

Use of ionic liquids as green solvents for extraction of Zn^{2+} , Cd^{2+} , Fe^{3+} and Cu^{2+} from aqueous solutions

Francisco José Hernández-Fernández *, Antonia Pérez de los Ríos*, A. Ginestá, Sergio Sánchez-Segado, Luis Javier Lozano, Juan Ignacio Moreno, C. Godínez
Technical University of Cartagena, Dep. Chemical and Environmental Engineering,
Campus Muralla del Mar,
C/ Doctor Fleming S/N, E-30202 Cartagena, Murcia, Spain
fjherfer@upct.es

This work analyzed the extraction of metal ions from aqueous solutions using ionic liquids in the absence of chelating agents. For this purpose, hydrochloride solutions of Zn^{2+} , Cd^{2+} , Cu^{2+} and Fe^{3+} were used as model systems and ionic liquids based on 1-n-alkyl-3-methylimidazolium and tetraalkyl ammonium cations combined with several anions (hexafluorophosphate, bis{(trifluoromethyl)sulfonyl}imide, tetrafluoroborate, and chloride) were used as extraction agents. It was found that the ionic liquid methyltrioctylammonium chloride, $[MTOA^+][Cl^-]$, allowed almost the nearly complete removal of Zn^{2+} , Cd^{2+} and Fe^{3+} and an extraction percentage around 80 % for Cu^{2+} , from the aqueous solutions. Furthermore, efficient selective separation of Zn^{2+} and Cd^{2+} from Fe^{3+} and Cu^{2+} was achieved using 1-methyl-3-octylimidazolium tetrafluoroborate, $[omim^+][BF_4^-]$, since high extraction percentages were reached for Zn^{2+} and Cd^{2+} (%E > 90) while this parameter is very low for Fe^{3+} and Cu^{2+} . 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 or into soils. The presence of traces of heavy metals in the environment is particularly dangerous, since most of them are toxic and persistent. Several technologies can be used to remove toxic metals from liquid effluents, including precipitation, solvent extraction and ion exchange (Alonso et al., 2006; Lozano and Godínez, 2003). Among these technologies, solvent extraction is widely used in the recovery and separation of metals from aqueous solutions, where 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. One disadvantage of solvent extraction is the loss of organic diluent via volatilisation, 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. 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*-alkylpyrindinium and tetraalkylammomium salts, and a polyatomic inorganic anion such as halides, $[\text{BF}_4^-]$, $[\text{PF}_6^-]$, $[\text{NTf}_2^-]$. From an environmental point of view, the most important advantage of ILs is their non-detectable vapour pressure, which makes them environmentally benign solvents compared with volatile organic solvents (VOCs). To date, ILs have recently been revealed as interesting clean alternatives to classical organic solvents in a wide range of processes (Ruiz et al., 2007; Hernández-Fernández et al., 2007) Over the last few years, extraction of several metal ions using ILs containing proper complexing agents such as crown ethers, Cyanex 923, dithizone and other organic ligands (Heitzman et al., 2006) has been carried out.

The present work aims to study the extraction of Zn^{2+} , Cd^{2+} , Fe^{3+} and Cu^{2+} from hydrochloride aqueous solutions with ionic liquids in the absence of a chelating agent. For that, six ionic liquids with different cations (1-*n*-alkyl-3-methylimidazolium and tetraalkylammomium) and anions (bis{(trifluoromethyl)sulfonyl}imide, hexafluorophosphate, tetrafluoroborate and chloride) were tested. The influence of the ionic liquid composition and the metal ion concentrations on the percentage extraction (% E) were evaluated.

2. Experimental

2.1. Chemicals

The ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate $[\text{bmim}^+][\text{BF}_4^-]$ (purity >99 %), $[\text{bmim}^+][\text{PF}_6^-]$ (purity >99 %), 1-octyl-3-methylimidazolium hexafluorophosphate $[\text{omim}^+][\text{PF}_6^-]$ (purity >99 %), 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, $[\text{bmim}^+][\text{NTf}_2^-]$ (purity >99 %) and 1-octyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, $[\text{omim}^+][\text{NTf}_2^-]$ (purity >99 %) were purchased from Iolitec GmbH (Denzlingen, Germany) and methyl trioctyl ammonium chloride (purity >97 %) was from Sigma-Aldrich-Fluka Chemical Co. (Madrid, Spain). The ILs were dried under anhydrous phosphorous pentoxide in vacuo and were stored in a desiccator to **ensure a long-term stability** of ionic liquids. Water content of the ionic liquids was measured by Karl Fischer titration, been in all cases lower 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 assure a better phase separation, the mixture was then centrifuged for 10 min at 5.000 rpm. Both phases were collected and the concentration of water in the IL was measured using a Karl-Fisher titrator. The stock aqueous solutions of metals were prepared by dissolving analytical grade chloride salts of the respective metals (from Sigma-Aldrich-Fluka Chemical Co, Madrid, Spain) in hydrochloric **acid**.

