–TOPO system (B). IL phase (1.0 cm$^3$): 1.0×10$^{-1}$ mol dm$^{-3}$ TOPO. Aqueous phase (1.0 cm$^3$): 1.0×10$^{-1}$ mol dm$^{-3}$ of (H, K)NO$_3$ and 1.0×10$^{-2}$ mol dm$^{-3}$ of KSCN.
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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.
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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.
Graphical Index

Third phase!

Aqueous phase

IL phase with TOPO

C₂mimTf₂N  C₄mimTf₂N  C₈mimTf₂N

C₆mimTf₂N