



# Dissolution of metal oxides in an acid-saturated ionic liquid solution and investigation of the back-extraction behaviour to the aqueous phase



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## ABSTRACT

The dissolution of metal oxides in an acid-saturated ionic liquid, followed by selective stripping of the dissolved metal ions to an aqueous phase is proposed as a new ionometallurgical approach for the processing of metals in ionic liquids. The hydrophobic ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) saturated with a concentrated aqueous hydrochloric acid solution was used to dissolve CaO, NiO, MnO, CoO, CuO, ZnO and Fe<sub>2</sub>O<sub>3</sub>. It was found that nickel(II) and calcium(II) could be separated from all other transition metals present in the ionic liquid phase by stripping at high chloride concentrations. By scrubbing the ionic liquid solutions phase with water, manganese(II) and cobalt(II) could be stripped together with a fraction of iron(III) and copper(II), leaving zinc(II) and the remainder of copper(II) and iron(III) in the ionic liquid phase. These metal ions could be removed from the ionic liquid using ammonia. Copper(II) and zinc(II) formed ammine complexes and were back-extracted, while iron(III) precipitated as iron(III) hydroxide. After removal of all the metals present in the ionic liquid phase, the ionic liquid was prepared for reuse. Unfortunately, the mutual separations nickel–calcium, cobalt–manganese, or zinc–copper could not be achieved. This system would be useful when nickel is the metal of interest, since separation of nickel from all other transition metals present in the solution is achieved by one stripping step.

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## 1. Introduction

Ionic liquids (ILs) are a relatively new class of solvents which are entirely made of ions and possess a melting point below 100 °C (Welton, 1999). Other characteristic properties include a high electrical conductivity, a large electrochemical window, a broad liquidus range, and a high thermal stability (Anthony et al., 2003). These properties make ionic liquids perfectly suitable solvents for a broad range of application fields such as catalytic and chemical reactions (Plechova and Seddon, 2008; Wasserscheid and Keim, 2000), membrane technology (Bara et al., 2010; Cserjesi and Belafi-Bako, 2011; Han and Row, 2010), separation technology (Han and Row, 2010), nanotechnology (Antonietti et al., 2004; Deshmukh et al., 2001; Fonseca et al., 2004), and analytical chemistry (Koel, 2005; Soukup-Hein et al., 2009). Solvent extraction (SX) is a technique often used to separate metal ions from each other (Rydberg et al., 1992), and there have been a number of reports of the utilisation of ionic liquids (Billard et al., 2011; Dai et al., 1999; Dietz, 2006; Stojanovic and Keppler, 2012; Visser et al., 2001). Trihexyl(tetradecyl)phosphonium chloride, the ionic liquid used in this study, has been shown to be an environmentally friendly extraction phase for metal ions when applied in undiluted form (Vander Hoogerstraete et al., 2013; Wellens et al., 2012). In addition,

ionic liquids can be used as solvents for the electrochemical recovery of metals (Abbott et al., 2011a,b). For electrowinning, ionic liquids should have a high solubilising power for metal salts, including metal oxides. However, the solubility of metal oxides in ionic liquids is in general very low, this is because no oxide-binding reagent able to react with the metal oxide is present and because of the high strength of many metal-oxide bonds. Nevertheless, some examples of ionic liquids that were able to dissolve metal oxides have been reported (Abbott et al., 2011b; Tian et al., 2010).

