



Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions

Guor-Tzo Wei*, Zusing Yang, Chao-Jung Chen

Department of Chemistry and Biochemistry, National Chung Cheng University, 160 San-Hsin, Ming-Hsiung, Chia-Yi 621, Taiwan

Received 2 January 2003; received in revised form 19 May 2003; accepted 22 May 2003

Abstract

Room temperature ionic liquids (RTILs) have been used as novel solvents to replace traditional volatile organic solvents in organic synthesis, solvent extraction, and electrochemistry. The hydrophobic character and water immiscibility of certain ionic liquids allow their use in solvent extraction of hydrophobic compounds. In this work, a typical room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [C₄mim][PF₆], was used as an alternative solvent to study liquid/liquid extraction of heavy metal ions. Dithizone was employed as a metal chelator to form neutral metal–dithizone complexes with heavy metal ions to extract metal ions from aqueous solution into [C₄mim][PF₆]. This extraction is possible due to the high distribution ratios of the metal complexes between [C₄mim][PF₆] and aqueous phase. Since the distribution ratios of metal dithizonates between [C₄mim][PF₆] and aqueous phase are strongly pH dependent, the extraction efficiencies of metal complexes can be manipulated by tailoring the pH value of the extraction system. Hence, the extraction, separation, and preconcentration of heavy metal ions with the biphasic system of [C₄mim][PF₆] and aqueous phase can be achieved by controlling the pH value of the extraction system. Preliminary results indicate that the use of [C₄mim][PF₆] as an alternate solvent to replace traditional organic solvents in liquid/liquid extraction of heavy metal ions is very promising.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Room temperature ionic liquid; 1-Butyl-3-methylimidazolium hexafluorophosphate; Solvent extraction; Metal ions extraction; Metal ions preconcentration

1. Introduction

Room temperature ionic liquids (RTILs) have aroused increasing interest for their promising role as alternative media in synthesis [1–11], separation [12–14], and electrochemistry [15,16] as a result of their unique chemical and physical properties [17–21]. RTILs can dissolve a wide spectrum of organic, organometallic, and inorganic compounds [18,19]. Also, they have no detectable vapor pres-

sure and are relatively thermal stable. So, there is no loss of solvent through evaporation with ionic RTILs. This will avoid environmental and safety problems due to volatilization, as is the case in traditional organic solvents. Therefore, they are proposed as novel solvent systems to replace traditional solvents that are generally toxic, flammable, and volatile. RTILs are regarded to have the potential to be alternative reaction media for “Green Chemistry” [22,23].

Applications of RTILs in analytical chemistry have also started to receive attention recently [12,14,24–28]. For the pioneer works of using RTILs in the extraction of metal ions, several groups presented the use of crown ethers for the extraction of

* Corresponding author. Tel.: +886-5-2428121;

fax: +886-5-2721040.

E-mail address: chegtw@ccunix.ccu.edu.tw (G.-T. Wei).

group 1 and 2 ions from aqueous phase [29–31]. RTILs were further extended to the extraction of heavy metal ions. Rogers and coworkers incorporated thiourea, thioether, and urea into derivatized imidazolium cations and used these functionized ILs as the extractant in liquid/liquid extraction of Hg^{2+} and Cd^{2+} [32]. In that report, low distribution ratios were obtained with less expensive ILs, such as 1-butyl-3-methylimidazolium hexafluorophosphate $[\text{C}_4\text{mim}][\text{PF}_6]$ as extractant for Hg^{2+} and Cd^{2+} . The distribution ratios were highly improved when functionized ILs were mixed with $[\text{C}_4\text{mim}][\text{PF}_6]$. Therefore, functionized ILs played the role of extractant and hydrophobic phase. Rogers and coworkers also utilized $[\text{C}_4\text{mim}][\text{PF}_6]$ with organic and inorganic extractants for the liquid/liquid extraction of heavy metal ions with radiotracer technique [33]. Hence, further analytical applications should be explored for the extraction of heavy metal ions with these novel media. In this work, dithizone, a popular organic metal chelator for analytical applications, was utilized as an organic extractant for liquid/liquid extraction of heavy metal ions with ionic liquid- $[\text{C}_4\text{mim}][\text{PF}_6]$. UV-Vis spectrometer was employed to examine the formation of metal–chelator complex by observing the spectra of dithizone and metal–dithizone complexes. Atomic absorption (AA) spectrometry, instead of isotope tracer [33], was then used to determine the liquid/liquid extraction efficiencies of metal ions at various conditions. To evaluate the potential use of RTILs to replace traditional volatile organic compounds (VOCs) in liquid/liquid extraction of heavy metal ions, the extractions of metal ions with VOCs and ionic liquid are compared.

