Mutual Separation of Fe(II) and Fe(III) Using Cyclohexane/Water/Ionic-liquid Triphasic Extraction System with 2,2’-Bipyridine and Tri-n-octylphosphine Oxide

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Abstract

Triphasic extraction system with two extract phases can be used to separate two materials simultaneously into each phase. In this article, possible mutual separation of Fe(II) and Fe(III) was studied using cyclohexane/water/ionic liquid (IL) triphasic extraction system for Fe speciation. For Fe(II) and Fe(III) extraction, 2,2'-bipyridine (bpy) and tri-n-octylphosphine oxide (TOPO) were selected as extractants, respectively. It was suggested that \([\text{Fe}^{II}(\text{bpy})_3]^{2+}\) and \(\text{Fe}^{III}(\text{TOPO})_4^{3+}-3\text{TF}_2\text{N}^-\) were extracted into the IL \((1\text{-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, } \text{C}_4\text{mimTf}_2\text{N})\) phase and the cyclohexane phase, respectively, and both the extractants also played as masking agents. On simultaneous separation using the triphasic system, Fe(II) and Fe(III) were quantitatively extracted into the IL phase and the cyclohexane phase, respectively, and their mutual separation was achieved.

Keywords  Mutual separation, iron(II), iron(III), ionic liquids, triphasic extraction system
Introduction

Iron is an essential trace metal element for almost all creatures, and biogeochemistry of iron has been studied including its concentration distribution and chemical species analysis in ocean.\(^1\) Since iron exists mainly as Fe(II) and Fe(III) and the oxidation states can change by redox reaction, its influence on nature can be studied with investigating the distribution of iron.\(^1,2\) In other words, it is important for Fe speciation to quantify iron concentration with distinguishing by the oxidation states.

For the determination of iron concentration in aqueous solution, several colorimetric methods have been reported with using thiocyanate ion,\(^3-6\) 1,10-phenanthroline (phen),\(^7-11\) 2,2’-bipyridine (bpy, Fig. 1)\(^12,13\) and so on. Thiocyanate ion forms stable bloody red-colored complex with Fe(III), and the complex is used for the quantification of Fe(III). In this case, Fe(II) can be quantified indirectly after oxidation to Fe(III). Conversely, phen and bpy form stable orange and pink-colored complex with Fe(II), respectively, and Fe(III) is quantified indirectly after reduction to Fe(II). However, these methods cannot be used for simultaneous direct determination of Fe(II) and Fe(III).

Conventional solvent extraction system, often used for isolation and/or purification of many chemical species, is biphasic one and, as a matter of course, only one target material can be selectively extracted due to the single extract phase. Triphasic extraction system with two extract phases, on the contrary, can be used to extract two materials separately into the different extract phases in one operation.\(^14\) Such triphasic system was reported first by Hartwig et al.\(^15\) in 1955. Triphasic system has been used for metal extraction such as platinum group metals,\(^16-23\) and it is expected that the system can be applied to mutual separation and fractional concentration of Fe(II) and
Fe(III).

In recent years, ionic liquids (ILs) have been paid attention as extraction solvents. ILs are generally defined as “liquids composed entirely of ions that are fluid around or below 100°C”\(^{24}\) and can be green solvents with ion-exchange ability, negligible volatility, low flammability and high thermal stability.\(^{25-29}\) Solvent properties of ILs, moreover, can be controlled by changing the combination of their constituent cations and anions.\(^{30}\) Solvent extraction using hydrophobic ILs has been studied since the late 1990s.\(^{31-41}\) Additionally, some hydrophobic ILs are also immiscible with non-polar organic solvents due to their relatively high polarity.\(^{42}\) For example, it was reported that a hydrophobic IL 1-butyl-3-methylimidazolium hexafluorophosphate and non-polar cyclohexane are mutually immiscible.\(^{43}\) By utilizing the properties, it is possible to construct novel organic-solvent/water/IL triphasic extraction systems or IL/water/IL triphasic ones.\(^{43-45}\)

