

Removal of Metal Ions from Aqueous Solutions by Extraction with Ionic Liquids[†]

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This work analyzed the extraction of Zn²⁺, Cd²⁺, and Fe³⁺ from aqueous hydrochloride solutions using ionic liquids in the absence of chelating agents. For this purpose, ionic liquids based on 1-(*n*-alkyl)-3-methylimidazolium and tetraalkylammonium cations and several anions (hexafluorophosphate, bis[(trifluoromethyl)sulfonyl]imide, tetrafluoroborate, and chloride) were tested. It was found that the ionic liquid methyltrioctylammonium chloride, [MTOA⁺][Cl⁻], allowed almost complete removal (extraction percentage > 94) of Zn²⁺, Cd²⁺, and Fe³⁺ from the aqueous solutions. Furthermore, efficient selective separation of Zn²⁺/Fe³⁺ and Cd²⁺/Fe³⁺ was achieved using 1-methyl-3-octylimidazolium tetrafluoroborate, [omim⁺][BF₄⁻], since high extraction percentages were reached for Zn²⁺ and Cd²⁺ (extraction percentage > 90) while this parameter was very low for Fe³⁺. These results indicate that the use of ionic liquids as an alternative to traditional extraction agents in liquid/liquid extraction of heavy metal ions is very promising.

1. Introduction

The rapid increase in the use of heavy metals over the past few decades has inevitably involved an increased flux of metallic substances into natural water bodies and soils. The presence of traces of heavy metals in the environment is particularly dangerous since most of them are toxic and persistent. One of the most toxic metals is cadmium, which finds its way to water bodies through wastewater from metal-plating industries, nickel cadmium batteries, phosphate fertilizers, mining, pigments, stabilizers, ceramics, and metallurgical and photographic products.¹ The presence of cadmium ions in many industrial aqueous waste solutions is a complex example of pollution because of its toxicity, which affects aquatic life and, in extreme cases, human life. Therefore, wastewater decontamination is of great importance in the environmental field of waste and pollution reduction.¹

Separation/concentration of metals not only involves environmental but also economic profits. Because of their economic value, recovery of metals has been attracting a great deal of attention from metallurgists. In this context, 95 % of cadmium comes as a byproduct of zinc hydrometallurgical processes. Another example of economic profit from recovery of metals is iron rejection in the zinc industry. Most operating zinc refineries use precipitation methods for zinc purification, in which iron and cadmium are usually precipitated as residues, followed by zinc recovery via electrowinning. This purification method has several problems from an environmental point of view. First, the residues generated are voluminous. For example, from a solution containing (25 to 45) % iron, 0.5 ton of jarosite (solid residue) is produced per ton of zinc metal. Second, the metal impurities entrained with these precipitates classify the residues as hazardous industrial waste. Consequently, as environmental regulations become increasingly more stringent, it is necessary to develop new purification methods.²

Several technologies can be used to remove toxic metals from liquid effluents, including precipitation, solvent extraction, ion exchange, etc.³ Among these technologies, solvent extraction is widely used in the recovery and separation of metals from aqueous solutions; the extraction agent [di(2-ethylhexyl)phosphoric acid, tris(2-ethylhexyl)amine, liquid phosphine oxides, etc.] is dissolved in an organic solvent (kerosene, toluene, etc.), which is used as the diluent.^{4,5} One disadvantage of solvent extraction is the loss of organic diluent via volatilization, which has a detrimental impact on the environment and human health. Consequently, greener extraction methods are being sought. The use of ionic liquids (ILs) could overcome this disadvantage.⁶ ILs are organic salts that are liquids over a temperature range around or below room temperature and normally consist of an organic cation, the most common used being dialkylimidazolium, *N*-alkylpyridinium, and tetraalkylammonium ions, and a polyatomic inorganic anion such as one of the halides, [BF₄⁻], [PF₆⁻], or [NTf₂⁻]. From an environmental point of view, the most important advantage of ILs is their nondetectable vapor pressure, which makes them environmentally benign solvents compared with volatile organic solvents (VOCs). They also show good chemical and thermal stability and can be used at high temperatures.⁷ Additionally, the properties of ILs (hydrophobicity, viscosity, solubility, etc.) can be varied by alternating the substituent group on the cation or the combined anion,⁸ making them more attractive for use as “green designer” solvents. Indeed, this feature is a key factor for realizing successful extraction processes, since appropriate combinations of the cationic and anionic parts of the solvent can be made.⁹ To date, ILs have recently been revealed as interesting clean alternatives to classical organic solvents in a wide range of chemical and biochemical processes.¹⁰ They have also been successfully applied in extraction processes, such as isolation of metal species,^{11,12} organic compounds (i.e., esters, alcohols, and organic acids),^{13,14} and even macromolecules (i.e., antibiotics).¹⁵

