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Techinical note

Regeneration of the ionic liquid tetraoctylammonium oleate after metal extraction

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ABSTRACT

Ionic liquids (ILs) have been presented as suitable candidates for metal extraction in the hydrometallurgy. It has already been proven that they have an adjustable selectivity towards metal ions. However, industrial applications of ILs are often limited due to their high price. Therefore, regeneration and reuse of ILs is necessary. In this study the regeneration of the fatty acid based IL tetraoctylammonium oleate was investigated, because in previous study excellent metal salt extraction efficiencies were obtained with this benign IL. Two methods for regeneration were investigated, i.e. electro-deposition and chemical regeneration. Electro-deposition turned out to be unfeasible for this IL. Chemical regeneration showed that the metal ions (Zn, Co and Mn) can be selectively back-extracted, so that metals can also be separated from each other in this step. The best stripping solution was aqueous sodium oxalate, which allowed the IL to be reused with no further treatment.

1. Introduction

Ionic liquids (ILs) are a class of molten salts that are liquid below 100 °C by definition, but mostly one refers to the room-temperature ionic liquids (RTILs), which are even liquid below room temperature. These liquids are composed of bulky organic cations in combination with organic or inorganic anions (Wilkes, 2002). They recently gained a lot of interest, because they have several interesting properties, i.e. negligible vapor pressure, low flammability, high thermal stability, and a broad chemical window and liquid range.

Solvent extraction is one of the applications in which ILs are promising alternatives due to their negligible vapor pressure compared to volatile organic compounds (VOCs). ILs for selective metal extraction can be created by using organic ions that have metal binding functionalities. It has already been proven that some ILs present excellent metal extraction efficiencies (Sun et al., 2010; Wellens et al., 2013; Zhang et al., 2012; Vander Hoogerstraete et al., 2013; Rout et al., 2011). Recently, non-fluorinated fatty acid based ILs were synthesized in the search for biocompatible, non-toxic metal selective ILs (Parmentier et al., 2012). Oleate and linoleate acid were selected as anion due to their affinity towards metals combined with the voluminous and hydrophobic tetraalkylammonium cations to prevent the loss of the IL to the water phase. These hydrophobic ILs have been applied for the extraction of several transition metals and rare earth metals and showed excellent extraction efficiencies (Parmentier et al., 2015).

Regeneration of ILs after extraction is much less investigated, but this step is very important, because one of the limiting factors for IL commercialization is their high price compared to VOCs. The pathways for IL regeneration after metal extraction depend on the properties of the IL and on the extraction mechanism.

The intrinsic IL properties are most important for non-chemical regeneration. For example, electro-deposition is only possible when the IL has a high conductivity, low viscosity and low water uptake (Chen and Chang, 2012; El Abedin et al., 2005; Endres, 2002; Papaiconomou et al., 2012). However, in some cases a higher water content was beneficial due to the decrease in viscosity and corresponding increase in conductivity, even though the electrochemical window also decreased (Abbott and McKenzie, 2006). Another option for recovery is fractional cementation, which is a type of precipitation that depends more on the selectivity of the IL towards one particular metal, which can then be co-precipitated together with a sacrificial metal with a more negative redox potential compared to the extracted metal (Abbott et al., 2011; Abbott et al., 2009).

On the contrary, chemical regeneration depends more on the extraction mechanism and not on the intrinsic properties of the IL. For metal salt extraction with ILs there are two main possible ways of extraction, i.e. the metal cation is extracted into the IL as a positive ion or as a negative complex. Extraction of the metal cation via a negative complex always proceeds via the cation of the IL by the uptake of a negatively

