Study of extraction of Zn (II) from ammoniacal media with ionic liquids

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Abstract. In this paper a systematic study on liquid-liquid extraction of Zn (II) from ammoniacal media using ionic liquids (IL) as extractants is presented. The ionic liquids used for this study were: trihexyl(tetradecyl)-phosphonium chloride (Cy IL 101), bis trihexyl(tetradecyl)-phosphonium-(trifluoromethylsulfonyl) imide (Cy IL 109) and 1-octyl bromide pyridinium (1-BOP). With bis trihexyl(tetradecyl)-phophonium-(trifluoromethylsulfonyl) imide (Cy IL 109), the efficiency of the liquid-liquid extraction system was evaluated as a function of the nature of the aqueous phase (HCl, H₂SO₄ and NH₄⁺/NH₃⁻), the pH, the diluents nature (kerosene, tributyl phosphate and toluene), and the modifier content. The results showed a very fast kinetic of the Zn(II) transfer to the organic phase, reaching the equilibrium within 10 minutes of contact between the phases (organic/aqueous). On the other hand, the Zn(II) extraction was better (percentage of extraction 98% at pH 9.2), when it was extracted from NH₄⁺/NH₃⁻ media with an organic phase composed by Cy IL 109 dissolved in kerosene with 50% of decanol. The results showed that the uses of ILs in the extraction of metals ions, instead of organic solvents, in the liquid-liquid extraction processes are ecologically viable alternatives that require further study for its application.

1. Introduction

Several technologies can be used to remove toxic metals from liquid effluents, including precipitation, solvent extraction, ion exchange, etc. [1]. Among these technologies, solvent extraction is highly used in the recovery and separation of metals from aqueous solutions; [2]. One disadvantage of solvent extraction is the losing of organic diluents by volatilization, which has a detrimental impact on the environment and human health. Consequently, greener extraction methods are being searched; the use of ionic liquids (ILs) could overcome this disadvantage [3]. Recently, considerable interest has been manifested in the use of room temperature ionic liquids as solvents for industrial catalytic reactions [4]. This approach appears to allow the controlled production of wanted products from reactants with a minimum waste of production through side reactions due to the tendency of ionic liquids to suppress conventional solvation and solvolysis phenomena. ILs are usually composed of heterocyclic organic cations and various anions that have unique properties such as non-volatility, non-flammability, and a wide temperature range to remain in liquid phase [5]. The most attractive property of ILs according to separation techniques is that ionic liquids can be designed to be water-immiscible salts by extending
the chain length of the cation and/or incorporating hydrophobic anions. These hydrophopic ILs, are
available for separation techniques that use a biphasic system, like liquid-liquid extraction [6].

The purpose of this researching work is to show the feasibility of ILs as alternative to traditional
organic solvents employed in liquid-liquid processes and to study the extraction of Zn(II) from sulfate
media using as extractant the ionic liquids (IL), trihexyl (tetradecyl)-phophonium chloride (Cy IL 101),
bis trihexyl(tetradecyl) - phophonium - (trifluoromethylsulfonyl) imide (Cy IL 109) and 1-octyl
bromide pyridinium (1-BOP).

1. Experiment

1.1. Reagents

As extractant phase (organic) we used three different ionic liquids: two commercial ionic liquids, Cy
IL 109, Cy IL 101, both provided by Cytec Industries, and 1-BOP (see Figure 1), which was
previously synthesized by our working group. They were prepared at 0.1 mol L$^{-1}$, diluted in kerosene
(98%, Aldrich) and n-decanol (98%, FAC). In this case, the experimental conditions were: Organic
phase=Cy IL 109, Cy IL 101, 1-BOP diluted in decanol/kerosene 50% v/v, Aqueous Phase=NH$_4$/NH$_3$
[Zn(II)]=10 ppm, pH=6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0.

![Chemical structure of ionic liquids used. a) Cy IL 109, b) Cy IL 101, (Cytec, 2004). c) 1-BOP.](image)

The effect of using different diluents (kerosene, tributyl phosphate (TBP (98%, Aldrich)) and toluene
(98%, Reasol)) in decanol proportion: modifier, 50:50 was studied. These tests were done only with
the ionic liquid Cy IL 109.

The aqueous phase was prepared from zinc sulfate (ZnSO$_4$·7H$_2$O, 98%, Merck) at 10 ppm. It was
diluted in deionized water in a different media: H$_2$SO$_4$ (98.08%, UT Baker), HCl (98%, Aldrich), NH$_3$
(analytical grade 25% v/v, Aldrich) and NH$_4$Cl (analytical grade, J. T. Baker).

Kinetic study was made only with Cy IL 109 because it was the IL that provided the best results. This
one was diluted in decanol / kerosene 50% v/v, using like aqueous phase a 0.01mol L$^{-1}$ ammoniacal
solution (pH 9.2).

1.2. Methodology

The Zn(II) extraction studies with different ionic liquids and diluents were carried out by contacting
equal volumes of both phases (aqueous and organic) in an erlenmeyer flask, which was placed in a
ping pong shaker (Eberbach model 6000), by 120 minutes. Subsequently the two phases were
separated (in a separatory funnel) and the content of Zn(II) into the aqueous phase was analysed by
atomic absorption spectrophotometry (AA) with a Perkin-Elmer 3110 (EAA) at a 213.9 nm
wavelength. The Zn(II) concentration in the organic phase was obtained by mass balance.