2. Experimental

2.1. Reagents

Dichloromethane, acetonitrile (ACN), ethyl acetate, tris(hydroxymethyl)-amionomethane, citric acid, buffer standards, and all metal ions standard solution (1000 ppm) were supplied by Merck (Darmstadt, Germany). Dithizone was obtained from Riedel-deHaen (Sleeze, Germany) and 1-chlorobutane was obtained from TEDIA (Fairfield, OH, USA). 1-Methylimidazole was supplied by ACROSS (Belgium) and potassium hexafluorophosphate was supplied by ProChem

(Rockford, IL, USA). Sodium hydroxide and anhydride magnesium sulfate were obtained from Hanawa (Osaka, Japan).

2.2. Apparatus

Atomic absorption measurements were performed with a Perkin-Elmer AA 3110 (Uerlingen, Germany). UV-Vis spectra were measured with Cary 3E (Varian, Palo Alto, CA, USA). The purity of ionic liquid was confirmed with the spectrum obtained from a Varian Gemini 200 MHz NMR. A Shimadzu (Tokyo, Japan) LC-10AT pump equipped with a SPD-10A UV-Vis detector and a Hypersil (Agilent, Palo Alto, CA, USA) ODS 5 μm , 4.6 mm \times 250 mm column was used to determine 1-butyl-3-methylimidazolium content in aqueous phase. The pH value of the extraction systems were measured with an Orion model 420A pH meter (Boston, MA, USA) that was calibrated with pH 4.00 and 10.00 buffer standards.

2.3. Preparation of ionic liquid

The synthesis of $[\text{C}_4\text{mim}][\text{PF}_6]$ was described elsewhere [12]. Briefly, 1-butyl-3-methylimidazolium chloride $[\text{C}_4\text{mim}][\text{Cl}]$ was prepared by adding equal amounts (0.3 mol) of 1-chlorobutane and 1-methylimidazole to a 250 ml round-bottom flask fitted with reflux condenser and reacting them for 24–48 h at 80 °C till the formation of a golden viscous liquid. The viscous liquid was cooled and washed three times with 50 ml portion of ethyl acetate in a separation funnel. Then, the lower liquid portion $[\text{C}_4\text{mim}][\text{Cl}]$ was slowly added to a 150 ml potassium hexafluorophosphate (0.3 mol) solution at 4 °C in 30 min, then stirred at room temperature for 30 min. A 25 ml dichloromethane was added to the lower liquid portion and this mixture was washed with water until the washing was no longer acidic. The washed IL was dried with anhydrous magnesium sulfate and heated under vacuum at 70 °C to remove the solvent. The purity of final product was characterized with ^1H NMR. The yield was about 60%.

2.4. Liquid/liquid extraction of metal–dithizone complexes

Dithizone was dissolved in a 5 ml aqueous phase to form an 8.4×10^{-5} M dithizone solution. The

aqueous phase was a mixture of ACN–water (10:90 (v/v)). UV-Vis measurement was performed to obtain the absorption spectrum of dithizone. Then, a metal ions solution (20 ppm) was added to the dithizone solution and the absorption spectrum of metal complexes was recorded. Consequently, the extraction of metal–dithizone complexes was performed by mixing 1 ml ionic liquid with metal–dithizone complexes and shaking for about 2 min and then centrifuging to separate the two phases. The UV-Vis spectrum of the aqueous phase was recorded.

2.5. Extraction efficiencies of metal ions with RTIL

Extraction efficiencies of metal ions at different pH values were determined by mixing 1 ml of RTIL with 5 ml aqueous phase that consisted of 20 ppm metal ions and 8.4×10^{-5} M dithizone. The effects of other ions co-existed in the aqueous phase on the extraction of metal ions were examined by mixing 500 ppm of different metal ions or anions in the aqueous phase before extraction with IL. The biphasic system was shaken to ensure it was fully mixed and then centrifuged to separate the two phases after extraction. The upper aqueous phase was taken out and measured with AA spectrometry to determine the concentration of metal ions that was left in the aqueous phase. Extraction efficiencies (E) were calculated by

$$E (\%) = \frac{(C_i)_{\text{aq}} - (C_f)_{\text{aq}}}{(C_i)_{\text{aq}}} \times 100 \quad (1)$$

where $(C_i)_{\text{aq}}$ and $(C_f)_{\text{aq}}$ are the concentration of metal ions in aqueous phase before and after extraction, respectively.

2.6. Preconcentration of metal ion by liquid/liquid extraction with $[C_4\text{mim}][\text{PF}_6]$

Aqueous phase containing metal ions and 8.4×10^{-5} M dithizone was mixed with 1 ml $[C_4\text{mim}][\text{PF}_6]$. The aqueous solution was removed after shaking and centrifuging. Different volume of acid solution was added to the ionic liquid to strip the metal ion from ionic liquid. Then, the acid solution was removed, diluted (if necessary), and measured with AA to determine the metal ions in aqueous phase. The recovery factor was then estimated from the ratio of metal ion

in acid solution to aqueous solution, with the correction of dilution factor.

