

Anomalous Suppressed Ion-exchange Extraction Behavior of Ni(II) into Ionic Liquids with Using *N,N,N',N'*-Tetrakis(2-pyridylmethyl)ethylenediamine as a Neutral Chelator

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In use of *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (**tpen**) as a hexadentate neutral chelator, ion-exchange extractability for Ni(II) into an ionic liquid (IL), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_4\text{mimTf}_2\text{N}$), was anomalously suppressed. From comparative extraction experiments with using different ILs and/or chelators corresponding to several substructures of **tpen**, it was suggested that **tpen** coordinates to Ni^{2+} as a tetradentate ligand in $C_4\text{mimTf}_2\text{N}$ and that two 2-pyridylmethyl pendant arms in **tpen** without coordinating to Ni^{2+} resulted in the extraction suppression due to their relatively high protonation ability.

1. Introduction

Hydrophobic ionic liquids (ILs), including 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_n\text{mimTf}_2\text{N}$, Figure 1), can extract many ionic species having hydrophobic and/or IL-philic nature from aqueous solutions via ion-exchange process. In extraction of metal cations into ILs via cation-exchange, their hydrophobization by forming complexes with monodentate neutral ligands or neutral chelators is imperative process.

N,N,N',N'-Tetrakis(2-pyridylmethyl)ethylenediamine (**tpen**, Figure 2) is a hexadentate neutral chelator having four 2-pyridylmethyl pendant arms, and can form cationic complexes with many metal cations. Several researchers have studied its possible use for ion-pair extraction of several metal cations into organic solvents [1,2] and that for their cation-exchange extraction into ILs [3].

In study on cation-exchange extraction of several divalent metals into $C_4\text{mimTf}_2\text{N}$ with using **tpen**, we wandered upon a curious fact that extraction of Ni(II) was dominantly suppressed. To clarify cause for the anomalous suppression, we investigated cation-exchange extraction behavior of Ni(II) with different chelators [*N,N'*-bis-(2-pyridylmethyl)ethylenediamine (**bpen**), bis(2-pyridylmethyl)amine (**bpa**) and 2-(aminomethyl)pyridine (**ap**),

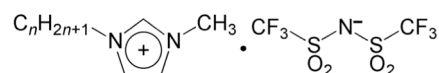


Figure 1. Chemical structure of $C_n\text{mimTf}_2\text{N}$.

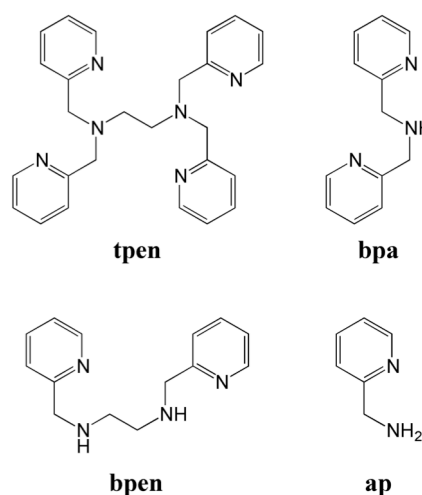


Figure 2. Chemical structures of the chelators used in this study.

Figure 2] corresponding to several substructures of **tpen**.

2. Experimental

2.1 Chemicals and apparatus

The three ILs (C_2mimTf_2N , C_4mimTf_2N and C_8mimTf_2N) were synthesized according to the previous reports [4,5]. The chelators (**tpen**, **bpen**, **bpa** and **ap**), nitrobenzene and other reagents were of reagent-grade materials purchased from Dojindo (Kumamoto, Japan), TCI (Tokyo, Japan) and other suppliers, and were used without further purification. High-purity water was produced with a Millipore Direct-Q water purification system.

A Thermo Fisher Model iCE3300 flame atomic absorption spectrometer was used for the determination of the metals in the aqueous phase. A Horiba Model F-72 pH meter equipped with a Horiba 9680-10D combined glass electrode was used to measure the pH values.

2.2 Extraction procedure

Aqueous phase (5 mL, pH 1–5) containing $2.0 \mu g mL^{-1}$ of Ni(II), Cu(II), Zn(II) or Mn(II), 0.1 M $NaClO_4$ (or KNO_3). 0.01M buffer (chloroacetic acid or acetic acid) was shaken to be equilibrated with extraction phase (1 mL, an IL or nitrobenzene) containing 1.0×10^{-3} M **tpen**, 2.0×10^{-3} M **bpen**, 2.0×10^{-3} M **bpa** or 4.0×10^{-3} M **ap**. On extraction at more acidic condition, suitable amount of HNO_3 was used instead of buffer and $-\log C_{HNO_3}$ value was used instead of aqueous phase pH. After phase separation by centrifugation, the metal contents in the both phases were determined with using flame AAS, and extraction ratio (%E) and distribution ratio (*D*) for the metal were calculated. (The content in the extraction phase was determined after back-extraction into 1–3 M HNO_3 .)

