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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The triphasic extraction system with two extract phases can be used to separate two materials simultaneously into each phase. In this article, a possible mutual separation of Fe(II) and Fe(III) was studied using the 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 $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ and $\text{Fe}^{\text{III}}(\text{TOPO})_4^{3+} \cdot 3\text{Tf}_2\text{N}^-$ were extracted into the IL (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $\text{C}_4\text{mimTf}_2\text{N}$) phase and the cyclohexane phase, respectively, and both of the extractants also acted 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

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Introduction

Iron is an essential trace metal element for almost all creatures, and the 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 a redox reaction, its influence on nature can be studied by investigating the distribution of iron.^{1,2} In other words, it is important for Fe speciation to quantify the iron concentration with distinguishing by the oxidation states.

For determining the 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 a 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 a 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).

The conventional solvent extraction system, often used for the isolation and/or purification of many chemical species, is a biphasic one and, as a matter of course, only one target material can be selectively extracted due to the single extract phase. The 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 a triphasic system was first reported by Hartwig *et al.*¹⁵ in 1955. The

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 the 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 an ion-exchange ability, negligible volatility, low flammability and high thermal stability.²⁵⁻²⁹ The 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

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

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Fig. 2 Structure of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C₄mimTf₂N).

bis(trifluoromethanesulfonyl)imide (C₄mimTf₂N, Fig. 2), and a non-polar organic solvent, cyclohexane were selected for investigating a possible mutual separation of Fe(II) and Fe(III) with using an 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 a 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 an 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 can be extracted into the IL phase by ion-exchange with the IL cation (C₄mim⁺), whereas the Fe(III)-TOPO complex is extracted into the cyclohexane phase by ion-pair extraction with the IL anion (Tf₂N[−]).

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. A 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. A 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(NO₃)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 cm³) containing 0.9–4.5 mg dm^{−3} Fe(II) and/or Fe(III), 0.1 mol dm^{−3} KNO₃ and 1 × 10^{−3} mol dm^{−3} bpy, the cyclohexane phase (1 cm³) containing 0.1 mol dm^{−3} TOPO, and the IL (C₄mimTf₂N) phase (1 cm³). In using the water/IL biphasic system, TOPO was not added to the IL phase because of possible third-phase formation under an acidic condition.⁵² In using the cyclohexane/water biphasic system without the IL

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

phase, 0.017 mol dm^{−3} LiTf₂N was added to the aqueous phase, which equals to the solubility of C₄mimTf₂N in water.⁵³

After shaking a stoppered tube including these phases for 30 min and centrifugation, the aqueous phase pH was measured. The Fe concentration in the aqueous phase was measured using a flame atomic absorption spectrophotometer. Those in the cyclohexane phase and the IL phase were determined in a similar manner after back-extraction into 1 mol dm^{−3} HNO₃. Additionally, the concentration of the extracted Fe(II)-bpy complex into the IL phase ($C_{\text{IL},[\text{Fe}(\text{bpy})_3]^{2+}}$) was calculated from the absorbance at 519 nm after suitable dilution, considering that the Fe(II) could not be back-extracted quantitatively even on using 6 mol dm^{−3} HNO₃.

The extractability into the IL phase (%*E*_{IL}) and that into the cyclohexane phase (%*E*_{org}) of Fe was calculated by using these values as follows:

$$\text{for Fe(II):} \quad \%E_{\text{IL}} = \frac{C_{\text{IL},[\text{Fe}(\text{bpy})_3]^{2+}}}{5C_{\text{ini}}} \times 100, \quad (1)$$

$$\text{for Fe(III):} \quad \%E_{\text{IL}} = \frac{C_{\text{IL}}}{5C_{\text{ini}}} \times 100, \quad (2)$$

$$\%E_{\text{org}} = \frac{C_{\text{org}}}{5C_{\text{ini}}} \times 100, \quad (3)$$

where *C*_{IL} and *C*_{org} are the extracted Fe concentration into the IL and the cyclohexane phase, respectively, and *C*_{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 the 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 the extraction mechanism of Fe(II) and Fe(III) on the triphasic system, these extraction behaviors were compared to those on the water/IL biphasic system and the cyclohexane/water biphasic system. Since Fe(II) was extracted into the IL

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: $1 \times 10^{-3} \text{ mol dm}^{-3}$ bpy. IL phase: $\text{C}_4\text{mimTf}_2\text{N}$.

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: $1 \times 10^{-3} \text{ mol dm}^{-3}$ bpy. IL phase: $\text{C}_4\text{mimTf}_2\text{N}$.

phase on the triphasic system, the 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 the TOPO-alone system without bpy, Fe(II) was not extracted into the IL phase. On the contrary, the use of bpy resulted in the quantitative extraction of Fe(II) into the IL phase at $\text{pH} > 1.5$, regardless of the co-presence or absence of TOPO. Namely, it was found that Fe(II) was quantitatively extracted into the IL phase as the bpy complex, and that TOPO showed no contribution to the Fe(II) extraction.

