Extraction Behavior of Divalent Metal Cations with 2-Mercaptopyridine N-Oxide in Ionic Liquid Chelate Extraction

Sumiyuki KIMURA,1 Yoshio SHIMIZU,2 Ayano EGUCHI1 and Naoki HIRAYAMA1,3

1 Department of Chemistry, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi 274-8510, Japan
2 Division of Material Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan
3 Research Center for Materials with Integrated Properties, Toho University, Miyama 2-2-1, Funabashi 274-8510, Japan

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The possible use of 2-Mercaptopyridine N-oxide (HSPyO) as an extractant in ionic liquid chelate extraction was investigated with using several divalent metals (M2+, M = Cu, Ni, Zn, Cd and Mn). The extraction performance of HSPyO in the 1-butyl-3-methyimidazolium bis(trifluoromethanesulfonyl)imide (C4mimTf2N) system was very similar to that in the chloroform system, except for Cd2+. Over wide pH range, Cu2+, Ni2+ and Zn2+ were extracted quantitatively into C4mimTf2N as neutral 1:2 complexes \( \text{M(SPyO)}_2 \). Furthermore, the strange extraction behavior for Cd2+ into C4mimTf2N was found to originate in the competitive extraction of neutral \( \text{Cd(SPyO)}_2 \) and anionic \( \text{Cd(SPyO)}_3^- \).

1. Introduction

Use of hydrophobic ionic liquids (ILs) as extraction solvents is an attractive research field in separation chemistry. Hydrophobic ILs have relatively high polarity compared to conventional hydrophobic organic solvents [1] and also have ion-exchange extraction abilities [2]. Although metal extraction requires some (neutral or anionic) extractants having complexation ability, use of ILs as extraction solvents for metal extraction separation has possible advantages in terms of actualization of unique extraction mechanisms (ion-exchange mode, etc.) and/or unique stabilization mechanisms (relatively high affinity to polar compounds, etc.). Therefore, many researchers have studied the development of metal extraction into ILs [3-11]. Among several approaches, ionic liquid chelate extraction using Brønsted acidic chelators as extractants [12,13] is of interest one because extraction selectivity can be controlled by changing the aqueous phase pH.

Sulfur is a soft Lewis donor and sulfur-containing chelators can act as extractants for selective extraction of soft or middle Lewis acid metal cations. Sulfur-containing anionic (Brønsted acidic) functional groups, dithiocarboxy, monothiocarboxy and thiol groups are well known. However, thiol-containing reagents often form disulfides. (For example, a monoanionic S,N-bidentate ligand 8-mercaptoquinoline is unstable and its use as an extractant is not possible without further tedious processing [14].)
2-Mercaptopyridine N-oxide (pyrithione, HSPyO, Figure 1, pK_\alpha = 4.49 [15]) is a monoanionic S,O-bidentate ligand and its Zn and Cu complexes are known as an antimicrobial agent and an antifouling paint, respectively. Although HSPyO has a thiol group, its intramolecular hydrogen bonding and tautomeric equilibrium with regard to the thione-form [16] (see Figure 1) prevents its dimerization by disulfide bond formation. Therefore, it is expected that HSPyO can be used as a stable sulfur-containing extractant for metal cations. In the past, several researchers studied the possible use of HSPyO as an extractant for several metals such as Fe^{3+} [17], UO_2^{2+} [18] and VO^{2+} [19]. Recently, Khayatian et al. used HSPyO in several microextraction techniques for Fe^{3+} and Cu^{2+}, including liquid-liquid microextraction into 1-octanol [20], directly suspended droplet microextraction using methyl isobutyl ketone [21] and ionic liquid dispersive liquid-liquid microextraction using 1-hexyl-3-methylimidazolium hexafluorophosphate [22]. However, the performance of HSPyO as a chelating extractant not only in ILs but also in conventional organic solvents has not been exhaustively investigated. Therefore, as a fundamental investigation, the extraction behavior of several divalent metal cations including Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Mn^{2+} into an IL, 1-buthyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C_4mimTf_2N), with HSPyO was compared to that into chloroform, a conventional organic extraction solvent. Finally, the possible availability of HSPyO as an extractant for metals in IL chelate extraction systems is discussed.