2.2. Extraction of Zn(II), Cd(II), Cu(II) and Fe(III) from hydrochloride aqueous solutions

Zn(II), Cd(II), Cu(II) and Fe(III) hydrochloride aqueous solutions were made up by dissolving solid ZnCl₂, CdCl₂, CuCl₂ and FeCl₃·6 H₂O and in 1 M hydrochloric acid. 1 mL of a metal aqueous 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. The mixture was shaken vigorously for 5 min to facilitate the transfer of compounds into the ionic liquid phase and centrifuged before being left at 303.15 K for 30 minutes in a thermostatic bath without stirring. Samples of the aqueous phase were taken from the tubes during at least three sampling events and the composition of the aqueous phase was analysed by atomic absorption spectrophotometry, as described 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 by the following equation:

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

where C_{IL} and $C_{H(t)}$ refer to the equilibrium concentration of the compounds in the ionic liquid and in the 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 are 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 spectra AA model) was used for the determination of metals (Zn, Cd, Cu and Fe). All aqueous solutions were prepared using deionised water.

3. Results and discussion

With the aim of evaluating the extraction of Zn(II), Cd(II), Fe(III) and Cu(II) by using ionic liquids, the extraction percentage values (%E) for 0.1 g/L of these metal ions from 1M hydrochloride solutions at 303.15 K were determined. For this purpose, six different ionic liquids [MTOA⁺][Cl⁻], [omim⁺][BF₄⁻], [omim⁺][PF₆⁻], [bmim⁺][PF₆⁻], [bmim⁺][NTf₂⁻] and [omim⁺][NTf₂⁻] were chosen on the basis of their low solubility in water, less than 1.4 %. The extraction percentage values (%E) for using the different ILs are presented in Figure 1.

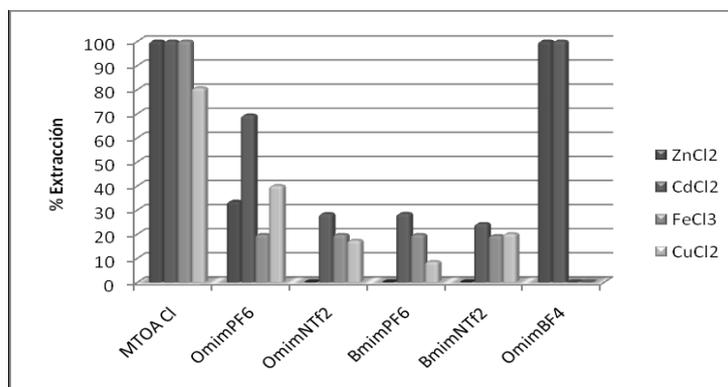


Figure 1: Extraction of 0.1 g/L Zn(II), 0.1 g/L Cd(II), 0.1 g/L Cu(II), and 0.1 g/L Fe(III) from 1M hydrochloride solutions using [MTOA⁺][Cl⁻], [omim⁺][BF₄⁻], [omim⁺][PF₆⁻], [bmim⁺][PF₆⁻], [bmim⁺][NTf₂⁻] and [omim⁺][NTf₂⁻] ionic liquids.

It is worthy of note that nearly complete removal of metal ions was achieved using [MTOA⁺][Cl⁻] for Zn²⁺, Cd²⁺ and Fe³⁺ and around 80% for Cu²⁺. The ionic liquid [omim⁺][BF₄⁻] also allows the quantitative extraction of Zn²⁺ and Cd²⁺. In contrast, non-extraction of Fe³⁺ and Cu²⁺ was observed by using the latter ionic liquid. Regarding the selective recovery of metal ions, important differences in the extraction percentage between Zn²⁺, Cd²⁺ / Cu²⁺, Fe³⁺ in [omim⁺][BF₄⁻] suggesting that these ionic liquids could be used for selective separation of these metal ions (see Figure 1). High extraction efficiencies for Cd²⁺ and less for Cu²⁺, Zn²⁺ and Fe³⁺ were also reached using [omim⁺][PF₆⁻]. With the rest of ionic liquids ([bmim⁺][PF₆⁻], [bmim⁺][NTf₂⁻], [omim⁺][NTf₂⁻]), the maximum extraction percentages was obtained for Cd²⁺ which was around 25 %, being decreasing for the rest of ion metal as follows: Fe³⁺ > Cu²⁺ > Zn²⁺. Almost non extraction of Zn²⁺ was found using [bmim⁺][PF₆⁻], [bmim⁺][NTf₂⁻] and [omim⁺][NTf₂⁻]. This fact allowed the selective separation of Zn²⁺ from Fe³⁺, Cu²⁺ and Cd²⁺, by using the latest ionic liquids. The above results have been analysed in order to evaluate the influence of the cation and anion composition of the ionic liquid on the recovery of metal ions. By comparing cation and anion effects in ionic liquid based on imidazolium cations, the greatest effect on the extraction percentage was observed by changing the nature of the anion of the ionic liquid. It can be concluded from the above results that it is possible to tailor ionic liquids for using as extraction agents for a specific metal ion separation.