In this study, a hydrophobic IL, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C\(_4\)mimTf\(_2\)N, Fig. 2), and a non-polar organic solvent, cyclohexane were selected for investigating possible mutual separation of Fe(II) and Fe(III) with using organic-solvent/water/IL triphasic extraction system. For Fe(II) extraction, bpy was used due to its high affinity with imidazolium-based ILs. Middle Lewis base bpy with N donor atoms can form stable complex with middle Lewis acid Fe(II). Moreover, tri-n-octylphosphine oxide (TOPO, Fig. 1)\(^{46-49}\) was selected as an extractant for Fe(III) due to its high affinity with aliphatic cyclohexane. Hard Lewis base TOPO with O donor atom can act as an effective ligand for hard Lewis acid Fe(III). As shown in Fig. 3, it is expected that the Fe(II)-bpy complex is extracted into the IL phase by ion-exchange with IL cation (C\(_4\)mim\(^+\)), whereas the Fe(III)-TOPO complex is extracted into the cyclohexane phase by ion-pair extraction with the IL anion.
Experimental

Reagents and chemicals

The IL C₄mimTf₂N was synthesized according to a reported procedure.⁵⁰,⁵¹ The extraction reagents bpy and TOPO were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan) and Dojindo (Kumamoto, Japan), respectively. Stock standard solution of Fe(II) (250 mg dm⁻³) was prepared by dissolving ammonium iron(II) sulfate hexahydrate (FUJIFILM Wako Pure Chemical Corporation, reagent grade) in 0.1 mol dm⁻³ HNO₃. Stock standard solution of Fe(III) (250 mg dm⁻³) was prepared by diluting 1000 mg dm⁻³ Fe atomic absorption spectrometry standard solution (Fe(NO)₃ in 0.275 mol dm⁻³ HNO₃) purchased from Nacalai Tesque (Kyoto, Japan) with 0.1 mol dm⁻³ HNO₃. Other chemicals and solvents included reagent-grade materials, and were used without further purification. High-purity water was produced with a Millipore Direct-Q water purification system.

Apparatus

The absorption spectra of the IL phase were recorded on a JASCO V-630 UV/visible spectrophotometer using 1 cm matched quartz cells. A Thermo Fischer Scientific iCE3000 flame atomic absorption spectrophotometer was used for determining the Fe concentration in the aqueous phase. A Horiba F-52 pH meter equipped with a Horiba 9680S-10D combined glass electrode was used to measure the pH values.
Extraction

The cyclohexane/water/IL triphasic system consisted of the aqueous phase (5 cm$^3$) containing 0.9-4.5 mg dm$^{-3}$ Fe(II) and/or Fe(III), 0.1 mol dm$^{-3}$ KNO$_3$ and 1×10$^{-3}$ mol dm$^{-3}$ bpy, the cyclohexane phase (1 cm$^3$) containing 0.1 mol dm$^{-3}$ TOPO, and the IL (C$_4$mimTf$_2$N) phase (1 cm$^3$). In use of the water/IL biphasic system, TOPO was not added to the IL phase because of possible third phase formation under acidic condition.$^{52}$ In use of the cyclohexane/water biphasic system without IL phase, 0.017 mol dm$^{-3}$ LiTf$_2$N was added to the aqueous phase, which equals to solubility of C$_4$mimTf$_2$N in water.$^{53}$

After shaking stoppered tube including these phases for 30 min and centrifugation, aqueous phase pH was measured. Fe concentration in the aqueous phase was measured using frame atomic absorption spectrophotometer. Those in the cyclohexane phase and the IL phase were determined using similar manner after back-extraction into 1 mol dm$^{-3}$ HNO$_3$. Additionally, the concentration of extracted Fe(II)-bpy complex into the IL phase ($C_{IL,[Fe(bpy)3]2^+}$) was calculated from absorbance at 519 nm after suitable dilution, considering the Fe(II) could not be back-extracted quantitatively even on using 6 mol dm$^{-3}$ HNO$_3$.