3. Results and Discussion

3.1 Extraction behavior of divalent metals into C_4mimTf_2N with **tpen**

Figure 3 shows extraction behavior of Ni(II), Cu(II), Zn(II) and Mn(II) into nitrobenzene and C_4mimTf_2N containing 1.0×10^{-3} M **tpen**. Changing $NaClO_4$ to KNO_3 in the nitrobenzene system resulted in the loss of metal extractability, whereas that in the C_4mimTf_2N system resulted in no change. Namely, the cationic **tpen** complexes were extracted as ion-pair with ClO_4^- in the former system and via cation-exchange mechanism in the latter system.

Cu(II), Zn(II) and Mn(II) showed similar extraction behavior between the nitrobenzene and C_4mimTf_2N systems. On the contrary, extraction of Ni(II) into C_4mimTf_2N was quite low compared to that into nitrobenzene. In addition, it was confirmed from slope analysis ($\log D$ vs. $\log [tpen]_e$) that the extracted species into nitrobenzene is

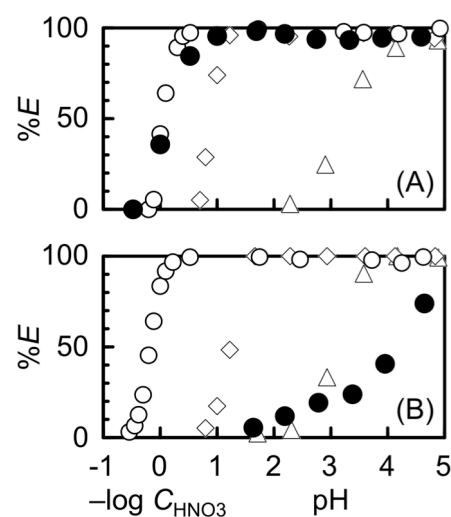


Figure 3. Extraction behavior of Ni (●), Cu (○), Zn (◇) and Mn (△) into nitrobenzene (A) or C_4mimTf_2N (B) with **tpen**.

$M(\text{tpen})^{2+} \cdot 2\text{ClO}_4^-$ ion-pair and that into $\text{C}_4\text{mimTf}_2\text{N}$ is $M(\text{tpen})^{2+}$ cation (except for Ni(II)).

3.2 Extraction behavior of Ni(II) into $\text{C}_4\text{mimTf}_2\text{N}$ with **bpen**, **bpa** and **ap**

To make the suppression of Ni(II) extractability clear, extraction behavior of Ni(II) with using **bpen**, **bpa** and **ap** was investigated. On each experiment, chelator concentration was set based on the number of the 2-pyridylmethyl pendant arm.

The results are shown in Figure 4. In use of **bpa** and **ap**, the nitrobenzene system and the $\text{C}_4\text{mimTf}_2\text{N}$ system showed similar extraction behavior. In use of **bpen**, intriguingly, the $\text{C}_4\text{mimTf}_2\text{N}$ system showed high extractability for Ni(II) , whereas the nitrobenzene system showed quite low one. Since **bpen** is a tetradentate chelator, $\text{Ni}(\text{bpen})^{2+}$ complex seems to be coordinatively-unsaturated (hydrated) one. $\text{C}_4\text{mimTf}_2\text{N}$ has lower hydrophobicity than nitrobenzene and, therefore, the **bpen**- $\text{C}_4\text{mimTf}_2\text{N}$ seems to show relatively high Ni(II) extractability.

On the contrary, hexadentate chelator **tpen** can form coordinatively-saturated complex with Ni(II) . Namely, structure of the extracted cationic Ni(II)-tpen complex in the $\text{C}_4\text{mimTf}_2\text{N}$ system seems to be different from that in the nitrobenzene system. In other words, it was suggested that the additional two 2-pyridylmethyl pendant arms in **tpen** play some role in the extraction suppression in the $\text{C}_4\text{mimTf}_2\text{N}$ system.

3.3 Extraction behavior of Ni(II) into various ILs with **bpen** and **tpen**

To evaluate the relationship between Ni(II) extractability and relative hydrophobicity of extraction phase solvent, extraction behavior of Ni(II) with **bpen** and **tpen** into $\text{C}_2\text{mimTf}_2\text{N}$ and $\text{C}_8\text{mimTf}_2\text{N}$ was investigated. The results are shown in Figure 5 with the data for the $\text{C}_4\text{mimTf}_2\text{N}$ and nitrobenzene systems.

In use of **bpen**, the order of Ni(II) extractability between solvents at pH 2–3 was $\text{C}_2\text{mimTf}_2\text{N} > \text{C}_4\text{mimTf}_2\text{N} > \text{C}_8\text{mimTf}_2\text{N} > \text{nitrobenzene}$, which is the inverse order of hydrophobicity of the solvents. This result is consistent with the relatively low hydrophobic nature of

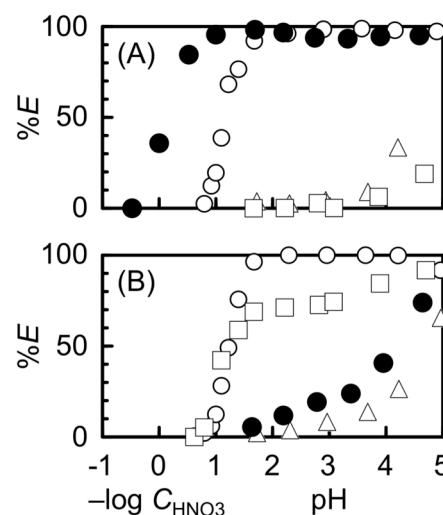


Figure 4. Extraction behavior of Ni(II) into nitrobenzene (A) or $\text{C}_4\text{mimTf}_2\text{N}$ (B).