3. Results and discussion

3.1. Examining the formation and extraction of metal complex with UV-Vis

Dithizone was selected as the organic extractant to study the liquid/liquid extraction of heavy metal ions with $[C_4\text{mim}][\text{PF}_6]$ because it is an organic colorimetric reagent that enables the use of UV-Vis spectrometer for measuring the concentration of metal ions [34]. It is widely used for the extraction and determination of metal ions [35]. Fig. 1a indicates two absorption peaks of dithizone in aqueous phase. It should be noted that 10% ACN was added in the aqueous phase to assist the dissolution of dithizone in aqueous phase. With the addition of Pb^{2+} into the aqueous dithizone solution, a new absorption maximum at about 480 nm was observed, as shown in Fig. 1b. This is due to the formation of lead–dithizone complex by mixing dithizone with Pb^{2+} . Once the solution of lead–dithizone complexes was mixed with $[C_4\text{mim}][\text{PF}_6]$, lead-dithizonate was removed from aqueous phase and the characteristic absorption peak of lead–dithizone complex in aqueous phase disappeared, as shown in Fig. 1c. UV-Vis spectrometer was also directly employed to observe the absorption spectrum of lead–dithizone complex in $[C_4\text{mim}][\text{PF}_6]$. Absorption spectra of lead-dithizonate and other metal-dithizonates in $[C_4\text{mim}][\text{PF}_6]$ are shown in Fig. 2. Results of Figs. 1 and 2 clearly indicate the formation of metal–dithizone complexes and the extraction of these complexes from aqueous phase into ionic liquid phase.

3.2. Influence of pH value on the extraction of metal ion with IL and chloroform

Although the results of Figs. 1 and 2 show that UV-Vis measurements can be employed to investigate the extraction of metal–dithizone complexes with $[C_4\text{mim}][\text{PF}_6]$, it is difficult to accurately determine the concentrations of dithizone and metal-dithizonate in $[C_4\text{mim}][\text{PF}_6]$. This is due to the spectral overlap of dithizone and metal-dithizonate in $[C_4\text{mim}][\text{PF}_6]$, as

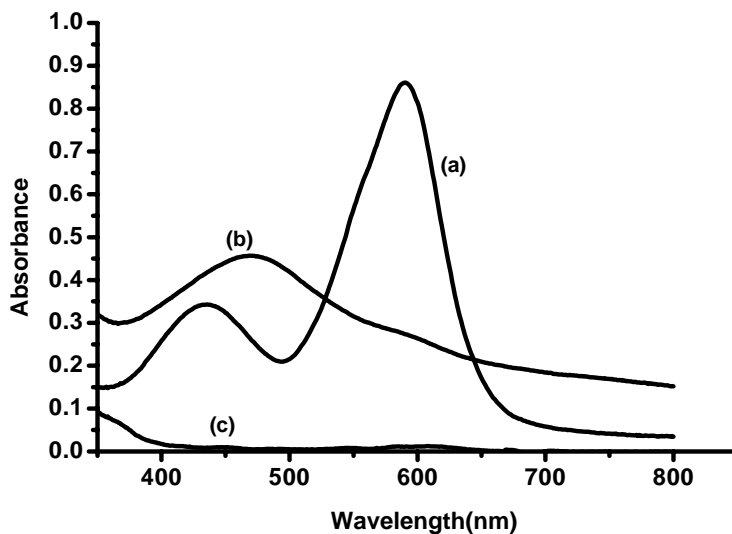


Fig. 1. UV-Vis absorption spectra of (a) dithizone in aqueous phase; (b) lead-dithizone in aqueous phase and; (c) aqueous phase after IL extraction.

shown in Fig. 2. Instead of using radioisotope tracer [33], AA was utilized to determine the concentration of metal ions in aqueous phase. The extraction efficiencies of metal ions with $[C_4mim][PF_6]$ can be estimated with Eq. (1).

The influence of pH value on the extraction of lead-dithizone complex with traditional solvent (chloroform) and IL are compared and shown in Fig. 3. Both biphasic systems show similar behavior that the extraction is strongly dependent on the pH value of