Dai et al. and later Bell et al. reported the solubility of uranium(VI) oxide and vanadium(V) oxide, respectively, in imidazolium chlororoaluminate ionic liquids (Bell et al., 1999; Dai et al., 1997). Unfortunately, chloroaluminate ionic liquids are not suitable for ionometallurgical processing of metal oxides, since these ionic liquids are extremely sensitive to moisture. Abbott and co-workers were able to dissolve a range of metal oxides in deep-eutectic solvents (DES), which are mixtures of choline chloride with a hydrogen-bond donor and are solvents with properties similar to those of ionic liquids (Abbott et al., 2003, 2005, 2006a,b). Nockemann et al. used protonated betaine bis(trifluoromethylsulfonyl)imide and similar ionic liquids for the dissolution of several metal oxides including the rare-earth oxides, uranium(VI) oxide, zinc(II) oxide, copper(II) oxide and nickel(II) oxide (Nockemann et al., 2006, 2008). These examples of ionic liquids were able to react with the oxides because of the presence of reactive protons in the cationic core of the ionic liquid. The availability of

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reactive protons is essential for the dissolution of metal oxides in ionic liquids. However, conventional protic ionic liquids cannot be used for this dissolution process, because upon reaction with the metal oxide, the ionic liquid is transformed into a neutral amine base. Moreover, many protic ionic liquids contain substantial amounts of neutral entities, unless they are prepared by very strong Brønsted acids (Greaves and Drummond, 2008). Ionic liquids with acid anions such as hydrogen sulphate have been used for the leaching of metals from ores. Unfortunately, the number of possible anions is limited to partially deprotonated polyprotic acids (Dong et al., 2009; Whitehead et al., 2004, 2007, 2009). Furthermore, hydrogen sulphate ionic liquids were used for the dissolution of alumina for electrolysis applications (Tian et al., 2010).

In this paper, we propose another approach to the dissolution of metal oxides in ionic liquids, namely by using an acid-saturated ionic liquid solution. More in particular, the dissolution of CaO, NiO, MnO, CoO, CuO, ZnO and Fe<sub>2</sub>O<sub>3</sub> in the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) saturated with hydrochloric acid has been investigated. The stripping of the dissolved metals from the ionic liquid phase to an aqueous phase is described and the selective removal of metals from the ionic liquid offers possibilities for the separation of mixtures of metal ions especially for nickel. Finally, the regeneration of the ionic liquid is considered.

## 2. Experimental

### 2.1. Chemicals

Trihexyl(tetradecyl)phosphonium chloride P<sub>66614</sub>Cl (>97%; Cyphos® IL101; Cytec Industries), HCl (37 wt.%, VWR), 1,4-dioxane (>99%; extra pure; stabilised, Acros Organics), ammonia (25 wt.%, Chem-Lab NV), Fe<sub>2</sub>O<sub>3</sub> (purified, Sigma–Aldrich), CaO (pieces made from marble, RPR), MnO (powder; 60 mesh; 99%, Sigma–Aldrich), NiO (76% Ni, Acros Organics), CoO (95%; powder, Alfa Aesar), CuO (≥99%, Sigma–Aldrich) and ZnO (≥99%, Sigma–Aldrich) were used as received, i.e. without further purification.

### 2.2. Instrumentation and methods

The metal content of the ionic liquid phases and aqueous phases was determined using a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). For analysis of the aqueous phase by TXRF, aqueous samples (1 mL) were measured after addition of gallium as an internal standard. The samples were diluted with MilliQ water (if necessary). A small aliquot of 10 µL was applied on a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with a measurement time of 200 s. For the determination of the metal content in an organic phase by TXRF, a certain weight of the extracted phase (±0.5 g) was diluted in dioxane (20 mL). Gallium (1000 mg L<sup>-1</sup>, in HNO<sub>3</sub> 2–3%) was added to the solution as an internal standard. A small aliquot of 5 µL was applied on a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with a measurement time of 400 s. Absorption spectra were measured with a Varian Cary 5000 spectrophotometer. A quartz cuvette with an optical path length of 0.1 mm was used. <sup>31</sup>P NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating at 161.98 MHz for <sup>31</sup>P. The samples were measured in an NMR tube containing a sealed capillary with deuterated chloroform (an external lock). A delay time (d1) of 60 s was applied in the NMR pulse sequence to avoid saturation effects in the <sup>31</sup>P NMR.

