



Understanding mercury extraction mechanism in ionic liquids



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ABSTRACT

In this paper the complete removal of mercury ions from aqueous solutions using hydrophobic ionic liquids in the absence of chelating agents is reported. Several parameters were studied; in particular, the anionic component of ionic liquid, the anion of the metal salt and the nature of the aqueous phase used to dissolve the mercuric salt were varied to understand the transfer mechanism of Hg(II) ions into "classical" imidazolium-based ionic liquid. Results seem to suggest that metal ion partition into 1-octyl-3-methylimidazolium salts involves neutral and/or anionic Hg(II) species and that the rate of the process is strongly dependent on the experimental conditions, such as the working temperature and the nature of the anionic component of the ionic liquid, of the buffer solution and of the counterion of Hg(II). Moreover, addition of inorganic salts, such as NaCl or NaBr, to the aqueous phase increases metal ion extraction rate, with more than 90% of metal ion being transferred into the organic phase within 30 min and total ion removal accomplished in just four hours. Salt effects could even overcome the high viscosity of the ionic liquid and then a simple method for large-scale Hg(II) extraction was developed.

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1. Introduction

Considerable attention has been recently focused onto ionic liquids (ILs) since they are considered as a promising alternative to classical organic solvents. Therefore they have been applied in many fields of chemical and industrial applications, as reported in some recent reviews [1–4]. Ionic liquids are a large class of low-melting salts that are liquids below 100 °C, usually comprised of large asymmetric organic cations and different inorganic or organic anions, with shielded or delocalised charges. Their most important feature is their remarkable structural tunability, and even slight changes in both the cationic and/or anionic components have been shown to produce different physicochemical properties of ILs [5].

Application of ionic liquids to separation technology has attracted great attention [2–4]; recently, liquid–liquid extraction of actinides and lanthanides has been reviewed and considerable attention has been focused to the extraction mechanism [6]. Understanding underlying mechanisms and finding the variables involved in the control of the processes is therefore a key-step to identify the ionic liquids best suited to a specific application and for a better design of novel extraction systems [7].

Efficient liquid/liquid extraction systems can be obtained by replacing traditional molecular solvents with water-immiscible

ionic liquids, since they have no detectable vapour pressure and are relatively thermally stable, allowing to avoid many environmental and safety problems related to the use of volatile organic compounds (VOCs). Therefore, IL-based extraction systems of a wide range of metal ions have been extensively investigated [8–10], generally with encouraging results.

Two main approaches have been adopted in liquid/liquid extraction of metal ions: (i) proper chelating agents can be solubilised in ionic liquid phase [11–14], or (ii) task-specific ionic liquids (TSILs) can be designed and synthesised not only to increase the affinity of a target species for the IL over a second phase but also to greatly diminish the chance for ligand loss to the aqueous phase. In fact, TSILs contain specific chelating groups covalently incorporated within one of the ionic liquid components, typically within the cation [15–18].

Recently, de los Ríos et al. [19,20] reported the extraction of Zn(II), Cd(II) and Fe(III) in ionic liquids in the absence of chelating agents. Among the selected ionic liquids, methyltrioctylammonium chloride ([MTOA][Cl]) allowed almost complete removal of the three metal ions from acidic aqueous solution, while the selective separation of Zn(II) and Cd(II) over Fe(III) and Cu(II) was accomplished with 1-methyl-3-octylimidazolium tetrafluoroborate [C₈MIM][BF₄].

Mercury is considered the most toxic nonradioactive metal and, taking into account its water-solubility and then its bioavailability, its removal from aqueous solutions is a very important issue. To date, the partition of Hg(II) into an IL extracting phase in

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liquid/liquid systems is accomplished by the use of TSILs containing a bis-imidazolium cation incorporating a short ethylene-glycol spacer [21] or thioether, thiourea and urea functional groups incorporated in the alkyl chains of the imidazolium cation [15,22].

In a previous work [23], we reported the first example of the complete spontaneous partition of Hg(II) ions into a “classical” imidazolium-based ionic liquid, i.e. 1-alkyl-3-methylimidazolium hexafluorophosphate, where the only “functionalisation” is related to the hydrophobic moiety. Interestingly, binding and transport properties of metal ions in such peculiar media could be controlled, by the working temperature and by the alkyl chain length on the imidazole ring.

In this work, a thorough study of the partitioning properties of ionic liquids towards mercuric ions is reported. The anionic component of ionic liquid, the anion of the metal salt and the nature of the aqueous phase used to dissolve the mercuric salt were varied to understand the transfer mechanism of Hg(II) ions in imidazolium-based ionic liquid. A better knowledge on these issues is indeed of primary importance not only in view of developing efficient back-extraction systems but also to understand if other metallic species could be spontaneously partitioned in ionic liquids by modifying specific experimental variables.

2. Experimental

2.1. Metal ion analysis

The concentration of Hg(II) ions in the aqueous phase was measured by following the sensitive spectrophotometric method described in an earlier paper [24]. A diode array Hewlett Packard 8452 A spectrophotometer was used for the quantitative determinations.