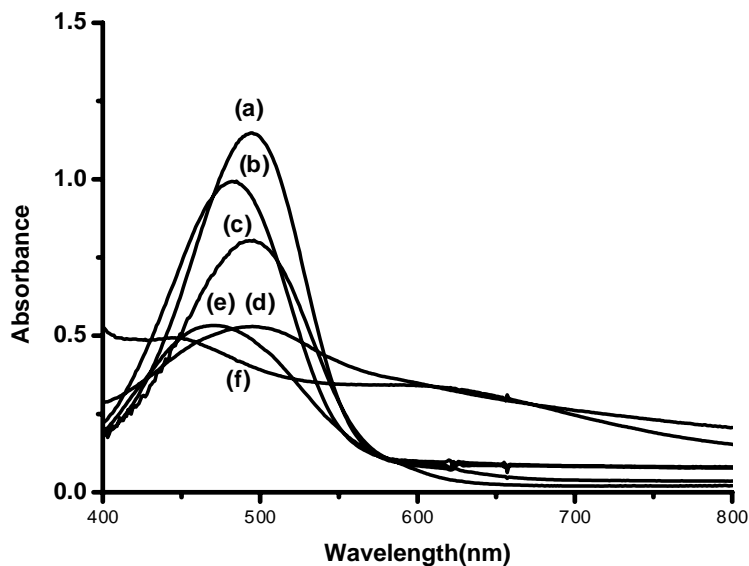


Fig. 2. UV-Vis absorption spectra of metal-dithizonates and dithizone in IL. (a) Cadmium-dithizonate; (b) mercury-dithizonate; (c) dithizone; (d) lead-dithizonate; (e) silver-dithizonate and; (f) copper-dithizonate. Absorption spectra of metal-dithizonates were corrected with IL as the blank.

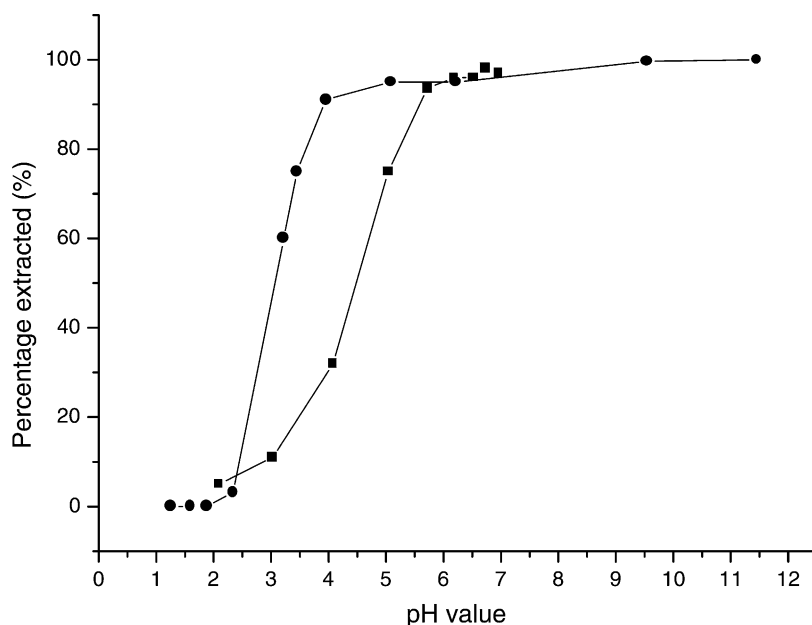


Fig. 3. Comparison of lead ion extraction with different solvents. Small amount of acetonitrile was added into the aqueous phase to extract 20 ppm lead with ionic liquid (●) and chloroform (■).

the extraction system. A schematic for the extraction of metal ion with dithizone can be represented by Fig. 4 [35]. At low pH, the majority of dithizone is in HL (neutral) form that prefers to distribute in organic phase. This leads to a very low concentration of metal-dithizonate because there is only a limited amount of deprotonated dithizone for the formation of metal-dithizonate. Also, highly hydrophilic metal ions prefer partition in aqueous phase and this results in

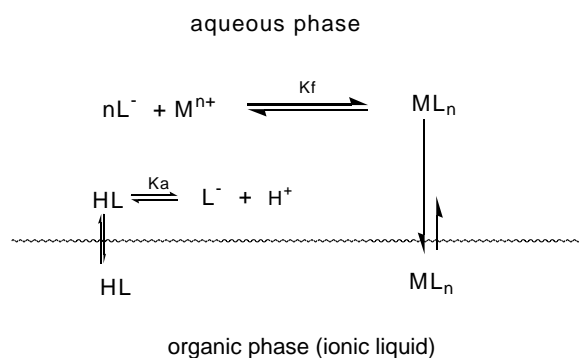


Fig. 4. Illustration of various equilibria involved in the metal ion extraction with an ionic liquid.

low extraction efficiency at low pH. On the contrary, high concentration of deprotonated dithizone at high pH leads to high concentration of metal-dithizonate and results in high extraction efficiency, due to the high solubility of metal-dithizonate in organic phase.