Over the past few years, extraction of several metal ions using ILs containing proper complexing agents such as crown ethers,¹⁶ Cyanex 923,¹⁷ dithizone,¹⁸ and other organic ligands¹⁹ has been

[†] Part of the “2009 Iberian Conference on Ionic Liquids”.

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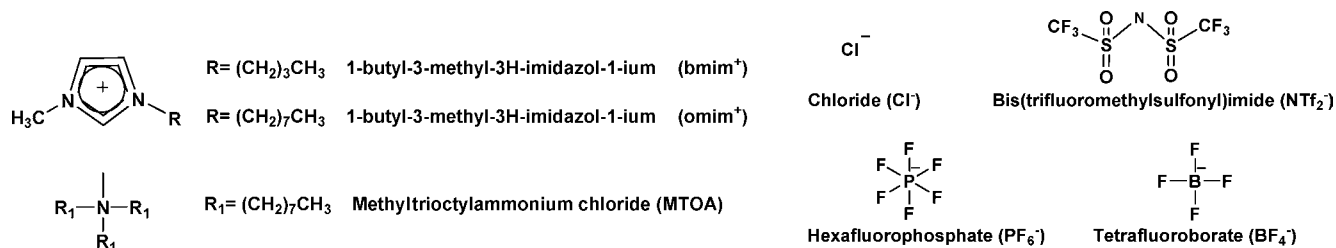


Figure 1. Ions involved in the assayed ionic liquids.

carried out. It is worthy of note that in comparison with conventional organic solvents, significant differences both in extraction efficiency and chemical equilibria can be found in ILs when they are employed in such biphasic systems.⁶ The present work studied the extraction of Zn^{2+} , Cd^{2+} , and Fe^{3+} from aqueous hydrochloride solutions in ILs in the absence of a chelating agent. For that, six ionic liquids with different cations [1-(*n*-alkyl)-3-methylimidazolium and tetraalkylammonium] and anions (bis[(trifluoromethyl)sulfonyl]imide, hexafluorophosphate, tetrafluoroborate, and chloride) were tested. The influence of the ionic liquid composition and metal ion concentrations on the extraction percentage (%E) were evaluated.

2. Experimental Section

2.1. Chemicals. The ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate [bmim^+][BF_4^-] (purity > 99 %), 1-butyl-3-methylimidazolium hexafluorophosphate [bmim^+][PF_6^-] (purity > 99 %), 1-octyl-3-methylimidazolium hexafluorophosphate [omim^+][PF_6^-] (purity > 99 %), 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide [bmim^+][NTf_2^-] (purity > 99 %), and 1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide [omim^+][NTf_2^-] (purity > 99 %) were purchased from Iolitec GmbH (Denzingen, Germany), and methyltrioctylammonium chloride (purity > 97 %) was obtained from Sigma-Aldrich-Fluka Chemical Co. (Madrid, Spain). The ILs were dried under anhydrous phosphorus pentoxide in vacuo and stored in a desiccator to ensure their long-term stability. The water content of the ILs was measured by Karl Fischer titrations and in all cases was found to be less than 150 ppm. The solubility of the different ILs in the water was determined by placing 2 mL of each phase in a test tube. The mixture was vigorously stirred at room temperature for 10 min. To ensure better phase separation, the mixture was then centrifuged for 10 min at 5000 rpm. Both phases were collected, and the concentration of water in the IL was measured using a Karl Fischer titrator.