2. Experimental

2.1 Chemicals and apparatus

The IL, C_4mimTf_2N, was synthesized according to the reported procedure [23]. The extractant, HSPyO, was purchased from Tokyo Chemical Industry (Tokyo, Japan). Other chemicals included reagent-grade materials and were used without further purification. High-purity water, produced with a Direct-Q water purification system (Millipore), was used throughout.

A Hitachi A-1000 flame atomic absorption spectrophotometer was used for the determination of metals in the aqueous phase. A Horiba F-52 pH meter equipped with a Horiba 9680-10D combined glass electrode was used to measure the pH values.

2.2 Distribution of metals

The distribution behavior of the metals was investigated at 25°C as follows. In a centrifuge tube, an aliquot (1 cm^3) of an extraction phase (C_4mimTf_2N or chloroform) containing 1.0×10^{-2} mol dm^{-3} HSPyO and 5 cm^3 of an aqueous phase containing 1×10^{-5} – 1×10^{-4} mol dm^{-3} of M^{2+} (M = Cu, Ni, Zn, Cd or Mn), 1.0×10^{-1} mol dm^{-3} KNO_3 and 1.0×10^{-2} mol dm^{-3} of a buffer (chloroacetic acid, acetic acid or 2-(N-morpholino)ethanesulfonic acid) were shaken mechanically for 30 min to achieve equilibrium. (For more acidic conditions (pH < 1), an aqueous phase containing 1×10^{-5} – 1×10^{-4} mol dm^{-3} of M^{2+} and a suitable concentration of HNO_3 was used.) After the two phases were separated by centrifugation, the aqueous phase pH was measured. The metal concentration in the aqueous phase and that in the extraction phase (after back-extraction for 30 min into a 10-fold volume of 1–3 mol dm^{-3} HNO_3) were determined by flame atomic absorption spectrophotometry.
3. Results and Discussion

3.1 Solubility and stability of HSPyO in C₄mimTf₂N and chloroform

HSPyO was readily soluble not only in chloroform but also in C₄mimTf₂N with a solubility of at least $1.0 \times 10^{-1}$ mol dm$^{-3}$. Furthermore, the solutions were stable for more than a few days with neither formation of the disulfide nor decomposition of the HSPyO. Thus, it was confirmed that an extraction phase with a large concentration of HSPyO is available.

3.2 Extraction behavior of the metals

The extracted ratios of $M^{2+}$ into C₄mimTf₂N and chloroform phases were plotted as a function of the aqueous phase pH. At pH < 1, initial HNO₃ concentration ($C(\text{HNO}_3)$) was used instead of pH. The results are shown in Figure 2. Except for Cd$^{2+}$, these two systems showed similar extraction performances. Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ showed high extractability in both the C₄mimTf₂N and chloroform systems in this order. In particular, Cu$^{2+}$ showed such a high extractability that it could not be back-extracted under the above-mentioned condition. (Therefore, the %$E$ values for Cu$^{2+}$ were calculated from mass balances.) In contrast, Mn$^{2+}$ showed quite low extractability.

Interestingly, Cd$^{2+}$ showed different extraction behavior in the chloroform system compared to the C₄mimTf₂N system. In the chloroform system (Figure 2(B)), the %$E$ values increased with the increasing pH up to ca. 3.5, above which the values decreased gradually. In the C₄mimTf₂N system (Figure 2(B)), in contrast, the %$E$ values reached a plateau at pH > ca. 3.5. This difference is discussed in Section 3.4 in detail.