Fig. 3 reveals that the extraction efficiency of ionic liquid is higher than that of chloroform at low pH. It can be attributed to either higher formation constant of lead-dithizonate or higher concentration of deprotonated dithizone in $[C_4mim][PF_6]$, as compared to that in chloroform. It is more likely that the ionic liquid facilitates the formation of deprotonated dithizone because the solvation energy of deprotonated dithizone in IL is higher than that in chloroform [31]. This argument is further supported by the absorption spectrum of dithizone in $[C_4mim][PF_6]$, as shown in Fig. 2, that only one absorption maximum at about 480 nm was observed. Yet, two absorption maximas at 440 and 620 nm for dithizone in a traditional VOCs, such as ACN, were observed [34]. The proton of dithizone may be partially solvated in ionic liquid. Thus, the absorption spectrum of dithizone in IL is similar to the spectrum of metal-dithizonate where dithizone is deprotonated. Therefore, the use of RTIL as the solvent

for liquid/liquid extraction of metal ions allows the extraction to be performed at lower pH. Another advantage of using RTIL in liquid/liquid extraction of metal ions is that this method eliminates the use of chlorinated solvents such as chloroform. Chloroform is highly toxic and listed as a potential carcinogen. Prolonged or repeated overexposure lead to liver and kidney damage and an increased risk of cancer. Detailed safety consideration for handling, disposal, and storage of chloroform can be found in the material safety data sheets (MSDS), and must be followed when handling this potential carcinogen.

One of the possibilities for the extraction of metal ions by RTIL is due to an ion exchange mechanism because of water solubility of ionic liquid. An experiment was designed to investigate the ion exchange mechanism by measuring the metal ions and $[\text{C}_4\text{mim}][\text{PF}_6]$ content in aqueous at different conditions and the results are shown in Table 1. A reversed-phase HPLC with 20% ACN in water as the mobile phase was used to determine the concentration of $[\text{C}_4\text{mim}][\text{PF}_6]$ in aqueous phase at different stages of extraction. Ion exchange between metal ions and $[\text{C}_4\text{mim}]$ before the addition of a metal chelator will lead to a decrease of metal ion concentration and an increase of $[\text{C}_4\text{mim}]$ concentration in aqueous phase. However, the data indicate that addition of Cu^{2+} in aqueous phase decreases the solubility of $[\text{C}_4\text{mim}][\text{PF}_6]$ at all pH values performed. This investigation indicates that the contribution of ion exchange between metal ions and $[\text{C}_4\text{mim}]$ for the extraction of

metal ions seems insignificant. However, the reduced solubility of ionic liquid in aqueous phase may due to ion exchange between metal ions and $[\text{C}_4\text{mim}]$. The conditions of the aqueous phase may also affect the solubility of ionic liquid in aqueous phase.

In the early stage of this work without the use of ACN, irreproducible and low extractions were obtained. This may be due to the high viscosity of ionic liquid and its immiscibility with water, resulting in poor mixing between aqueous phase and IL and hence poor extraction. Since ACN is miscible with aqueous phase and ionic liquid phase, it can promote a better mixing between aqueous phase and viscous IL and improve extraction reproducibility. This argument is confirmed by the reproducibility study of Pb^{2+} extraction. The extraction efficiencies of Pb^{2+} with ACN at pH 3.8 and without ACN at pH 3.5 are 58.3 ± 5.6 and $37.5 \pm 12.5\%$, respectively, from five replicate extractions. Nevertheless, our recent results indicate that reproducible extraction of metal ions with RTIL can be obtained without addition of ACN in aqueous phase [36].

Fig. 5 summarizes the pH effect on the extraction of different metal ions with $[\text{C}_4\text{mim}][\text{PF}_6]$. All curves have the similar trend that the extractions of metal ions with RTIL are strongly pH dependent. The characteristic pH with 50% extraction efficiency depends on the stability of metal-dithizonate (K_f). Complete extraction of metal ion can be accomplished at lower pH for metal ion with more stable metal–dithizone complex (higher K_f). Consequently, this behavior can be applied for the separation of metal ions by controlling the pH value of the separation medium.

3.3. Separation of metal ions in liquid/liquid extraction of metal ion with IL

The feasibility for the separation of metal ion in liquid/liquid extraction with IL was examined. An aqueous phase containing Cu^{2+} , Pb^{2+} , and Zn^{2+} was extracted with $[\text{C}_4\text{mim}][\text{PF}_6]$ at pH 2.0. Only Cu^{2+} was extracted into ionic phase, whereas Pb^{2+} and Zn^{2+} remained in the aqueous phase. This allows the separation of Cu^{2+} from Pb^{2+} and Zn^{2+} . This is in agreement with the results of Fig. 5. To further confirm this feasibility, a mixture of Cu^{2+} and Cd^{2+} at pH 1.9 was investigated. About 97% of Cu^{2+} were extracted into $[\text{C}_4\text{mim}][\text{PF}_6]$, whereas Cd^{2+} remained

Table 1

The solubility of $[\text{C}_4\text{mim}][\text{PF}_6]$ in the aqueous phase at various extraction conditions

pH	Aqueous phase condition	Percentage of Cu^{2+} extracted ^a (%)	$[\text{C}_4\text{mim}][\text{PF}_6]$ ^b (mg/ml)
0.66	Aqueous phase only	–	1.96
0.66	Cu^{2+} in aqueous phase	0	1.02
0.66	CuL_2 in aqueous phase	60.7	4.75
1.21	Aqueous phase only	–	5.19
1.21	Cu^{2+} in aqueous phase	0	2.86
1.21	CuL_2 in aqueous phase	94.6	6.05
2.09	Aqueous phase only	–	5.51
2.09	Cu^{2+} in aqueous phase	0	4.33
2.09	CuL_2 in aqueous phase	95.0	7.69

^a Determined by AA.