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charged metal complexes (e.g., $ZnCl_4^{2-}$, $PdCl_4^{2-}$, ReO_4^-) (Regel-Rosocka and Wisniewski, 2011; Rohal et al., 2007; Cieszynska and Wisniewski, 2011; Regel-Rosocka, 2009; Vander Hoogerstraete and Binnemans, 2014). This usually occurs at high acid conditions (low pH) and high chloride concentrations (Yang et al., 2011). Regeneration of this type of ILs can be done by adding strong acids (e.g., H_2SO_4, HTf_2N) or strong bases (e.g., NH_4OH) that are able to break the negatively charged metal complexes. Recently, stripping of the metals out of this type of ILs has also been performed by applying the weak acid, oxalic acid (Dupont and Binnemans, 2015a; Dupont and Binnemans, 2015b; Vander Hoogerstraete et al., 2014). In this case, the metals form very strong water insoluble complexes that precipitates out of the IL.

Extraction of the positively charges metal ions (e.g., Ni^{2+}, Pd^{2+}, Co^{2+}) proceeds via functionalized ILs. These are ILs that contain a metal binding functionality most often in the anion (Vander Hoogerstraete et al., 2013; Rout et al., 2011; Rout et al., 2013; Egorov et al., 2010; Fischer et al., 2011; Biswas et al., 2014), but sometimes also in the cation (Visser et al., 2001; Harjani et al., 2008; Nockemann et al., 2008) of the IL. Regeneration of these functionalized IL is mainly done by reducing the metal interaction of the functionality due to protonation or oxidation, which can also be achieved with weaker acids and/or bases (Rout et al., 2011; Rout et al., 2013; Biswas et al., 2014; Visser et al., 2001; Rout and Binnemans, 2014; Holbrey et al., 2003). In most cases, these ILs cannot be directly reused for metal extraction.

In the present paper different options for the regeneration of the functionalized IL tetraoctylammonium oleate after metal extraction are to our knowledge investigated for the first time. Good extraction efficiencies were observed for the extraction of the transition metals (Mn^{2+}, Fe^{2+}, Zn^{2+}) in a previous investigation (Parmentier et al., 2012) and the presented work is a continuation of the research that was performed in this first article. Only difference is that iron (Fe) was changed by cobalt (Co), because Fe could easily precipitate and we replaced it by Co, because this has a nice visual color in the aqueous phase (red/pink) and ionic liquid phase (blue). Resulting that the visual observation gives already a first indication of the processes that are happening during regeneration. Preferably regeneration is done in a sustainable way, i.e. performed by a minimal consumption of electric energy and without the use of toxic chemicals. Insights of the regeneration process will help us to evaluate if this specific IL can be applied in a future continuous setup for metal extraction.

2. Experimental

2.1. Materials

The IL tetraoctylammonium oleate ($[N_{8888}][C18:1]$) used throughout this research was synthesized conform literature (Parmentier et al., 2012). Copper chloride anhydrous 98 wt.% ($CuCl_2$) and manganese chloride dihydrate 99 wt.% ($MnCl_2 \cdot 2H_2O$) were supplied by Boom BV (Meppel, The Netherlands). Zinc chloride 99 wt.% ($ZnCl_2$), cobalt chloride hexahydrate 98 wt.% ($CoCl_2 \cdot 6H_2O$) and sodium oxalate ≥99.5 wt.% ($Na_2C_2O_4$) were obtained from Sigma-Aldrich (Zwijndrecht, Belgium). Sulfuric acid 95 wt.% (H_2SO_4), acetic acid 99–100 wt.% (CH_3COOH), hydrogen chloride 1 M (HCl), ammonium hydroxide 25 wt.% (NH_4OH), sodium hydroxide pellets 99.2 wt.% (NaOH), sodium sulfate anhydrous 99 wt.% (Na_2SO_4), sodium acetate trihydrate 100 wt.% ($NaCH_3CO_2 \cdot 3H_2O$), sodium bicarbonate 99 wt.% ($NaHCO_3$) and sodium chloride 99 wt.% (NaCl) were supplied by VWR chemicals (Leuven, Belgium). Milli-Q water (≥18 MΩ cm) was obtained from a Millipore Milli-Q® Biocel, which used a Q-grade® column or a Synergy UV water purification system.