The extractability into the IL phase ($%E_{IL}$) and that into the cyclohexane phase ($%E_{org}$) of Fe was calculated with using these values as follows:

for Fe(II): $$\%E_{IL} = \frac{C_{IL,[Fe(bpy)3]2^+}}{5C_{ini}} \times 100 \quad (1)$$
for Fe(III) : \[
\%E_{\text{IL}} = \frac{C_{\text{IL}}}{5C_{\text{ini}}} \times 100
\]  \hspace{1cm} (2)

\[
\%E_{\text{org}} = \frac{C_{\text{org}}}{5C_{\text{ini}}} \times 100
\]  \hspace{1cm} (3)

where \( C_{\text{IL}} \) and \( C_{\text{org}} \) are extracted Fe concentration into the IL and the cyclohexane phase respectively and \( C_{\text{ini}} \) is the initial Fe concentration in the aqueous phase.

**Results and Discussion**

*Analysis of the triphasic extraction behavior*

To avoid possible interference originating in hydrolysis of Fe(III), the extraction was carried out at pH < 3.5 in this study. At first, the triphasic extraction behavior for each of Fe(II) and Fe(III) was investigated separately. Figure 4 shows the results on co-using bpy and TOPO. Iron(II) was quantitatively extracted at pH > 1.5 into the IL phase, whereas Fe(III) was quantitatively extracted into the cyclohexane phase at pH > 2.7. These results suggested that the fractional extraction of Fe(II) and Fe(III) can be achieved at 2.7 < pH < 3.5.

To reveal extraction mechanism of Fe(II) and Fe(III) on the triphasic system, these extraction behavior was compared to those on the water/IL biphasic system and the cyclohexane/water biphasic system. Since Fe(II) was extracted into the IL phase on the triphasic system, extraction behavior of Fe(II) on the water/IL biphasic system was investigated and compared to that on the triphasic system. The results are shown in Fig.
5. On using TOPO alone system without bpy, Fe(II) was not extracted into the IL phase. On the contrary, use of bpy resulted in quantitative extraction of Fe(II) into the IL phase at pH > 1.5 regardless of the co-presence or absence of TOPO. Namely, it was found that Fe(II) was quantitatively extracted into the IL phase as bpy complex and TOPO showed no contribution to the Fe(II) extraction.

To determine the extracted Fe(II)-bpy complex species, absorbance in the IL phase was measured under different bpy concentration at a fixed Fe(II) concentration on the water/IL biphasic system. The result is shown in Fig. 6, in which the obtained absorbance was plotted as a function of bpy/Fe(II) concentration ratio. Two asymptotes intersected at molar ratio of ca. 3. Additionally, calculated molar absorption coefficient of Fe(II)-bpy complex in the IL phase (9.1×10^3 mol^-1 dm^3 cm^-1, λ_{max} = 519 nm) was similar to that of [Fe(bpy)_3]^{2+} in aqueous solution (8.7×10^3 mol^-1 dm^3 cm^-1, λ_{max} = 522 nm). The results indicated that [Fe(bpy)_3]^{2+} was extracted into the IL phase based on cation exchange with C_4mim^+ as follows:

\[
[\text{Fe(bpy)}_3]^{2+} + 2\text{C}_4\text{mim}^+_{\text{IL}} \rightleftharpoons [\text{Fe(bpy)}_3]^{2+}_{\text{IL}} + 2\text{C}_4\text{mim}^+_{\text{IL}} \tag{4}
\]

Iron(III) was extracted slightly into the IL phase on bpy alone system without TOPO. However, addition of TOPO resulted in no extraction of Fe(III) regardless of the presence or absence of bpy. It was suggested that hard Lewis acid Fe(III) was formed more suitable complex with hard base TOPO than middle base bpy, and aliphatic TOPO complex had relatively low affinity with imidazolium based ILs having some aromaticity.