To determine the extracted Fe(II)-bpy complex species, the absorbance in the IL phase was measured under different bpy concentrations at a fixed Fe(II) concentration on the water/IL biphasic system. The result is shown in Fig. 6, in which the obtained absorbance is plotted as a function of the bpy/Fe(II) concentration ratio. Two asymptotes intersected at a molar ratio of *ca.* 3. Additionally, the calculated molar absorption coefficient of the Fe(II)-bpy complex in the IL phase ($9.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$, $\lambda_{\text{max}} = 519 \text{ nm}$) was similar to that of $[\text{Fe}(\text{bpy})_3]^{2+}$ in the aqueous solution ($8.7 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$, $\lambda_{\text{max}} = 522 \text{ nm}$ ⁵⁴).

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

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: $0.017 \text{ mol dm}^{-3}$ LiTf_2N and $1 \times 10^{-3} \text{ mol dm}^{-3}$ bpy. IL phase: $\text{C}_4\text{mimTf}_2\text{N}$.

The results indicated that $[\text{Fe}(\text{bpy})_3]^{2+}$ was extracted into the IL phase based on cation exchange with C_4mim^+ , as follows:

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

Since Fe(III) was extracted into the cyclohexane phase on the triphasic system, the 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 the bpy-alone system without TOPO, Fe(III) was not extracted into the cyclohexane phase. The addition of TOPO resulted in the quantitative extraction of Fe(III), provided that the triphasic system showed a slightly less Fe(III) extractability compared to the cyclohexane/water biphasic system, probably due to the formation of an ion-pair of the TOPO-oxonium complex and Tf_2N^- .⁵² With using the cyclohexane/water biphasic system, the extracted species of Fe(III)-TOPO complex into the cyclohexane phase was determined. Equation (5) represents the extraction equilibrium of Fe(III) into the cyclohexane in the biphasic system,

Fig. 8 $\log D_{\text{org}}$ vs. $\log[\text{TOPO}]_{\text{org}}$ plot on the cyclohexane/water biphasic system for extraction of Fe(III). Cyclohexane phase: $2.5 \times 10^{-3} - 4.5 \times 10^{-3} \text{ mol dm}^{-3}$ TOPO. Aqueous phase: $0.017 \text{ mol dm}^{-3}$ LiTf_2N .

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

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

The distribution ratio of Fe(III) into the cyclohexane phase (D_{org}) is defined as

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

$$\log D_{\text{org}} = \log K_{\text{ex}} + n \log [\text{TOPO}]_{\text{org}} + 3 \log [\text{Tf}_2\text{N}^-]_{\text{org}} \\ \sim n \log [\text{TOPO}]_{\text{org}} + \text{const.} \quad (8)$$

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

Iron(II) was extracted slightly into the cyclohexane phase on the TOPO-alone system without bpy. On adding bpy, a 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) formed a more suitable complex with the middle base bpy than the 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, the simultaneous separation of Fe(II) and Fe(III) was carried out. Table 1 shows the simultaneous separation of Fe(II) and Fe(III) using the cyclohexane/water/IL triphasic extraction system. The extraction pH condition was fixed at *ca.* 3 and the initial amount of substance of Fe(II) ($M_{\text{ini,Fe(II)}}$) and that of Fe(III) ($M_{\text{ini,Fe(III)}}$) ranged over $0.8 \times 10^{-7} - 4.0 \times 10^{-7} \text{ mol}$. The recovery rate of Fe(II) ($\%R_{\text{Fe(II)}}$) and that of Fe(III) ($\%R_{\text{Fe(III)}}$) are defined as follows:

$$\%R_{\text{Fe(II)}} = \frac{M_{\text{IL, [Fe(bpy)3]2+}}}{M_{\text{ini, Fe(II)}}} \times 100, \quad (9)$$

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

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

Initial value		Measured values			
$M_{\text{ini, Fe(II)}} / 10^{-7} \text{ mol}$	$M_{\text{ini, Fe(III)}} / 10^{-7} \text{ mol}$	$M_{\text{IL, [Fe(bpy)3]2+}} / 10^{-7} \text{ mol}$	$\%R_{\text{Fe(II)}}$	$M_{\text{org, Fe}} / 10^{-7} \text{ mol}$	$\%R_{\text{Fe(III)}}$
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: $1 \times 10^{-3} \text{ mol dm}^{-3}$ bpy. IL phase: $\text{C}_4\text{mimTf}_2\text{N}$.

where $M_{\text{IL, [Fe(bpy)3]2+}}$ is the amount of the Fe(II)-bpy complex extracted into the IL phase, and $M_{\text{org, Fe}}$ is the amount of Fe extracted into the cyclohexane phase. In this case, $\%R_{\text{Fe(III)}}$ is defined by considering that all Fe extracted into the cyclohexane phase is Fe(III). Under all experimental conditions, $\%R_{\text{Fe(II)}}$ 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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