^b Determined by HPLC.

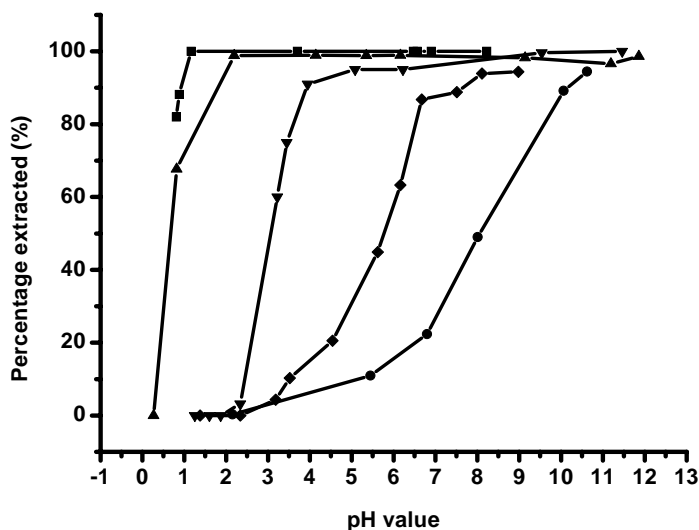


Fig. 5. The effect of pH value on the extraction efficiencies of metal ions with $[C_4mim][PF_6]$. The aqueous phase contain 8.4×10^{-5} M dithizone with 20 ppm of silver ion (■), copper ion (▲), lead ion (▼), cadmium ion (◆), and zinc ion (●).

in the aqueous phase. Furthermore, a mixture of Ag^+ and Pb^{2+} at pH 1.9 was examined. About 92% of Ag^+ were extracted into $[C_4mim][PF_6]$, whereas Pb^{2+} remained in the aqueous phase. These examples clearly indicate that IL can be employed for the separation of metal ions by tailoring the pH value of the aqueous phase.

3.4. Interference in the extraction of metal ions with ionic liquid

Fig. 5 also implies that extraction of a particular metal ion may be interfered by other metal ions. Fig. 6 displays the effect of cations on the extraction of Cu^{2+} . The data indicate that Ag^+ or Hg^{2+} reduces the

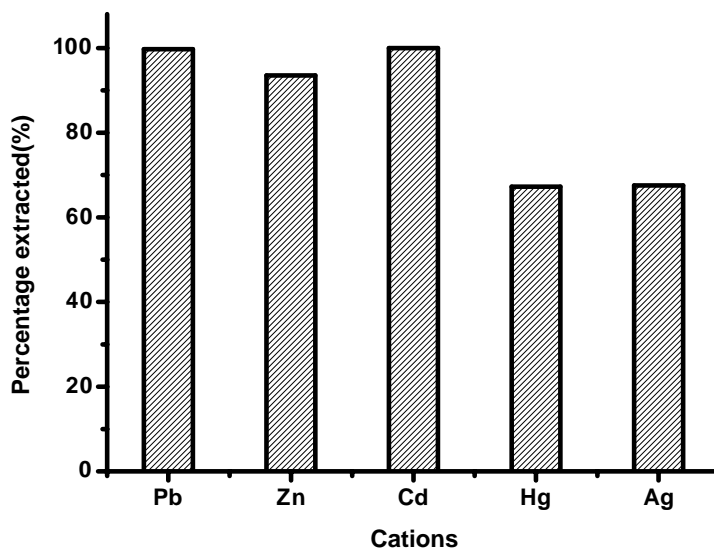


Fig. 6. Cations effect on the extraction of copper ion with $[C_4mim][PF_6]$. Five hundred parts per million of interference ion were added to pH 6.5, 8.4×10^{-5} M dithizone aqueous phase with 20 ppm copper solution.

extraction efficiency of Cu^{2+} . The effect of Hg^{2+} or Ag^+ on the extraction of Cu^{2+} is concentration dependent (not shown here). This is attributed to the greater formation constant of Ag^+ or Hg^{2+} with dithizone than that of Cu^{2+} . Therefore, dithizone prefers to form a neutral metal complex with Ag^+ or Hg^{2+} rather than with Cu^{2+} when the concentration of dithizone is less than the stoichiometric concentration of the metal ions. Hence, the effect of cation on the extraction of metal ions depends on the formation constant of the metal complex and the concentration of the metal chelator. Fig. 7 displays the effect of anions on the extraction of Cu^{2+} . Here, the anions are assumed to compete with dithizone for complex formation and may lead to interference. Fig. 7 indicates that the interference of anions on the extraction of Cu^{2+} is negligible. This is due to large formation constant of copper–dithizone complex.