Since Fe(III) was extracted into the cyclohexane phase on the triphasic system, extraction behavior of Fe(III) on the cyclohexane/water biphasic system was investigated and compared to that on the triphasic system. The results are shown in Fig.
7. On bpy alone system without TOPO, Fe(III) was not extracted into the cyclohexane phase. Addition of TOPO resulted in quantitative extraction of Fe(III), provided that the triphasic system showed slightly less Fe(III) extractability compared to the cyclohexane/water biphasic system probably due to formation of ion-pair of TOPO–oxonium complex and Tf$_2$N$^-$. With using the cyclohexane/water biphasic system, the extracted species of Fe(III)-TOPO complex into the cyclohexane phase was determined. Equation (5) represents extraction equilibrium of Fe(III) into the cyclohexane in the biphasic system,

$$
    \text{Fe}^{3+} + n \text{TOPO}_{\text{org}} + 3\text{Tf}_2\text{N}^- \rightleftharpoons \text{Fe(TOPO)}_{\text{org}}^{3+} \cdot 3\text{Tf}_2\text{N}^- \quad (5)
$$

where $n$ is number of TOPO coordinating to Fe(III). In this case, extraction constant ($K_{\text{ex}}$) is defined as Eq. (6).

$$
    K_{\text{ex}} = \frac{[\text{Fe(TOPO)}_{\text{org}}^{3+} \cdot 3\text{Tf}_2\text{N}^-]_{\text{org}}}{[\text{Fe}^{3+}][\text{TOPO}]_{\text{org}}^n[\text{Tf}_2\text{N}^-]^3} \quad (6)
$$

Distribution ratio of Fe(III) into the cyclohexane phase ($D_{\text{org}}$) is defined as Eq. (7).

$$
    D_{\text{org}} = \frac{[\text{Fe(TOPO)}_{\text{org}}^{3+} \cdot 3\text{Tf}_2\text{N}^-]_{\text{org}}}{[\text{Fe}^{3+}]} = K_{\text{ex}} [\text{TOPO}]_{\text{org}}^n [\text{Tf}_2\text{N}^-]^3 \quad (7)
$$

$$
    \log D_{\text{org}} = \log K_{\text{ex}} + n \log [\text{TOPO}]_{\text{org}} + 3 \log [\text{Tf}_2\text{N}^-] \\
    \sim n \log [\text{TOPO}]_{\text{org}} + \text{const.} \quad (8)
$$
Equation (8) means that slope of log $D_{\text{org}}$-log $[\text{TOPO}]_{\text{org}}$ plot is number of TOPO coordinating to Fe(III). As shown in Fig. 8, the slope of the plot is ca. 4. It was suggested that ion pair $\text{Fe(TOPO)}_4^{3+} \cdot 3\text{Tf}_2\text{N}^-$ was extracted into the cyclohexane phase.

Iron(II) was extracted slightly into the cyclohexane phase on TOPO alone system without bpy. On adding bpy, red Fe(II)-bpy complex was precipitated in the aqueous phase and Fe(II) was not extracted into the cyclohexane phase. It was suggested that middle Lewis acid Fe(II) was formed more suitable complex with middle base bpy than hard base TOPO, and the aromatic bpy complex had low affinity with aliphatic cyclohexane.

**Simultaneous extraction separation of Fe(II) and Fe(III)**

Based on the above-mentioned results, simultaneous separation of Fe(II) and Fe(III) was carried out. Table 1 shows simultaneous separation of Fe(II) and Fe(III) using the cyclohexane/water/IL triphasic extraction system. Extraction pH condition was fixed as ca. 3 and initial amount of substance of Fe(II) ($M_{\text{ini}, \text{Fe(II)}}$) and that of Fe(III) ($M_{\text{ini}, \text{Fe(III)}}$) were ranged in $0.8 \times 10^{-7}$-$4.0 \times 10^{-7}$ mol. Recovery rate of Fe(II) ($\%R_{\text{Fe(II)}}$) and that of Fe(III) ($\%R_{\text{Fe(III)}}$) are defined as follows:

