

## Organic-solvent/Water/Ionic-liquid Triphasic System for the Fractional Extraction of Divalent Metal Cations

Takeshi TAKATA\* and Naoki HIRAYAMA\*\*†

\*Division of Material Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

\*\*Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

A novel cyclohexane/water/ionic-liquid (1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF<sub>6</sub>]) triphasic extraction system was studied for a possible fractional extraction of divalent metal cations with co-using 8-quinolinol (HQ) and tri-*n*-octylphosphine oxide (TOPO) as competitive extractants. In this system, Ni<sup>2+</sup> was extracted into the [bmim][PF<sub>6</sub>] phase as a Q<sup>-</sup>-complex, whereas each of Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> was extracted into the cyclohexane phase as an ion-pair of a cationic TOPO-complex and PF<sub>6</sub><sup>-</sup>. A suitable selection of extractants and ionic liquid can result in developing a powerful triphasic fractional extraction system.

(Received October 8, 2009; Accepted October 9, 2009; Published November 10, 2009)

Solvent extraction is a traditional separation technique using an organic-solvent/water biphasic system. This method, however, has only one extraction (organic) phase, and is not suitable for the simultaneous fractional separation of various components.

Recently, various extraction systems using several hydrophobic ionic liquids (ILs), such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][Tf<sub>2</sub>N]), instead of organic solvents as an extraction phase have been investigated for the extraction of metal cations and other species.<sup>1,2</sup> These hydrophobic ILs are not only immiscible to water, but also immiscible to various non-polar aliphatic solvents. Namely, a non-polar-aliphatic-solvent/water/hydrophobic-IL three-component system can form three separate phases.<sup>3</sup>

Previously, one of the authors reported that several divalent metal cations (M<sup>2+</sup>) including Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> can be extracted effectively into [bmim][PF<sub>6</sub>] with 8-quinolinol (HQ) as hydrated neutral complexes (MQ<sub>2</sub>(H<sub>2</sub>O)<sub>n</sub>) and that the coexistence of tri-*n*-octylphosphine oxide (TOPO) results in the interfering extraction of Zn<sup>2+</sup> and Cd<sup>2+</sup>.<sup>4,5</sup> These facts have suggested that the co-use of HQ and TOPO as extractants in the triphasic system can actualize the fractional extraction of metal cations. In this communication, we report on a fundamental study concerning a novel triphasic fractional extraction system for divalent metals, consisting of cyclohexane and [bmim][PF<sub>6</sub>] as competitive extraction phases and HQ and TOPO as competitive extractants. In addition, this is the first report on use of an IL-containing triphasic system in analytical chemistry.

### Experimental

Chemicals were of reagent-grade, and were used without further

purification. Ionic liquid [bmim][PF<sub>6</sub>] was synthesized according to a reported procedure.<sup>6</sup> Distilled and deionized water was used throughout.

An extraction study was performed as follows. In a centrifuge tube, an aliquot (1 cm<sup>3</sup>) of cyclohexane containing 1 × 10<sup>-2</sup> mol dm<sup>-3</sup> of HQ and 1 × 10<sup>-1</sup> mol dm<sup>-3</sup> of TOPO, 1 cm<sup>3</sup> of [bmim][PF<sub>6</sub>] and 5 cm<sup>3</sup> of an aqueous phase containing 1 × 10<sup>-5</sup> to 1 × 10<sup>-4</sup> mol dm<sup>-3</sup> of M<sup>2+</sup> (M = Mn, Ni, Cu, Zn, Cd or Pb), 1 × 10<sup>-1</sup> mol dm<sup>-3</sup> of potassium nitrate and 1 × 10<sup>-2</sup> mol dm<sup>-3</sup> of buffer (chloroacetic acid, acetic acid or Good's buffers) were shaken mechanically at 25 ± 1°C for 45 min. After the three phases were separated by centrifugation, the pH in the aqueous phase was determined. The metal concentration in the aqueous phase and those in the two extraction phases (after back-extraction into 10-fold volume of 1 mol dm<sup>-3</sup> nitric acid) were determined by flame atomic absorption spectrophotometry.