● **tpen**, □ **bpen**, ○ **bpa**, △ **ap**

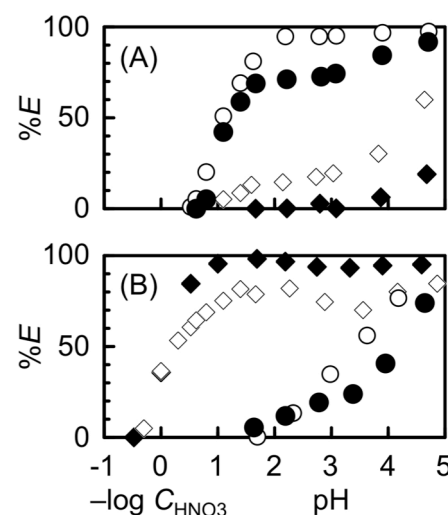


Figure 5. Extraction behavior of Ni(II) with **bpen** (A) and **tpen** (B) into $\text{C}_2\text{mimTf}_2\text{N}$ (○), $\text{C}_4\text{mimTf}_2\text{N}$ (●), $\text{C}_8\text{mimTf}_2\text{N}$ (◇) or nitrobenzene (◆).

coordinatively-unsaturated (hydrated) $\text{Ni}(\text{bpen})^{2+}$. In addition, the order between ILs, $\text{C}_2\text{mimTf}_2\text{N} > \text{C}_4\text{mimTf}_2\text{N} > \text{C}_8\text{mimTf}_2\text{N}$, accorded with conventional order in cation-exchange extraction into ILs [6].

In use of **tpen**, on the contrary, the order of Ni(II) extractability between solvents at pH 1–2 was nitrobenzene $> \text{C}_8\text{mimTf}_2\text{N} \gg \text{C}_4\text{mimTf}_2\text{N} \approx \text{C}_2\text{mimTf}_2\text{N}$. Interestingly, $\text{C}_8\text{mimTf}_2\text{N}$ having higher hydrophobicity than $\text{C}_4\text{mimTf}_2\text{N}$ showed similar Ni(II) extractability to nitrobenzene, whereas $\text{C}_2\text{mimTf}_2\text{N}$ having lower hydrophobicity showed similar one to $\text{C}_4\text{mimTf}_2\text{N}$. Probably, coordinatively-saturated (unhydrated) hydrophobic $\text{Ni}(\text{tpen})^{2+}$ complex prefers more hydrophobic solvents.

The $\text{p}K_a$ values for $\text{H}_4\text{tpen}^{4+}$, $\text{H}_3\text{tpen}^{3+}$, $\text{H}_2\text{tpen}^{2+}$ and Htpen^+ are 2.95, 3.35, 4.86 and 7.19, respectively [7], whereas respective ones for the protonated **bpen** are 1.62, 1.81, 5.45 and 8.23 [8]. These values show that the pendant arms on **tpen** have high affinity for H^+ compared to those on **bpen**. In less-hydrophobic ILs such as $\text{C}_4\text{mimTf}_2\text{N}$ and $\text{C}_2\text{mimTf}_2\text{N}$, it was suggested that **tpen** coordinates to Ni^{2+} not as a hexadentate ligand but as a tetradentate one to form relatively less-hydrophobic complex and that non-coordinating pyridine-N atoms on the free pendant arms are protonated, resulting in distribution of the more-charged (protonated) complex into the aqueous phase.

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References

- 1) M. Watanabe, R. Mirvaliev, S. Tachimori, K. Takeshita, Y. Nakano, K. Morikawa, R. Mori, *Chem. Lett.*, 1230-1231 (2002).
- 2) N. Hirayama, S. Iimuro, K. Kubono, H. Kokusen, T. Honjo, *Anal. Chim. Acta*, **339**, 115-121 (1997).
- 3) K. Shimojo, H. Naganawa, F. Kubota, M. Goto, *Chem. Lett.*, **35**, 484-485 (2006).
- 4) S. V. Dzyuba, R. A. Bartsch, *ChemPhysChem*, **3**, 161-166 (2002).
- 5) A. K. Burrell, R. E. Del Sesto, S. N. Baker, T. M. McCleskey, G. A. Baker, *Green Chem.*, **9**, 449-454 (2007).
- 6) T. Hamamoto, M. Okai, S. Katsuta, *J. Phys. Chem. B*, **119**, 6317-6325 (2015).
- 7) G. Anderegg, F. Wenk, *Helv. Chim. Acta*, **50**, 2330-2332 (1967).
- 8) R. G. Lacoste, A. E. Martell, *Inorg. Chem.*, **3**, 881-884 (1964).