The stock aqueous solutions of metals were prepared by dissolving analytical-grade chloride salts of the respective metals (from Sigma-Aldrich-Fluka Chemical) in hydrochloric acid.

2.2. Extraction of Zn(II), Cd(II), and Fe(III) from Aqueous Hydrochloride Solutions. Zn(II), Cd(II), and Fe(III) aqueous hydrochloride solutions were prepared by dissolving solid CdCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and ZnCl_2 in 1 M hydrochloric acid. One milliliter of an aqueous metal solution containing a known concentration of metal ion was brought into contact with 1 mL of pure IL. The phase-contacting experiments were carried out in carefully stoppered centrifuge tubes. Each mixture was shaken vigorously for 5 min to facilitate the transfer of compounds into the IL phase and then centrifuged before being left at 303.15 K for 30 min in a thermostatic bath without stirring. Samples of the aqueous phase were taken from the tube during at least three sampling events, and the composition of the aqueous phase was analyzed by atomic absorption spectrophotometry, as described

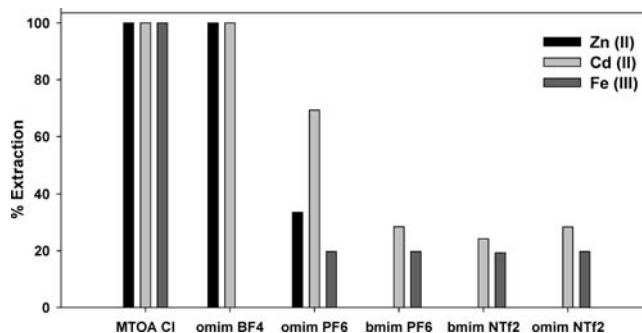


Figure 2. Extraction of 0.1 g/L Zn(II), 0.1 g/L Cd(II), and 0.1 g/L Fe(III) from 1 M hydrochloride solutions using the different ionic liquids.

in section 2.3. Sampling ceased when the metal ion concentration stabilized. The efficiency of the extraction process was evaluated by the extraction percentage (%E), which was calculated using the following equation:

$$\%E = \frac{C_{\text{IL}(t)}}{C_{\text{IL}(t)} + C_{\text{H}(t)}} \cdot 100 \quad (2)$$

where $C_{\text{IL}(t)}$ and $C_{\text{H}(t)}$ refer to the equilibrium concentrations of the compounds in the IL and aqueous phases, respectively. The concentration of metal ions in the IL phase was deduced from the difference between the initial concentration of metal ions in the aqueous phase and the concentration of metal ions in the raffinate. It should be noted that the ILs employed in this work were immiscible with the aqueous phase. Determinations were made in triplicate to ensure the repeatability of the tests, and mean values are reported. The repeatability of the assay, as measured by the relative standard deviation, was 3 % or less.

2.3. Analytical Method. The uptake of metal ions was monitored by removing samples of the aqueous solutions periodically for analysis. Atomic absorption spectrophotometry (Varian model Spectra AA) was used for determination of the metals (Zn, Cd, and Fe). All of the aqueous solutions were prepared using deionized water.