2.2. Electro-deposition experiments

First a test solution was made by dissolving 0.1 g $CuCl_2$ in 5 mL of the pure IL $[N_{8888}][C18:1]$ (0.117 mol Cu/L or 7.45 g Cu/L). The IL had a water content of 7.2 wt.%. This concentration was used for all test solutions throughout all electro-deposition experiments. Initially, 2 electrodes were applied based on titanium coated with platinum (1 cm by 3 cm). Afterwards, these electrodes were changed for 2 copper plates (1 cm by 3 cm). In this study, the cell was connected in series with a galvanostat (IviumStat, Ivium Technologies, The Netherlands) to maintain a constant potential. The conductivity of the IL was calculated via the measured resistance. Detailed information on how these calculations were done can be found in the supplementary info. Resistance of the IL was measured via a resistance meter (Agilent 4338B, Agilent Technologies), with a 0.4% relative precision.

2.3. Chemical regeneration experiments

First the IL phase was loaded with the metals of interest. A standard solution was prepared by dissolving a mixture of 3 salts (0.5 g of each salt: $ZnCl_2$, $MnCl_2$ and $CoCl_2$) in 100 mL Milli-Q water. Then, 1 mL of this salt solution was added to 1 g of the IL $[N_{8888}][C18:1]$ as extractant and was mixed in a Heidolph Multi Reax vortex mixer at 2500 rpm for 2 h at room temperature. Later, the mixture was centrifuged on an Allegra X-12R Centrifuge of Beckman Coulter at 3000 rpm for 10 min to accelerate the separation of the water phase.

Regeneration experiments with the loaded extractant were executed similar to the extraction experiments except for the fact that a 1 M solution of acid, base or salt was applied instead of the standard metal solution. After each extraction and regeneration experiment, the aqueous phases were analyzed with a Perkin Elmer, precisely Induced Coupled Plasma (ICP), which used an optical atomic emission spectrometer (AES) Optima 5300DV to detect if metal extraction/regeneration occurred. Results were obtained via a Winlab 32 ICP continuous automated analysis. The ICP-AES has a detection limit of 50 μg/L with an uncertainty of 2%.

Analysis of the metal precipitates was done by a JEOL JSM-6480LV scanning electron microscope (SEM) for imaging and with energy dispersive X-ray analysis (EDXA) for element analysis. Precipitates were recovered by decantation of the samples.

The percentage extraction (%E) in case of equal volumes of the aqueous and organic phase can be calculated by

$$\%E = \left(\frac{C_{aq,0} - C_{aq}}{C_{aq,0}}\right) \times 100\% \tag{1}$$

where C_{aq} is the metal concentrations in the aqueous phase after extraction, and $C_{aq,0}$ is the metal concentration of the initial aqueous phase.

After the metal extraction experiments, the regeneration of the IL was investigated. The percentage stripped from the organic phase was calculated by:

$$\%S = \left(\frac{C_{aq,s}}{C_{org,0}}\right) \times 100\% \tag{2}$$

where $C_{org,0}$ is the metal concentration in the IL before stripping ($C_{org,0} = C_{aq,0} - C_{aq}$) and $C_{aq,s}$ is the metal concentration in the aqueous phase after the stripping process.

2.4. IL recycling experiments

Cycle experiments were performed by repeating the extraction and regeneration procedures as explained in the chemical regeneration section in a subsequent order. In this case, 5 mL of IL and 5 mL of the start solution were applied. Extraction after regeneration was only once performed when testing acids as stripping solution, and three times when a salt solution or Milli-Q water were used as stripping agents. The sum of the stripping efficiency was reported when different stripping steps were directly performed after each other. A cycle experiment was also performed with a metal salt solution containing 1000 ppm NaCl and 1000 ppm $CoCl_2$ using two different stripping solutions, e.g. 0.05 M