In the kinetic study, it was used a double layer glass reactor, placing equal volumes of both phases
(aqueous and organic). The mix was kept stirred in a magnetic stirring grid at constant temperature
(298 K). After each test, the phases were separated for their subsequent Zn(II) analysis by AA. In the
experiments, the pH of the aqueous solutions was measured using an automatic titrator (716 DMS
Titriino Metrohm) with a glass electrode.
2. Results and Discussion

2.1. Effect of different ionic liquids

The results obtained in the Zn(II) extraction with three different ionic liquids, Cy IL 109, Cy IL 101 and 1-BOP, as a function of pH are showed in the figure 2. It is possible to see that the pH drastically influences on the extraction of the metal ion. There is a high zinc extraction of 98% at pH 9.2 with Cy IL 109 and 69% at pH = 3.2 with Cy IL 101. The Cy IL 101 extracts better in an acid medium, otherwise occurs with Cy IL 109 that has a better performance in basic media. This phenomenon is attributed to the nature of the different anions containing in each ionic liquid. Regarding to the ionic liquid 1-BOP, we could obtain 100% extraction at pH 7.6. However, this compound showed high solubility in water and for this reason it does not accomplish the required characteristics to be considered as a good solvent or IL [9].

3.2 Effect of the aqueous media

The results of the Zn(II) extraction from H$_2$SO$_4$ and HCl media showed that there is no a relevant extraction of this ion, reaching a maximum extraction percentage of 9.5% to pH 2.0 when H$_2$SO$_4$ was used, and 10.8% with HCl at pH 2.4 (see Fig. 3). The behavior of the system did not show a stable trend, which can be attributed to the appearance of a third phase. Nevertheless, it is possible to say that the extraction of Zn(II) by the Cy IL 109 form acidic media is inefficient. When we worked the aqueous phase in an ammoniacal solution the Zn(II) extraction was better than the one obtained in an acidic media.

It is necessary to remark that a second organic phase is formed during the liquid-liquid extraction of Zn(II), which is attributed to the insolubility of Cy IL 109 in kerosene. The presence of n-decanol, besides helping to have a good phase separation, it helps to solubilise the Cy IL 109 in the organic phase. However, in relation kerosene / decanol (90:10) the solubility is still limited. When the organic phase is only composed by kerosene, the insolubility of ionic liquid is evident. In fact, we verified the presence of Zn (II) in the second organic phase, which agrees with Dingsheng et al [7].

3.3 Effect of diluent

In solvent extraction is often added to the organic phase a third component called “modifier” [8], in order to prevent the formation of a third phase or the presence of stable emulsions in the extraction systems. In this sense, we studied the behavior modifier dissolved in three different diluents (see Fig. 4), kerosene, tributyl phosphate and toluene in decanol (proportion: 1:1). The results showed that with TBP and toluene was possible to get extractions of 99 and 97% at pH 10.4 and 8.4, respectively. When kerosene is used as diluent, the Zn(II) extraction was of 98% at pH 9.2, comparing it with that reported by Regel-Rosocka [10]. The Cy IL 109 in toluene extracted only 20% of Zn(II) from HCl solutions.

3.4 Effect of decanol/kerosene proportion
The Zn(II) extraction from ammoniacal media at pH 9.2, using Cy IL 109 as extractant, at different kerosene / decanol rate, shows that the Zn(II) extraction percentage increases as the relation of decanol / kerosene increases, reaching percentage of extraction up to 98% using a rate decanol / kerosene 1:1, (see Fig. 5).

3.5 Effect of time
The results obtained from the kinetic study, in the case of the Zn(II) by the Cy IL 109, showed that after 10 minutes of stirring it was possible to obtain 81% of Zn (II), this value increased until 160 minutes, time when we achieved a maximum extraction percentage (98%) which was maintained constant.

3. Conclusions
The liquid-liquid extraction of Zn (II) using Cy IL 109 as extractant dissolved in kerosene and n-decanol was possible in an ammoniacal medium (98% at pH 9.2). When the Cy IL 101 was used the Zn(II) extraction from acidic media was possible. When the 1-BOP was used as extractant the extraction of Zn(II) was very high, but the use of this extractant it is not recommended because of its high solubility in water. The most suitable conditions for the extraction of Zn (II) are: Cy IL 109 diluted in decanol-kerosene ratio of 1:1 at pH 9.2. The use of ionic liquids could be competitive and in the future they could be applied to systems containing different metal species.

4. References
[1] Lozano L J and Godínez C 2003 Comparative Study of SX of Vanadium from Sulphate Solutions by Primene 81R and Alamine Miner Eng 16 291-294
[2] Agrawal A Kumari S and Sahu K K 2008 Liquid-Liquid Extraction of H₂SO₄ From Zinc Bleed Stream Hydrometallurgy 42–47
[3] Rogers R D and Voth G A 2007 Ionic Liquids Acc. Chem. Res 40 1077–1078
[4] Wilkes J S 2004 Properties of IL Solvents for Catalysis J. Mol. Catal. A Chem 11-17
[5] Kazunori N 2005 Ind. Eng. Chem. Res 44 4368-4372
[6] Luo H., Dai, S. and Bonnesen P.V 2004 Anal. Chem 76 2773-2779
[7] He X 2006 Study of transport and separation of Zn(II) by a combined SLM strip dispersion process containing D2EPHA in kerosene as the carrier Desalinization 40-51
[8] Juáñ D Meseguer D 1998 Extracción de cromo con disolventes orgánicos. Extracción con DEHPA Rev. Metal 3 253-260
[9] Papaiconomou N Lee J L 2007 Selective Extraction of Copper, Mercury, Silver and Palladium Ions from Water Using Hydrophobic Ionic Liquids American Chemical Society A-G
[10] Regel-Rosocka M 2008 Extractive removal of Zn(II) from chloride liquors with phosphonium ionic liquids/toluene mixtures as novel extractants Separation and Purification Technology 960-965