3. Results and Discussion

To evaluate the extraction of Zn(II), Cd(II), and Fe(III) using ILs, the extraction percentages (%E) from 0.1 g/L solutions of these metal ions in 1 M hydrochloric acid at 303.15 K were determined. For this purpose, the six ILs [MTOA^+][Cl^-], [omim^+][BF_4^-], [omim^+][PF_6^-], [bmim^+][PF_6^-], [bmim^+][NTf_2^-], and [omim^+][NTf_2^-] (see Figure 1) were chosen on the basis of their low solubilities in water {[MTOA^+][Cl^-] < 0.02 % (v/v), [omim^+][BF_4^-] < 1.4 % (v/v), [omim^+][PF_6^-] < 0.04 % (v/v), [bmim^+][PF_6^-] < 0.501 % (v/v), [bmim^+][NTf_2^-] < 0.280 % (v/v), [omim^+][NTf_2^-] < 0.1 % (v/v)}. The %E values obtained using the different ILs are presented in Figure 2.

It is worthy of note that nearly complete removal was achieved for all three metal ions using [MTOA^+][Cl^-] and for Zn^{2+} and Cd^{2+} using [omim^+][BF_4^-]. High extraction

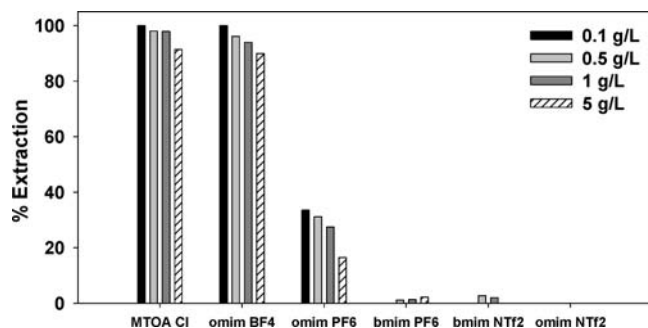


Figure 3. Effect of ionic liquid composition and metal ion concentration in the extraction percentage of Zn(II) from hydrochloride solutions.

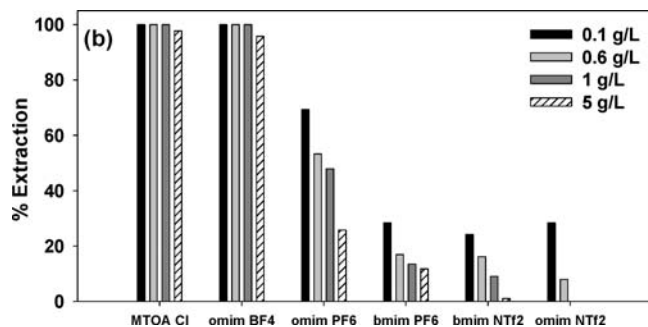


Figure 4. Effect of ionic liquid composition and metal ion concentration in the extraction percentage of Cd(II) from hydrochloride solutions.

efficiencies for Cd^{2+} and less for Zn^{2+} were also obtained using $[\text{omim}^+][\text{PF}_6^-]$. With the rest of ILs ($[\text{bmim}^+][\text{PF}_6^-]$, $[\text{bmim}^+][\text{NTf}_2^-]$, and $[\text{omim}^+][\text{NTf}_2^-]$), the extraction percentages of Cd^{2+} were around 25 %; for Fe^{3+} , the extraction efficiency was lower. Almost no extraction of Zn^{2+} was found using $[\text{bmim}^+][\text{PF}_6^-]$, $[\text{bmim}^+][\text{NTf}_2^-]$, or $[\text{omim}^+][\text{NTf}_2^-]$.

In regard to the selective recovery of metal ions, important differences in the extraction percentages for Zn^{2+} versus Fe^{3+} and Cd^{2+} versus Fe^{3+} were observed when $[\text{omim}^+][\text{BF}_4^-]$ and $[\text{omim}^+][\text{PF}_6^-]$ were used as extraction agents, suggesting that these ILs could be used for selective separation of these metal ions (see Figure 2). Furthermore, appreciable extraction percentage differences were observed for Cd^{2+} and Zn^{2+} in $[\text{bmim}^+][\text{PF}_6^-]$, $[\text{bmim}^+][\text{NTf}_2^-]$, and $[\text{omim}^+][\text{NTf}_2^-]$ and for Fe^{3+} and Zn^{2+} in $[\text{bmim}^+][\text{NTf}_2^-]$ and $[\text{omim}^+][\text{NTf}_2^-]$, which could allow the selective separation of these metals. It can be concluded from the above results that it is possible to tailor ILs for use as extraction agents for specific metal ion separations.