$$\%R_{\text{Fe(II)}} = \frac{M_{\text{IL}, [\text{Fe(bpy)}_3]^{2+}}}{M_{\text{ini}, \text{Fe(II)}}} \times 100 \quad (9)$$

$$\%R_{\text{Fe(III)}} = \frac{M_{\text{org, Fe}}}{M_{\text{ini}, \text{Fe(III)}}} \times 100 \quad (10)$$

where $M_{\text{IL}, [\text{Fe(bpy)}_3]^{2+}}$ is amount of Fe(II)-bpy complex extracted into the IL phase, $M_{\text{org, Fe}}$ is amount of Fe extracted into the cyclohexane phase. In this case, $\%R_{\text{Fe(III)}}$ is defined
under considering that all Fe extracted into the cyclohexane phase is Fe(III). At all experimental condition, $\%R_{\text{Fe(II)}}$ and $\%R_{\text{Fe(III)}}$ showed approximately quantitative values. This suggested that Fe(II) and Fe(III) were quantitatively extracted into the IL phase and the cyclohexane phase respectively. From these results, it was found that Fe(II) and Fe(III) can be mutually separated using the cyclohexane/water/IL triphasic extraction system.

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Table 1  Results on simultaneous separation of Fe(II) and Fe(III) using the cyclohexane/water/IL triphasic extraction system

| Initial value | Measured values |
|---------------|----------------|
| $M_{\text{ini, Fe(II)}}$ / $10^{-7}$ mol | $M_{\text{IL,[Fe(bpy)3]2+}}$ / $10^{-7}$ mol | $\% R_{\text{Fe(II)}}$ | $M_{\text{org,Fe}}$ / $10^{-7}$ mol | $\% R_{\text{Fe(III)}}$ |
| 4.0 / 4.0 | 3.9 | 97 | 4.1 | 101 |
| 1.3 / 4.0 | 1.4 | 102 | 4.1 | 101 |
| 4.0 / 1.3 | 3.8 | 95 | 1.5 | 110 |
| 0.81 / 4.0 | 0.83 | 102 | 4.2 | 104 |
| 4.0 / 0.81 | 3.9 | 98 | 0.82 | 102 |

a. Cyclohexane phase: 0.1 mol dm$^{-3}$ TOPO. Aqueous phase: $1 \times 10^{-3}$ mol dm$^{-3}$ bpy. IL phase: C$_4$ mimTf$_2$N.
Figure Captions

Fig. 1 Structure of extractants used in this study. (a) 2,2'-bipyridine (bpy), (b) tri-n-octylphosphine oxide (TOPO).

Fig. 2 Structure of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C$_4$mimTf$_2$N).

Fig. 3 Schematic diagram of mutual separation of Fe(II) and Fe(III) using cyclohexane/water/IL triphasic extraction system.

Fig. 4 Extraction behavior of Fe(II) (○) and Fe(III) (●) into the cyclohexane phase (upper) and the IL phase (lower) on the triphasic extraction system. Cyclohexane phase: 0.1 mol dm$^{-3}$ TOPO. Aqueous phase: 1×10$^{-3}$ mol dm$^{-3}$ bpy. IL phase: C$_4$mimTf$_2$N.

Fig. 5 Extraction behavior of Fe(II) into the IL phase on the water/IL biphasic system and the triphasic system. The water/IL biphasic system: bpy alone (◇). The triphasic system: bpy alone (□), TOPO alone (△), bpy + TOPO (○). Cyclohexane phase: 0.1 mol dm$^{-3}$ TOPO. Aqueous phase: 1×10$^{-3}$ mol dm$^{-3}$ bpy. IL phase: C$_4$mimTf$_2$N.