### Results and Discussion

In the cyclohexane/water/[bmim][PF<sub>6</sub>] triphasic system, the extracted ratios of M<sup>2+</sup> into the cyclohexane phase (%E<sub>org</sub>) and those into the [bmim][PF<sub>6</sub>] phase (%E<sub>IL</sub>) were plotted as a function of the aqueous-phase pH. The results co-using HQ and TOPO as extractants are shown in Fig. 1 along with plots obtained when using HQ alone.

Upon using HQ alone, all metals were extracted only into the [bmim][PF<sub>6</sub>] phase, and the extraction behavior was almost the same as that in the water/[bmim][PF<sub>6</sub>] biphasic system. The results are consistent with our opinion that an IL as the extraction phase can stabilize extracted hydrated neutral metal complexes.<sup>7</sup> Upon co-using HQ and TOPO, on the contrary, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> were extracted mainly to the cyclohexane phase, whereas Ni was extracted quantitatively extracted into the [bmim][PF<sub>6</sub>] phase. At pH 5, the %E<sub>org</sub> values for Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> were 73, 83, 76 and 87%, respectively, and these

† To whom correspondence should be addressed.  
E-mail: hirayama@cacheibm.s.kanazawa-u.ac.jp

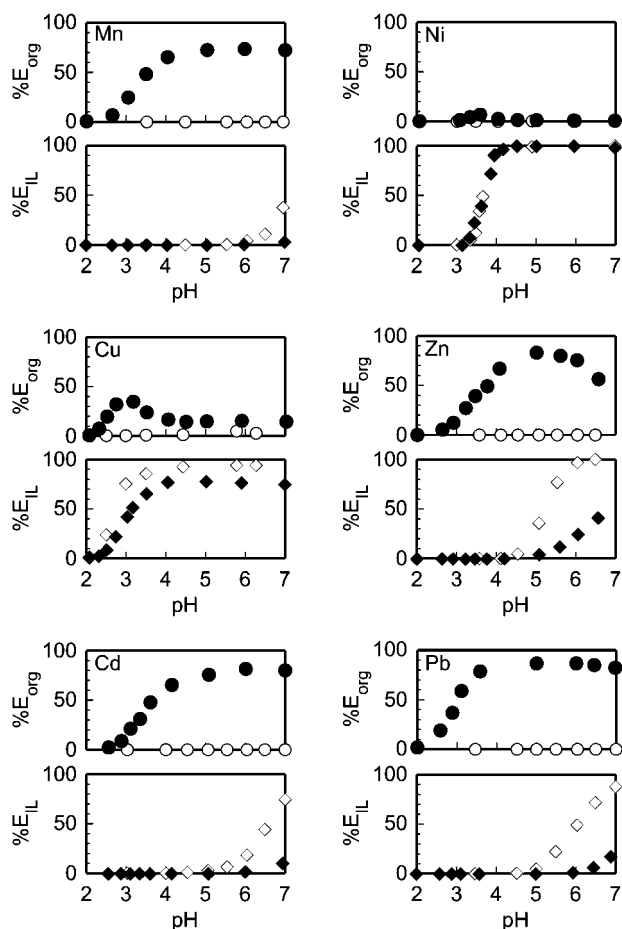


Fig. 1 Plots of  $\%E_{\text{org}}$  (upper) and  $\%E_{\text{IL}}$  (lower) for  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  as a function of the aqueous-phase pH in the cyclohexane/water/[bmim][PF<sub>6</sub>] triphasic extraction system using HQ and TOPO (solid symbols) or HQ alone (open symbols) as extractant(s). The initial HQ and TOPO concentrations in the cyclohexane phase were  $1 \times 10^{-2}$  and  $1 \times 10^{-1}$  mol dm<sup>-3</sup>, respectively.

metals were not extracted into the [bmim][PF<sub>6</sub>] phase. Namely, the extraction of these TOPO-containing complexes into the cyclohexane phase seem to have a competitive advantage over the extraction of respective hydrated neutral complexes into the [bmim][PF<sub>6</sub>] phase (at higher pH, in fact, these metals were gradually extracted into the [bmim][PF<sub>6</sub>] phase). In addition,  $\text{Cu}^{2+}$  was extracted into both phases, and this system seemed to be unfavorable for the extraction of  $\text{Cu}^{2+}$ .