The effect of initial metal ion concentration, from 0.1 g/L to 5 g/L, in the aqueous solution on the efficiency of the extraction process for Zn²⁺, Cd²⁺, Fe³⁺ and Cu²⁺ was also studied. It was observed that the extraction percentage of Zn²⁺ slightly decreases when metal ion concentrations increases when [MTOA⁺][Cl⁻] and [omim⁺][BF₄⁻] were used as extraction agents. This effect is prominent for [omim⁺][PF₆⁻]. The rest of ionic liquids were not suitable for the extraction of Zn²⁺ in all assayed conditions.

In the case of Cd²⁺, almost complete recovery was reached with the ILs [MTOA⁺][Cl⁻] and [omim⁺][BF₄⁻] for all metal ion concentrations. It was also observed that the extraction percentage decreases sharply for the rest of the ionic liquids.

On the other hand, a high efficiency of extraction of Fe^{+3} was reached with $[\text{MTOA}^+][\text{Cl}^-]$, observing that this parameter slightly decreases with an increase in the metal ion concentration up to about 95 %. Nearly no recovery of Fe^{3+} was achieved with $[\text{omim}^+][\text{BF}_4^-]$ in all 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 maximum percentages of extraction reached was around 20%, decreasing with the increase in ion metal concentrations.

In the case of Cu^{2+} , the extraction percentage decrease around 20% from 0.1 g/L to 5 g/L metal concentration for all ionic liquids assayed except for $[\text{omim}^+][\text{PF}_6^-]$ being the decrease of 40%.

Regarding the transfer mechanism of metal ions in ionic liquids, 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. 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. (2004) for the extraction as Zn(II) and Cd(II) from chloride solutions with Aliquat 336. Currently a great deal of interest is being shown in studying the interaction between metal ions and ionic liquids (Williams et al., 2005; Dhumal and Krishnan, 2009) For instance, Williams et al. (2005) (Williams et al., 2005) reported that room temperature ionic liquids composed of bis(trifluoromethylsulfonyl) imide anions and 1,3-ethylmethylimidazolium (EMI) cations stabilize monomeric ligand deficient transition metal complexes (iron, titanium and ruthenium) via four distinct binding modes: monodentate nitrogen or oxygen coordination and/or bidentate oxygen–oxygen' or nitrogen–oxygen coordination. Clearly, an understanding of the transfer mechanism of metal ions in ionic liquids is of primary importance to be able to establish 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 about the extraction of Zn^{+2} , Cd^{+2} , Fe^{+3} and Cu^{+2} from hydrochloride aqueous solutions in ionic liquids in the absence of chelating agents are shown. It is worthy of note that nearly complete removal of metal ions was achieved using $[\text{MTOA}^+][\text{Cl}^-]$ for Zn^{2+} , Cd^{2+} and Fe^{3+} and with $[\text{omim}^+][\text{BF}_4^-]$ for Zn^{2+} and Cd^{2+} . High extraction efficiencies for Cd^{2+} and less for Zn^{2+} were also reached using $[\text{omim}^+][\text{PF}_6^-]$. In the case of Cu^{2+} , the highest extraction percentage ($\cong 80\%$) was reached using $[\text{MTOA}^+][\text{Cl}^-]$. The composition of the ionic liquid used as the extraction agent was seen to strongly influence the efficiency of the extraction process. By comparing cation and anion effects in ionic liquid based on imidazolium cations, the greatest effect on the extraction percentage was observed by changing the nature of the anion of the ionic liquid. Regarding the effect of the metal ion concentrations, it was found that the extraction percentage increased with the decrease in the metal ions concentrations of the aqueous solutions.

In conclusion, 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 ionic liquid for each metal ion by changing either the anion or the cation in order to create more efficient processes.

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