Selective separation of Zn(II) over Fe(III) from acidic media using ionic liquids as sole extraction agents

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This work analysed the extraction of \( \text{Zn}^{2+} \) and \( \text{Fe}^{3+} \) from hydrochloride aqueous solutions using ionic liquids in the absence of chelating agents. For this purpose, ionic liquids based on 1-n-alkyl-3-methylimidazolium and tetraalkyl ammonium cations and several anions (hexafluorophosphate, bis{(trifluoromethyl)sulfonyl}imide, tetrafluoroborate, and chloride) were tested. It was found that the ionic liquid methyltrioctylammonium chloride, \([\text{MTOA}^+]\text{[Cl}^-] \), allowed almost complete removal (%E > 94) of \( \text{Zn}^{2+} \) and \( \text{Fe}^{3+} \) from the aqueous solutions. Furthermore, efficient selective separation of \( \text{Zn}^{2+}/\text{Fe}^{3+} \) was achieved using 1-methyl-3-octylimidazolium tetrafluoroborate, \([\text{omim}^+]\text{[BF}_4^-] \), since high extraction percentages were reached for \( \text{Zn}^{2+} \) (%E > 90) while this parameter is very low for \( \text{Fe}^{3+} \).

1. Introduction

Separation/concentration of metals not only involves environmental but also economical profits. One example of the economic profit from recovery of metals is the iron rejection in the zinc industry. Most operating zinc refineries use precipitation methods for zinc purification, in which iron are usually precipitated as residues, followed by zinc recovery by electrowinning. This purification method has several problems from an environmental point of view. Firstly, the residues generated are voluminous. For example, from a solution containing 25 to 45 % iron, 0.5 tonne jarosite (solid residue) are produced per tonne zinc metal. Secondly, 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 environmentally friendly purification methods. Among the alternative technologies, solvent extraction is being considered (Lozano and Godinez, 2003). Until now, a number of extractants have been proposed for the extraction of iron from zinc process solutions, such as \( \text{D}_2\text{EHPA and M}_2\text{EHPA (organophosphorus acids), NED (hydroxamic acid), TEHA (tris-(2-ethylhexyl)amine) and EU2 (aminophosphonic acid) dissolved in organic diluents (Agrawal at al., 2008). One disadvantage of the solvent extraction is the loss of organic diluent via volatilization which has a detrimental impact
on the environment and human health. The use of ionic liquids (ILs), which are liquid in a temperature range around or below room temperature, could overcome this disadvantage (de los Ríos et al., 2009). ILs are fused salts containing an organic cation, such as dialkylimidazolium cation or N-alkylpyridinium cation, and an inorganic anion, such as halides, \([\text{BF}_4^-]\), \([\text{PF}_6^-]\), \([\text{NTf}_2^-]\) or other complex anions. From an environmental point of view, the most important properties of ionic liquids are their negligible vapour pressure and their good chemical and thermal stabilities.

The aim of the present work was the study of the selective separation of \(\text{Zn}^{2+}\) and \(\text{Fe}^{3+}\) from hydrochloride aqueous solution using ionic liquid as extraction agent in replacement of conventional organic solvents. For that, six ionic liquids with different cation (1-n-alkyl-3-methylimidazolium and tetraalkyl ammonium) and anion (bis{(trifluoromethyl)sulfonyl}imide, hexafluorophosphate, tetrafluoroborate and chloride) compositions were tested for the selective separation of the target metal ions. The influence of the ionic liquid composition, the metal ion concentrations and the pH of the aqueous solutions on the percentage extraction and selectivity 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 5000 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) and Fe(III) from hydrochloride aqueous solutions

Zn(II), Fe(III) hydrochloride aqueous solutions were made up by dissolving solid FeCl₃·6 H₂O and ZnCl₂ 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:

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\%E = \frac{C_{IL}}{C_{IL} + C_{H(t)}} \times 100
\]

(1)

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 and Fe). All aqueous solutions were prepared using deionised water.

3. Results and Discussion

With the aim of evaluating the extraction of Zn(II) and Fe(III) 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 \([\text{MTOA}^+]\text{[Cl]}\), \([\text{omim}^+]\text{[BF}_4^-\]), \([\text{omim}^+]\text{[PF}_6^-\]), \([\text{bmim}^+]\text{[PF}_6^-\]), \([\text{bmim}^+]\text{[NTf}_2^-\]) and \([\text{omim}^+]\text{[NTf}_2^-\]) were chosen on the basis of their low solubility in water (\([\text{MTOA}^+]\text{[Cl]}\) < 0.02 % (v/v), \([\text{omim}^+]\text{[BF}_4^-\]) < 1.4 % (v/v), \([\text{omim}^+]\text{[PF}_6^-\]) < 0.04 % (v/v), \([\text{bmim}^+]\text{[PF}_6^-\]) < 0.501 % (v/v), \([\text{bmim}^+]\text{[NTf}_2^-\]) < 0.280 % (v/v), \([\text{omim}^+]\text{[NTf}_2^-\]) < 0.1 % (v/v)). 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) and 0.1 g/L Fe(III) from 1M hydrochloride solutions using the different ionic liquids.