3.5. Preconcentration of metal ion with ionic liquid

One of the analytical applications for liquid/liquid extraction of a metal ion with a metal chelator is preconcentration of the metal ion to increase the sensitiv-

ity of analysis. A trace metal ion can be removed from aqueous phase into organic phase by the formation of a neutral metal–dithizone complex. With addition of acid to decrease the pH value to a certain value, the extraction efficiency of a metal ion is reduced. So, the metal ion can be stripped from IL phase into aqueous phase by the dissociation of metal–dithizone complex. Since the extraction and stripping between aqueous and IL phase are pH dependent, the recovery of a metal ion is possible by controlling pH value. Therefore, the concentration of a metal ion can be increased from extraction and stripping cycle by using a large volume of aqueous phase with a small volume of IL during extraction and a small volume of acid solution during the stripping. With this extraction and stripping cycle, a metal ion in a large volume of aqueous phase is transferred to a small volume of acid solution. This results in an increase of metal ion concentration. The magnitude of the concentration factor depends on the volume ratio of the original aqueous solution to the stripping acid solution. Results for the preconcentration of Cd^{2+} and Pb^{2+} are shown in Table 2. These data show that the preconcentration and recovery of metal ions with ionic liquid from diluted solutions are possible.

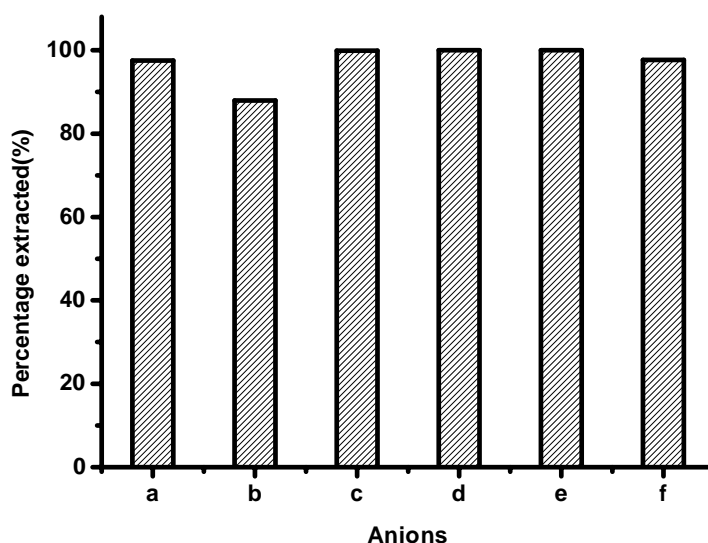


Fig. 7. Anions effect on the extraction of copper ion with $[\text{C}_4\text{mim}][\text{PF}_6]$. Five hundred parts per million of interference ion were added to pH 6.5, 8.4×10^{-5} M dithizone aqueous phase with 20 ppm copper solution. (a) Cl^- ; (b) CO_3^{2-} ; (c) PO_4^{3-} ; (d) acetate; (e) SCN^- and; (f) citrate.

Table 2
Preconcentration of Cd²⁺ and Pb²⁺ by liquid/liquid extraction with [C₄mim][PF₆]

Concentration factor	Theoretical value (ppm)	Experimental value (ppm)	Recovery (%)
Cd ²⁺ ^a			
5	10.0	10.1	101
10	20.0	20.2	101
20	40.0	38.2	97.4
25	50.0	45.8	91.6
50	100	99.2	99.2
Pb ²⁺ ^b			
2	40.0	38.0	97.2
2.5	50.0	49.0	98.2
4	80.0	79.0	98.8
5	100	99.9	99.9

^a Two parts per million Cd²⁺.

^b Twenty parts per million Pb²⁺ aqueous phase at pH 7.0.

3.6. Recycling ionic liquid for reuse

Ionic liquid is regarded as a “Green Solvent”[22]. The feasibility of recycling RTIL in liquid/liquid extraction of 20 ppm Pb²⁺ at pH 6.5 with dithizone was examined. After the extraction, the ionic liquid phase was mixed with 0.1 M HNO₃ solution to remove Pb²⁺ from the ionic liquid. Then, the ionic liquid was recycled for reuse. This extraction and stripping process was repeated five cycles. AA was used to measure the concentration of Pb²⁺ in acidic aqueous phase after each stripping process. Average extraction efficiency of 98.4 ± 0.2% was obtained. Similar results were obtained with other metal ions. The results indicate that ionic liquid can be recycled for reuse in liquid/liquid extraction of metal ions. The extraction process is also shown to be very reproducible from these data.

3.7. Conclusions

The extraction of metal ions with dithizone in a biphasic system consisting of an ionic liquid and an aqueous phase was demonstrated. This novel extraction system can be employed for separation and preconcentration of metal ions. RTILs are environmentally benign because of their nonvolatile and nonflammable properties. Recycling ionic liquid for reuse is also possible. Hence, they have the potential to replace traditional VOCs in liquid/liquid extraction of metal ions.