To evaluate the extracted species into the cyclohexane phase, the relationships between the logarithmic cyclohexane/water distribution ratios for the metals ( $\log D_{\text{org/aq}}$ ) and the logarithmic initial HQ concentration in the cyclohexane phase ( $\log C_{\text{org}}(\text{HQ})$ ) or the logarithmic initial TOPO concentration in the cyclohexane phase ( $\log C_{\text{org}}(\text{TOPO})$ ) were investigated. These plots for  $\text{Cd}^{2+}$  are shown in Fig. 2 as examples. The  $\log D_{\text{org/aq}}$  values were independent of  $C_{\text{org}}(\text{HQ})$ , showing no contribution of HQ to the extraction. On the contrary, the  $\log D_{\text{org/aq}}$  vs.  $\log C_{\text{org}}(\text{TOPO})$  plot showed a straight line with a slope of ca. 3, and it was found that three TOPO molecules reacted with one  $\text{M}^{2+}$  in this extraction. Furthermore, the use of a cyclohexane/water biphasic system with the same extractant condition resulted in

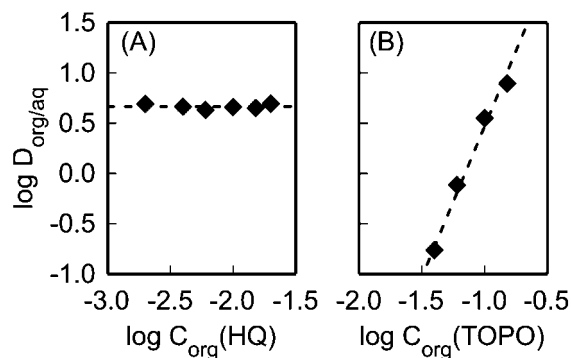
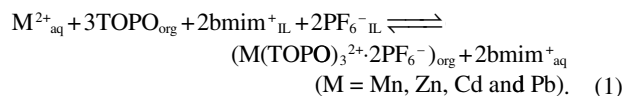


Fig. 2 Plots of  $\log D_{\text{org/aq}}$  for  $\text{Cd}^{2+}$  in the cyclohexane/water/[bmim][PF<sub>6</sub>] triphasic extraction system with co-using HQ and TOPO as a function of the logarithmic initial HQ concentration in the cyclohexane phase (A) and the logarithmic initial TOPO concentration in the cyclohexane phase (B). The aqueous-phase pH was 3.5, the initial HQ concentration on (B) was  $1 \times 10^{-2}$  mol dm<sup>-3</sup> and the initial TOPO concentration on (A) was  $1 \times 10^{-1}$  mol dm<sup>-3</sup>. The broken lines, of which the slope is 0 and 3 for (A) and (B), respectively, were obtained by a least-squares fitting.

no extraction of these metals at pH < 5. These facts suggested that the extraction equilibria of these metals into the cyclohexane phase in the triphasic system is expressed as follows:



In this mechanism, it is impressive that the counter anion (PF<sub>6</sub><sup>-</sup>) for ion-pair extraction into the cyclohexane phase is fed from the [bmim][PF<sub>6</sub>] phase. Namely, in the triphasic extraction system, the [bmim][PF<sub>6</sub>] phase seems to act not only as an extraction phase for Q-complexes, but also as a counter-anion storage for ion-pair extraction into another extraction phase.

As mentioned above, a cyclohexane/water/[bmim][PF<sub>6</sub>] triphasic system co-using HQ and TOPO can be used as fractional extraction of several divalent metal cations ( $\text{Ni}^{2+}$  vs.  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$ ). Insufficient extractability of the metals into the cyclohexane phase can be improved by increasing the phase volume. Furthermore, it is expected that the selection of more suitable extractants and/or IL results in the development of a much powerful triphasic functional extraction system for various metals.

## References

1. F. Kubota and M. Goto, *Solv. Extr. Res. Dev., Jpn.*, **2006**, 13, 26, and references therein.
2. N. Hirayama, *Bunseki*, **2006**, 519, and references therein.
3. P. Wasserscheid, *Nature*, **2006**, 439, 797.
4. N. Hirayama, *JAERI-Conf*, **2004**, 2003-021, 103.
5. N. Hirayama, *Bunseki Kagaku*, **2008**, 57, 949.
6. J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, and R. D. Rogers, *Chem. Commun.*, **1998**, 1765.
7. N. Hirayama, M. Deguchi, H. Kawasumi, and T. Honjo, *Talanta*, **2005**, 65, 255.