### 2.3. Dissolution experiments

10 wt.% hydrochloric acid (12 M HCl) was added to the ionic liquid trihexyl(tetradecyl)phosphonium chloride (50 mL). To this solution, NiO, CuO, Fe<sub>2</sub>O<sub>3</sub>, ZnO, CaO, MnO and CoO were added with a metal concentration of 1 g L<sup>-1</sup> for each metal. The ionic liquid solutions

were analysed for their metal content after intensively stirring for 2 h at 60 °C.

### 2.4. Stripping experiments

To carry out the stripping experiments, a sample (4 mL) of the P<sub>66614</sub>Cl–HCl phase containing the dissolved metal ions was taken and mixed with an aqueous solution (4 mL). This aqueous solution contained HCl concentrations ranging from 0 M (pure water) to 12 M. The solutions were stirred for 30 min at 60 °C. After phase separation, the phases were centrifuged (3000 rpm, 3 min) and both phases were analysed for their metal content.

The recovery of the ionic liquid was tested after stripping of copper, zinc and iron. To three individual batches of the P<sub>66614</sub>Cl–HCl solution (5 mL), Fe<sub>2</sub>O<sub>3</sub> and CuO and ZnO were added, respectively, so that after dissolution the ionic liquid phase had a metal content of 5 g L<sup>-1</sup>. After the dissolution of the metal oxides, the ionic liquid solution was washed twice with water (5 mL). Thereafter, the ionic liquid phase was mixed with an aqueous ammonia solution (5 wt.% NH<sub>3</sub>, 5 mL). After centrifugation the ionic liquid phases were analysed for their metal content. After the stripping step at 6 M HCl, the ionic liquid phase (4 mL), was subsequently mixed three times with a pure water solution (4 mL). Finally, an ammonia solution (5 wt.%) was used as stripping solution (4 mL). The stripping conditions were the same as described in the previous paragraph; after each stripping step the phases were separated and after centrifugation the metal content was analysed in both phases.

The results of all the stripping experiments are represented by the stripping percentage (%S), which describes the percentage of a particular metal that is back-extracted from the ionic liquid phase to the aqueous phase. Depending on the metal concentration of the specific metal, either Eq. (1) or Eq. (2) was used to calculate the stripping percentage.

$$\%S = \frac{[M]_{aq}}{[M]_0} \quad (1)$$

$$\%S = \frac{[M]_0 - [M]_{IL}}{[M]_0} \quad (2)$$

Here  $[M]_{aq}$  is the concentration of the metal in the aqueous phase after stripping,  $[M]_{IL}$  is the concentration of the metal in the ionic liquid after stripping and  $[M]_0$  is the initial concentration of the metal in the ionic liquid phase before stripping. Eq. (1) was used when the metal element concentration was lower in the aqueous phase than in the ionic liquid phase after stripping. On the other hand, Eq. (2) was used when the ionic liquid phase contained the lowest metal element concentration. The lowest concentration was measured, because the absolute errors are much smaller and thus the %S value is more accurate.

## 3. Results and discussion

### 3.1. Dissolution experiments

For the dissolution of metal oxides in an acid-saturated ionic liquid several preconditions need to be fulfilled. First of all, the ionic liquid has to be able to dissolve a sufficiently large amount of acid to convert the required amount of metal oxides. Secondly, the ionic liquid must form two phases in contact with water to carry out the stripping experiments with an aqueous phase. Thirdly, a low solubility of the ionic liquid in water is required to minimise losses of the organic cations to the aqueous phase in order to make the system viable from both an economic and environmental point of view (Abbott et al., 2011b). Fourthly, the ionic liquid needs to be able to keep the metals dissolved, which can be achieved by using an ionic liquid with coordinating anions. Finally, in order to avoid a complicated extraction system it is favourable to choose the anion of the ionic liquid identical with the conjugated base of the

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