3.3 Determination of the extracted species for Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$

Since HSPyO is a monoanionic bidentate chelator, the general extraction equilibrium for $M^{2+}$ in the chloroform system is represented as follows:

$$M^{2+} + 2\text{HSPyO}(e) \rightleftharpoons M(\text{SPyO})_2(e) + 2\text{H}^+$$

where subscript e denotes the extraction phase. The extraction constants ($K_{ex}$) can be defined as follows:

$$K_{ex} = \frac{[\text{M(\text{SPyO})}_2]_e[H^+]^2}{[M^{2+}][\text{HSPyO}]_e^2}$$

Moreover, the same extraction equilibrium is expected also in the C₄mimTf₂N system because these two systems showed similar extraction behavior as shown in Figure 2. In this case, the logarithmic distribution ratio ($\log D$) for the metal can be expressed from Equation (2) as follows:

$$\log D = \log K_{ex} + 2\log [\text{HSPyO}]_e + 2\text{pH}$$
To confirm the hypothesis, log \( D \) for \( \text{Ni}^{2+} \) and that for \( \text{Zn}^{2+} \) were plotted as a function of the logarithmic initial concentration of HSPyO in the extraction phase (log \( C_e(\text{HSPyO}) \)) at fixed aqueous phase pH, and that of the aqueous phase pH (or \(-\log C(\text{HNO}_3)\)) at fixed HSPyO concentration. The results for the \( \text{C}_4\text{mimTf}_2\text{N} \) system are shown in Figure 3 as examples. In all cases, the plots showed straight lines the slopes of which were closed to 2. Therefore, it was found that \( \text{Ni}^{2+} \) and \( \text{Zn}^{2+} \) are extracted not only into chloroform but also into \( \text{C}_4\text{mimTf}_2\text{N} \) as described by Equation (1).

For \( \text{Cu}^{2+} \), which shows a very high extractability, a loading test was conducted. Figure 4 shows the relationship between the initial amount of \( \text{Cu}^{2+} \) in the aqueous phase and that remaining after extraction into the \( \text{C}_4\text{mimTf}_2\text{N} \) phase. (The results for the chloroform system are also shown in the figure.) If extraction of \( \text{Cu}^{2+} \) is based on Equation (1), the maximum extractable \( \text{Cu}^{2+} \) is 5.0 \( \mu \text{mol} \) (= \( 1.0 \times 10^{-2} \text{ mol dm}^{-3} \times 1.0 \text{ cm}^3 / 2 \)). The obtained results validate the hypothesis.

In these cases, the \( K_{ex} \) values can be calculated from Equation (3) by using the \( D \) values. Table 1 shows the log \( K_{ex} \) values obtained for the \( \text{Cu}^{2+} \), \( \text{Ni}^{2+} \) and \( \text{Zn}^{2+} \) in the two extraction systems.

### Table 1. The log \( K_{ex} \) values

<table>
<thead>
<tr>
<th>Cation</th>
<th>Extraction phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{C}_4\text{mimTf}_2\text{N} )</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} )</td>
<td>&gt; 6</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} )</td>
<td>2.38±0.04</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} )</td>
<td>1.13±0.04</td>
</tr>
<tr>
<td>( \text{Cd}^{2+} )</td>
<td>ca. –0.5 \text{a)}</td>
</tr>
</tbody>
</table>

\( \text{a)} \) Estimated value.

### 3.4 Analysis of the complicated extraction behavior of \( \text{Cd}^{2+} \)

To clarify the complicated extraction behavior of \( \text{Cd}^{2+} \) with HSPyO, the extraction behavior of \( \text{Cd}^{2+} \) at different extractant concentrations was investigated. Figure 5 shows the relationship between log \( D \) for \( \text{Cd}^{2+} \) and the aqueous phase pH for different extractant concentration conditions.