2.2. Extraction experiments

In a screw cap, flat-bottomed vial, 1 mL of ionic liquid and 1 mL of a 5×10^{-3} M HgX₂ solution in 0.15 M sodium acetate buffer, pH 4.68 were added. They were kept under stirring in a glycerine/water bath at constant temperature and the metal ion concentration in the upper aqueous phase was monitored. Then, Hg(II) ion concentration in ionic liquid was calculated as a difference. Each experiment was done at least in triplicate and results agreed to within 5%.

2.3. Materials

All chemicals were analytical grade, purchased from Sigma-Aldrich and used as received.

Ionic liquids were synthesised by following the reported procedures [8,25]; 1-octyl-3-methylimidazole bromide [C₈MIM][Br] was synthesised and used as a precursor to produce 1-octyl-3-methylimidazole hexafluorophosphate [C₈MIM][PF₆], 1-octyl-3-methylimidazole tetrafluoroborate [C₈MIM][BF₄] and 1-octyl-3-methylimidazole bis(trifluoromethyl)sulfonylimide [C₈MIM][Tf₂N].

[C₈MIM][Br] was prepared by adding equimolar amounts of freshly distilled 1-methylimidazole and 1-octylbromide into a 500 mL round-bottomed flask fitted with a reflux condenser for 48 h at 60–70 °C with stirring until two phase formed. Unreacted starting materials were extracted with ethyl acetate and traces of solvent were removed under vacuum (50 mTorr) at 80 °C. Finally a pale yellow and slightly viscous liquid was obtained.

The ¹H NMR spectrum (200 MHz, CD₃OD), consists of the following peaks: δ = 0.87 (t, *J* = 7.3 Hz, 3H, CH₃); 1.09–1.29 (m, 10H, 5CH₂); 1.81–1.87 (m, 2H, CH₂); 3.85 (s, 3H, N-CH₃); 4.15 (t,

J = 7.4 Hz, 2H, N-CH₂); 7.51 (d, *J* = 1.8 Hz, 1H, CH); 7.59 (d, *J* = 1.8 Hz, 1H, CH); 8.95 (s, 1H, N-CH-N).

2.4. Synthesis of [C₈MIM][PF₆]

To a stirring solution of [C₈MIM][Br] (186.41 g, 0.6773 mol) and water (150 mL) at 0 °C, 50% excess hexafluorophosphoric acid (200 mL of 60% aqueous solution) was slowly added. The resulting biphasic system was stirred for 4 h followed by dichloromethane extraction (5 × 80 mL) to remove the ionic liquid. Water wash (10 × 100 mL) using distilled water was used to eliminate unreacted acid. The dichloromethane and water were removed under vacuum overnight at 120 °C. The absence of bromide ions in the colourless liquid was verified by testing with silver nitrate.

2.5. Synthesis of [C₈MIM][BF₄]

Fluoroboric acid (89.36 g of 48% aqueous solution, 0.44 mol) was added to an aqueous solution of [C₈MIM][Br] (121.10 g, 0.44 mol in 140 mL) at 0 °C. Addition of the acid was gradually done with continuous stirring. When addition of the fluoroboric acid was completed, the temperature of the reaction medium was increased to 20 °C and the mixture left overnight. Traces of unreacted fluoroboric acid were removed with distilled water (10 × 100 mL); then, portions of dichloromethane (5 × 80 mL) were used to extract the ionic liquid. Removal of the remaining dichloromethane and water occurred in vacuum at 110 °C overnight. The absence of bromide ions in the liquid was verified by testing with silver nitrate.

2.6. Synthesis of [C₈MIM][Tf₂N]

To an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (Li(Tf₂N)) (25.00 g, 0.087 mol in 50 mL) an aqueous solution of [C₈MIM][Br] (23.67 g, 0.086 mol in 30 mL) was added and the mixture was stirred for 2 h at RT. The [C₈MIM][Tf₂N] produced was separated from the aqueous layer and washed with distilled water (5 × 100 mL) to remove residual LiBr salt and traces of unreacted Li(Tf₂N). The colourless ionic liquid was subsequently heated at 110 °C under vacuum overnight to remove traces of water. The absence of bromide ions in the liquid was verified by testing with silver nitrate.

3. Results and discussion

As previously reported [23], water/ionic liquid biphasic systems can be successfully employed to obtain a quantitative transfer of Hg(II) ions into the ionic liquid phase even in the absence of a chelating agent. In the previous paper we have shown that Hg(II) extraction from the buffered aqueous phase depends on both the working temperature and hydrophobicity of ionic liquid; when [C₈MIM][PF₆] was used, complete partitioning occurred in 12 h at 60 °C, while at lower temperatures the process was much slower (for example, just at 40 °C, the quantitative transfer of metal ions required 3 days to be completed). The extraction efficiency was evaluated solely by analysing the effects of working temperature variation (range 25–60 °C), and those related to the alkyl chain length linked to the imidazolium ring.

In this paper, 1-octyl-3-methylimidazolium, as cation of ionic liquid, and the operating temperature of 60 °C were selected; the effects of others factors and of experimental conditions on Hg(II) extraction were here evaluated, to better understand the extraction mechanism. In particular, extraction efficiency was investigated as a function of the anion of both ionic liquid and metal

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