The effects of initial metal ion concentration in the aqueous solution on the efficiency of the extraction process for Zn^{2+} , Cd^{2+} , and Fe^{3+} are shown in Figures 3, 4, and 5, respectively.

As can be seen from Figure 3, the extraction percentage of Zn^{2+} slightly decreased as the metal ion concentration increased when $[\text{MTOA}^+][\text{Cl}^-]$ or $[\text{omim}^+][\text{BF}_4^-]$ was used as the extraction agent. This effect was prominent for $[\text{omim}^+][\text{PF}_6^-]$. The rest of ILs were not suitable for the extraction of Zn^{2+} under any of the assayed conditions.

In the case of Cd^{2+} (see Figure 4), almost complete recovery was reached with the ILs $[\text{MTOA}^+][\text{Cl}^-]$ and $[\text{omim}^+][\text{BF}_4^-]$ for all metal ion concentrations. Figure 4 also shows that the extraction percentage decreased sharply with increasing metal ion concentration when $[\text{omim}^+][\text{PF}_6^-]$ was used. Similar behavior was observed for the rest of the ILs.

On the other hand, a high efficiency of extraction of Fe^{3+} was reached with $[\text{MTOA}^+][\text{Cl}^-]$, and it was observed that this

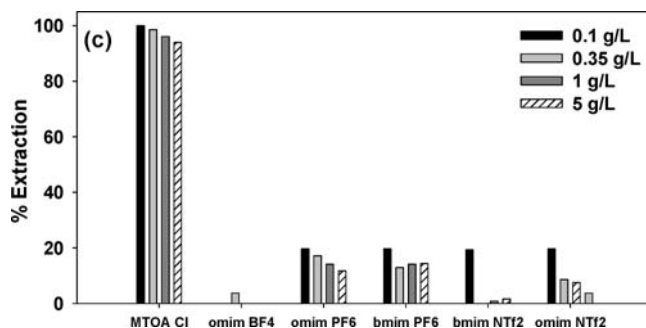


Figure 5. Effect of ionic liquid composition and metal ion concentration in the extraction percentage of Fe(III) from hydrochloride solutions.

parameter decreased slightly with an increase in the metal ion concentration up to about 95 % (see Figure 5). Nearly no recovery of Fe^{3+} was achieved with $[\text{omim}^+][\text{BF}_4^-]$ under any of the assayed conditions. In the cases of $[\text{omim}^+][\text{PF}_6^-]$, $[\text{bmim}^+][\text{PF}_6^-]$, $[\text{bmim}^+][\text{NTf}_2^-]$, and $[\text{omim}^+][\text{NTf}_2^-]$, the extraction percentages reached a maximum at around 20 % and decreased with increasing metal ion concentration.

It can be concluded from Figures 3, 4, and 5 that selective separation of Zn^{2+} from Fe^{3+} and Cd^{2+} from Fe^{3+} could be successfully carried out at all metal ion concentrations with $[\text{omim}^+][\text{BF}_4^-]$ and, to a lesser extent, with $[\text{omim}^+][\text{PF}_6^-]$. Furthermore, selective separation of Cd^{2+} from Zn^{2+} and Fe^{3+} from Zn^{2+} is possible using $[\text{bmim}^+][\text{PF}_6^-]$, $[\text{bmim}^+][\text{NTf}_2^-]$, and $[\text{omim}^+][\text{NTf}_2^-]$, since the extraction of Zn^{2+} was insignificant over the range of concentrations studied.