It is worthy of note that nearly complete removal of metal ions was achieved using [MTOA]+[Cl] for the two metal ions (Zn$^{2+}$ and Fe$^{3+}$) and with [omim][BF$_4$] for Zn$^{2+}$. With the rest of ionic liquids ([omim'][PF$_6$], [bmim'][PF$_6$], [bmim'][NTf$_2$], [omim'][NTf$_2$]) the extraction percentages of Fe$^{3+}$ were around 25%, except for Fe$^{3+}$ using [bmim'][PF$_6$] in which case the extraction efficiency was lower. Almost no extraction of Zn$^{2+}$ was found using [bmim'][PF$_6$], [bmim'][NTf$_2$] and [omim'][[NTf$_2$], being the extraction with [omim'][PF$_6$] near 40%. Regarding the selective recovery of metal ions, important differences in the extraction percentage between Zn$^{2+}$/Fe$^{3+}$ were observed when [omim'][BF$_4$] were used as extraction agents, suggesting that these ionic liquids could be used for selective separation of these metal ions (see Figure 1). Furthermore, appreciable extraction percentage differences were observed between Fe$^{3+}$ and Zn$^{2+}$ in [bmim'][NTf$_2$] and [omim'][NTf$_2$], since these ionic liquids do not extract the Fe$^{3+}$ cation. The effect of initial metal ion concentration in the aqueous solution on the efficiency of the extraction process for Zn$^{2+}$ and Fe$^{3+}$ have been also studied. An example is shown in Figure 2, which shows the effect of ionic liquid composition and metal ion concentration on the extraction percentage (%E) of Zn(II).

Figure 2: Effect of ionic liquid composition and metal ion concentration on the extraction percentage (%E) of Zn(II) from hydrochloride solutions.

As can be seen from Figure 2, the extraction percentage of Zn$^{2+}$ slightly decreases when metal ion concentrations increases when [MTOA][Cl] and [omim'][BF$_4$] were used as extraction agents. This effect is prominent for [omim'][PF$_6$]. The rest of ionic liquids were not suitable for the extraction of Zn$^{2+}$ in all assayed conditions. On the other hand, a high efficiency of extraction of Fe$^{3+}$ was reached with [MTOA][Cl], observing that this parameter slightly decreases with an increase in the metal ion concentration up to about 95% (Figure not shown). Nearly no recovery of Fe$^{3+}$ was achieved with [omim'][BF$_4$] in all assayed conditions. In the cases of [omim'][PF$_6$], [bmim'][PF$_6$], [bmim'][NTf$_2$] and [omim'][NTf$_2$], the maximum percentages of extraction reached was around 20%, decreasing with the increase in ion metal concentrations.
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. As can be observed from Figures 1 and 2 the extraction percentage for Zn$^{+2}$ using imidazolium based ionic liquids increased in the sequence: [NTf$_2$] < [PF$_6$] < [BF$_4$], which is in agreement with the anion hydrophilicity sequence (de los Ríos et al, 2008; Ropel et al. 2005). Furthermore, the increase in the chain length of the alkyl substituent of the 3-methylimidazolium cation from [bmim$^+$] to [omim$^+$] for the anion [PF$_6$] resulted in an increased extraction efficiency for both metal ions. Similar results were found by Germani et al. (2007) in the extraction of Hg$^{+2}$ with these ionic liquids. In the case of Fe$^{+3}$, it is worthy to note that higher efficiencies were reached with the tetraalkylammonium cation than that obtained with imidazolium cations. Among imidazolium based ionic liquids, higher extraction percentages of Fe$^{+3}$ were reached with ionic liquids based on [PF$_6$] anions respect to those based on [NTf$_2$] anions. The influence on the extraction percentage of Fe$^{+3}$ and Zn$^{+2}$ of the HCl concentration in the aqueous media was also studied in the case of [omim$^+$][PF$_6$]. For that, a metal solution of 0.1g/L was used and the HCl concentration of the aqueous phases was range from 0.1M to 5M. The increased in the HCl concentration (Figure not shown) involves an increased in the extraction percentage, reaching maximum value around 80% and near 100% for Zn$^{+2}$ and Fe$^{+3}$, respectively.

4. Conclusions

In this work, the extraction of Zn$^{+2}$ and Fe$^{+3}$ from hydrochloride aqueous solutions in ionic liquids in the absence of chelating agents are shown. It was found that the ionic liquid methyltriocytalammonium chloride, [MTOA$^+$][Cl$^-$], allowed almost the complete removal of Zn$^{+2}$ and Fe$^{+3}$ from the aqueous solutions. Furthermore, efficient selective separation of Zn$^{+2}$/Fe$^{+3}$ was achieved using 1-methyl-3-octylimidazolium tetrafluoroborate, [omim$^+$][BF$_4$], since high extraction percentages were reached for Zn$^{+2}$ while this parameter was very low for Fe$^{+3}$. The ionic liquids [bmim$^+$][PF$_6$], [bmim$^+$][NTf$_2$] and [omim$^+$][NTf$_2$] made also possible the selective recovery of Fe$^{+3}$/Zn$^{+2}$. It was also found that the extraction percentage increased with the increase in the HCl concentration. To sum up, in this study we highlight the possibility of using ionic liquids as sole extraction agents for the selective separation of Zn$^{+2}$ and Fe$^{+3}$ from hydrochloride aqueous solutions.

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References