Fig. 6 Relationship between absorbance in the IL phase and bpy/Fe(II) concentration ratio. [Fe(II)]$_{ini}$ = 2.7×10$^{-5}$ mol dm$^{-3}$. Aqueous phase: 0-1.6×10$^{-4}$ mol dm$^{-3}$ bpy. IL phase: C$_4$mimTf$_2$N.

Fig. 7 Extraction behavior of Fe(III) into the cyclohexane phase on the
cyclohexane/water biphasic system (gray) and that on the triphasic system (black). Extractant: bpy alone (■), TOPO alone (▲), bpy + TOPO (●). Cyclohexane phase: 0.1 mol dm$^{-3}$ TOPO. Aqueous phase: 0.017 mol dm$^{-3}$ LiTf$_2$N and 1×10$^{-3}$ mol dm$^{-3}$ bpy. IL phase: C$_{4}$mimTf$_2$N.

Fig. 8 log $D_{\text{org}}$ vs. log [TOPO]$_{\text{org}}$ plot on the cyclohexane/water biphasic system for extraction of Fe(III). Cyclohexane phase: 2.5×10$^{-3}$-4.5×10$^{-3}$ mol dm$^{-3}$ TOPO. Aqueous phase: 0.017 mol dm$^{-3}$ LiTf$_2$N.
Fig. 1 Structure of extractants used in this study. (a) 2,2’-bipyridine (bpy), (b) tri-\textit{n}-octylphosphine oxide (TOPO).
Fig. 2  Structure of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C₈mimTf₂N).
Fig. 3  Schematic diagram of mutual separation of Fe(II) and Fe(III) using cyclohexane/water/IL triphasic extraction system.
Fig. 4 Extraction behavior of Fe(II) (○) and Fe(III) (●) into the cyclohexane phase (upper) and the IL phase (lower) on the triphasic extraction system. Cyclohexane phase: 0.1 mol dm$^{-3}$ TOPO. Aqueous phase: $1 \times 10^{-3}$ mol dm$^{-3}$ bpy. IL phase: C$_4$ mimTf$_2$N.
Fig. 5  Extraction behavior of Fe(II) into the IL phase on the water/IL biphasic system and the triphasic system. The water/IL biphasic system: bpy alone (◇). The triphasic system: bpy alone (□), TOPO alone (△), bpy + TOPO (○). Cyclohexane phase: 0.1 mol dm$^{-3}$ TOPO. Aqueous phase: 1×10$^{-3}$ mol dm$^{-3}$ bpy. IL phase: C$_{4}$mimTf$_{2}$N.
Fig. 6  Relationship between absorbance in the IL phase and bpy/Fe(II) concentration ratio. [Fe(II)]_{ini} = 2.7 \times 10^{-5} \text{ mol dm}^{-3}. Aqueous phase: 0-1.6 \times 10^{-4} \text{ mol dm}^{-3} \text{ bpy}. IL phase: C_{4}mimTf_{2}N.
Fig. 7  Extraction behavior of Fe(III) into the cyclohexane phase on the cyclohexane/water biphasic system (gray) and that on the triphasic system (black). The cyclohexane/water biphasic system: TOPO alone (▲), bpy + TOPO (●). The triphasic system: bpy alone (■), TOPO alone (▲), bpy + TOPO (●). Cyclohexane phase: 0.1 mol dm$^{-3}$ TOPO. Aqueous phase: 0.017 mol dm$^{-3}$ LiTf$_2$N and 1×10$^{-3}$ mol dm$^{-3}$ bpy. IL phase: C$_4$mimTf$_2$N.
Fig. 8  log $D_{\text{org}}$ vs. log [TOPO]$_{\text{org}}$ plot on the cyclohexane/water biphasic system for extraction of Fe(III). Cyclohexane phase: $2.5 \times 10^{-3}$-$4.5 \times 10^{-3}$ mol dm$^{-3}$ TOPO. Aqueous phase: 0.017 mol dm$^{-3}$ LiTf$_2$N.
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