The above results were analyzed in order to evaluate the influence of the cation and anion composition of the IL on the recovery of metal ions. By comparison of cation and anion effects in ILs based on imidazolium cations, the greatest effect on the extraction percentage was observed when the nature of the anion of the IL was changed. As can be observed from Figures 3 and 4, the extraction percentages for Zn^{2+} and Cd^{2+} using imidazolium-based ILs increased in the sequence: $[\text{NTf}_2^-] < [\text{PF}_6^-] < [\text{BF}_4^-]$, which is in agreement with the anion hydrophilicity sequence.^{13,20} Furthermore, an increase in the chain length of the alkyl substituent of the 3-methylimidazolium cation from $[\text{bmim}^+]$ to $[\text{omim}^+]$ for the anion $[\text{PF}_6^-]$ resulted in increased extraction efficiencies for both metal ions. Similar results were found by Germani et al.¹² in the extraction of Hg^{2+} with these ILs. In the case of Fe^{3+} , it is worthy of note that higher efficiencies were reached with the tetraalkylammonium cation than with imidazolium cations. Among the imidazolium-based ILs, higher extraction percentages of Fe^{3+} were reached with those based on $[\text{PF}_6^-]$ anions than with those based on $[\text{NTf}_2^-]$ anions.

In regard to the transfer mechanism of metal ions in ILs, the ionic nature of these solvents can result in a variety of extraction mechanisms, including solvent ion-pair extraction, ion exchange, and simultaneous combinations of these.⁶ In the case of $[\text{MTOA}^+][\text{Cl}^-]$, which is a quaternary amine, the extraction mechanism could be ion exchange, as proposed by Juang et al.²¹ for the extraction of $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ from chloride solutions with Aliquat 336. Currently, a great deal of interest in studying the interaction between metal ions and ILs is being shown.^{22,23} For instance, Williams et al.²² reported that the room-temperature IL composed of bis[(trifluoromethyl)sulfonyl]imide anion and 1-ethyl-3-methylimidazolium (emim) cation stabilizes monomeric ligand-deficient transition-metal complexes (iron, titanium, and ruthenium) via four distinct binding modes: monodentate N or O coordination and/or bidentate O–O' or

N–O coordination. Clearly, an understanding of the transfer mechanism of metal ions in ILs is of primary importance for establishing a predictive model that may be used in practical operations. For this reason, this issue is now being studied in our laboratories.

4. Conclusions

In this work, preliminary results on the extraction of Zn^{2+} , Cd^{2+} , and Fe^{3+} from aqueous hydrochloride solutions in ionic liquids in the absence of chelating agents are shown. The composition of the IL used as the extraction agent was seen to strongly influence the efficiency of the extraction process. Nearly complete extraction was reached with $[MTOA^+][Cl^-]$ for the three metal ions and with $[omim^+][BF_4^-]$ for Zn^{2+} and Cd^{2+} . Furthermore, the use of $[omim^+][BF_4^-]$ allowed the selective separation of Zn^{2+} from Fe^{3+} and Cd^{2+} from Fe^{3+} while $[bmim^+][PF_6^-]$, $[bmim^+][NTf_2^-]$, and $[omim^+][NTf_2^-]$ made possible the selective recovery of Cd^{2+} from Zn^{2+} and Fe^{3+} from Zn^{2+} . It was also found that the extraction percentage increased with a decrease in the metal ion concentrations.

This work demonstrates the exciting potential of ionic liquids for use as extraction agents in green extraction processes, since it is possible to design a specific IL for each metal ion by changing either the anion or the cation in order to create more efficient processes.

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Received for review June 13, 2009. Accepted November 2, 2009. This work was partially supported by the SENECA Foundation-Agency of Science and Technology of Murcia Region 11087/AC/09 and 11087/AC/09 grants in the framework of II PCTRM 2007-2010 and by the CICYT ENE2006-09395 and SENECA Foundation 05649/PI/07 grants.

JE9005008