Acknowledgements

The authors would like to thank National Chung Cheng University and the National Science Council, Taiwan for financially supporting this research with grant (NSC91-2113-M-194-021). The authors thank Professor L.-K. Chau for editorial assistance.

References

- [1] J.S. Wilkes, M.J. Zaworotko, *J. Chem. Soc., Chem. Commun.* (1992) 965.
- [2] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. de Souza, *Polyhedron* 15 (1996) 1217.
- [3] C.J. Adam, M.J. Earle, G. Robert, K.R. Sneddon, *Chem. Commun.* (1998) 2097.
- [4] P.J. Dyson, D.J. Ellis, D.C. Parker, T. Welton, *Chem. Commun.* (1999) 25.
- [5] C.J. Adam, M.J. Earle, K.R. Sneddon, *Green Chem.* 2 (2000) 21.
- [6] G. Toma, B. Gotov, E. Solcaniova, *Green Chem.* 2 (2000) 149.
- [7] C.E. Song, E.J. Roh, *Chem. Commun.* (2000) 837.
- [8] J.N. Rosa, C.A.M. Afonso, A.G. Santos, *Tetrahedron* 57 (2001) 4189.
- [9] D.J. Bauer, K.W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt, P. Wasserscheid, *J. Organomet. Chem.* 630 (2001) 177.
- [10] S.T. Handy, X.L. Zhang, *Org. Lett.* 3 (2001) 233.
- [11] F. Favre, H. Olivierbourbigou, D. Commercuc, L. Saussine, *Chem. Commun.* (2001) 1360.
- [12] J.G. Huddleston, H.D. Willauer, R.P. Swatoski, A.N. Visser, R.D. Rogers, *Chem. Commun.* (1998) 1765.
- [13] L.A. Blanchard, D. Hancut, E.J. Beckman, J.F. Brennecke, *Nature* 399 (1999) 28.
- [14] A.G. Fadeev, M.M. Meagher, *Chem. Commun.* (2001) 295.
- [15] C.L. Hussey, in: G. Mamantov, A.I. Popov (Eds.), *Chemistry of Nonaqueous Solvents: Current Progress*, VCH, New York, 1994.
- [16] I.W. Sun, C.L. Hussey, *Inorg. Chem.* 28 (1989) 2731.
- [17] M. Freemantle, *Chem. Eng. News* 79 (2001) 21.
- [18] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 3772.
- [19] T. Welton, *Chem. Rev.* 99 (1999) 2071.
- [20] J.A. Anthony, E.J. Maginn, J.F. Brennecke, *J. Phys. Chem. B* 105 (2001) 10942.
- [21] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, *Green Chem.* 3 (2001) 156.
- [22] K.P. Stephen, *Chem. Eng. News* 79 (2001) 27.
- [23] P. Wasserscheid, R. van Hal, A. Bosmann, *Green Chem.* 4 (2002) 400.
- [24] R.A. Osteryoung, in: *Advances in Molten Salt Chemistry*, G. Mamantov, C. Mamantov (Eds.), Elsevier, New York, 1987, pp. 6–329.

- [25] D.W. Armstrong, L. He, Y.S. Liu, *Anal. Chem.* 71 (1999) 3873.
- [26] D.W. Armstrong, L. Zhang, L. He, M.L. Gross, *Anal. Chem.* 73 (2001) 3679.
- [27] E.G. Yanes, S.R. Gratz, M.J. Baldwin, S.E. Robison, A.M. Stalcup, *Anal. Chem.* 73 (2001) 3838.
- [28] L.A. Blanchard, J.F. Brennecke, *Ind. Eng. Chem. Res.* 40 (2001) 287.
- [29] A.N. Visser, R.P. Swatloski, W.M. Reichert, S.T. Griffin, R.D. Rogers, *Ind. Eng. Chem. Res.* 39 (2000) 3596.
- [30] S. Dai, Y.H. Ju, C.E. Barnes, *J. Chem., Dalton Trans.* (1999) 1201.
- [31] S. Chun, S.V. Dzyuba, R.A. Bartsch, *Anal. Chem.* 73 (2001) 3737.
- [32] A.N. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davis Jr., R.D. Rogers, *Chem. Commun.* (2001) 135.
- [33] A.N. Visser, R.P. Swatloski, S.T. Griffin, D.H. Hartman, R.D. Rogers, *Sep. Sci. Technol.* 36 (2001) 785.
- [34] R.P. Paradkar, R. Williams, *Anal. Chem.* 66 (1994) 2752.
- [35] D. Harris, *Quantitative Chemical Analysis*, fifth ed., W.H. Freeman, New York, 1998, p. 644.
- [36] G.-T. Wei, J.-C. Chen, Z. Yang, *J. Chin. Chem. Soc.*, in press.