In the chloroform system (Figure 5 (B)), the plots had asymptotes with slopes of ca. 2 in the lower pH region, and those with slopes of ca. –1 in the higher pH region. The former shows extraction of \( \text{Cd}^{2+} \) as...
Cd(SPyO)₂ based on Equation (1). The latter, in contrast, suggests that the extracted species returns to the aqueous phase by forming anionic Cd(SPyO)₃⁻, as follows:

\[
\text{Cd(SPyO)₂}^{(e)} + \text{HSPyO}^{(e)} \rightarrow \text{Cd(SPyO)₃}^{−} + \text{H}^+ \quad (4)
\]

Because Cd²⁺ is a relatively large cation compared to the other investigated cations, Cd²⁺ can form a stable anionic 1:3 complex.

In the C₄mimTf₂N system (Figure 5(A)), interestingly, an extractant-concentration-independent log \( D \) value (0.38± 0.01) was obtained at pH > ca. 5. This means the existence of another extraction mechanism under this condition. Considering Equation (4), a possible mechanism is anion-exchange extraction of Cd(SPyO)₃⁻ with the IL anion Tf₂N⁻, as follows:

\[
\text{Cd(SPyO)}^{3−} + \text{Tf}_2\text{N}^{−} \rightarrow \text{Cd(SPyO)}^{3−}_{(e)} + \text{Tf}_2\text{N}^{−}_{(e)} \quad (5)
\]

This equilibrium depends on the concentration of Tf₂N⁻ in the aqueous phase. Actually, addition of 1.0×10⁻² mol dm⁻³ lithium bis(trifluoromethanesulfonyl)imide (LiTf₂N) to the aqueous phase at pH > 5 resulted in a significant decrease in the log \( D \) value for Cd²⁺. (The results are also plotted in Figure 5(a).) Since the activity of Tf₂N⁻ in the C₄mimTf₂N phase is defined as unity, the anion-exchange extraction constant (\( K_{\text{exchange}} \)) can be defined as follows:

\[
K_{\text{exchange}} = \frac{[\text{Cd(SPyO)}^{3−}]_{(e)}[\text{Tf}_2\text{N}^{−}]_{(e)}}{[\text{Cd(SPyO)}^{3−}]} 
\]

and, at pH >5, log \( D \) for Cd²⁺ can be expressed as follows:

\[
\log D = \log K_{\text{exchange}} − \log [\text{Tf}_2\text{N}^{−}] \quad (7)
\]

From the extraction data at pH > 5, the log \( K_{\text{exchange}} \) value was calculated as -1.41±0.01 with using Equation (7) and the solubility product for C₄mimTf₂N (2.70×10⁻⁴ [24]).

As mentioned above, the extraction mechanism for Cd²⁺ with HSPyO is very complicating, and it is difficult to determine the log \( K_{\text{ex}} \) values corresponding to Equation (2) in the two systems correctly. For reference, the estimated values obtained from the extraction data are also shown in Table 1.

4. Conclusion

The present study showed the possible use of HSPyO as a chelating extractant in ionic liquid chelate extraction. The reagent has a preferential solubility in an IL, C₄mimTf₂N. The extractability order between divalent metals with HSPyO in the C₄mimTf₂N system was Cu²⁺ > Ni²⁺ > Zn²⁺ > Cd²⁺ >> Mn²⁺, which was the same as that in the chloroform system, and the three metals, Cu²⁺, Ni²⁺ and Zn²⁺, were extracted quantitatively. The extracted species in the IL system were neutral M(SPyO)₂, and, for Cd²⁺, also anionic.
Cd(SP\text{PyO})_3^- was competitively extracted based on anion-exchange. Since Cd\textsuperscript{2+} is relatively soft and large compared to the other metals studied, it is expected that the ionic liquid chelate extraction system using HSP\text{PyO} can be used as a conventional chelate extraction system at pH < ca. 3 and as specific anion-exchange extraction system for relatively soft and large metals at pH > ca. 5.

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