



Recycling and recovery of ammonium-based ionic liquids after extraction of metal cations from aqueous solutions



M.A. Valdés Vergara^a, I.V. Lijanová^{a,*}, N.V. Likhanova^b, O. Olivares Xometl^c, D. Jaramillo Viguera^a, A.J. Morales Ramirez^a

^a Instituto Politécnico Nacional, CIITEC, Cerrada Cecati S/N, Colonia Santa Catarina de Azcapotzalco, CP 02250 México, D.F., Mexico

^b Instituto Mexicano del Petróleo, Gerencia de Ingeniería de Recuperación Adicional, Eje Central Norte Lázaro Cárdenas No. 152, Col. San Bartolo Atepehuacan, CP 07730 México, D.F., Mexico

^c Benemérita Universidad Autónoma de Puebla, Facultad de Ingeniería Química, Av. San Claudio y 18 Sur, Col. San Manuel, Ciudad Universitaria, Puebla 72570, Mexico

ARTICLE INFO

Article history:

Received 20 August 2014

Received in revised form 14 May 2015

Accepted 22 May 2015

Available online 23 May 2015

Keywords:

Ionic liquids

Extraction

Recycle

Recovery

Heavy metals

Aqueous solutions

ABSTRACT

The recycling and recovery of ionic liquids (ILs) after the extraction of metal ions were investigated by using trioctylmethyl ammonium camphorate and trioctylmethyl ammonium dodecanedioate, which were synthesized from trioctylamine. The metal ions used in the aqueous solutions were: cadmium, copper and lead with initial concentrations of 50 and 100 ppm. In all the cases, the extraction percentage results were above 90%. After the extraction, the IL recovery was carried out by using solvents with medium polarity indexes. The present work features an extraction mechanism that goes through the use, recycling, recovery and reuse of ILs applied in the metal extraction process.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In the last decades, ionic liquids (ILs) have generated rising interest because of their diversified range of applications. These solvents include a large number of molecular structures and consist entirely of cations and anions, featuring low melting points as low as 100 °C with low viscosities [1–4].

IL properties such as melting point, viscosity, density, and hydrophobicity can be designed and task-specifically adjusted, choosing either the structure of the cation or anion or both to meet the requirements of specific applications [5–7]. ILs are found increasingly in a number of fields such as catalysis, electrochemistry, separation processes and liquid–liquid extractions [8–17].

The liquid–liquid extraction is an important kind of separation method that is based on the distribution of chemicals between two different liquid phases [18]. In recent years, many researchers have studied the liquid–liquid extraction by using ILs as ‘green’ solvents in the partition of substituted-benzene derivatives between water and a hydrophobic IL [19], the removal of sulfides and

nitrides from diesel and gasoline [20–24], and the removal of heavy metals from water [17,25].

In the first studies of heavy metal extractions that were performed with ILs assisted by crown ethers, the metals were removed from the aqueous phase, but in many cases, the ILs remained in the aqueous phase, and the whole extraction depended on the hydrophobicity of the extracting agent. The selectivity towards certain metal ions and extraction efficiency depend on the IL structure [26–28]. Other research works on metal ion extractions without extracting agents, only using IL/aqueous systems, have shown extremely high metal ion partitionings to the IL phase [17,19,27,28], which is leading to the development of new water treatment methods. Some extractions without using an extracting agent have been done, like in the work published by Germani [29] and his group, where Cu cations were removed with 1-alkyl-3-methylimidazolium-based ILs, showing that the extraction can occur without a chelating agent. Another work was done by de los Ríos et al. [30], where the extraction of Zn²⁺, Cd²⁺, and Fe³⁺ from aqueous hydrochloride solutions using ILs, in the absence of chelating agents, is shown. In this sense, our research group accomplished the extraction of five different heavy metals from aqueous solutions, in neutral pH, with 7 quaternary-ammonium-based ILs, obtaining a metal removal between 80% and 90 % [31].

* Corresponding author.

E-mail addresses: irinalijanova@yahoo.com.mx (I.V. Lijanová), nvictoro@imp.mx (N.V. Likhanova).

As it can be seen from the facts stated above, ILs are very interesting compounds for performing extraction and separation processes, but actually, there are few methods for purifying them and less about ammonium-based ILs, which are the ones used in the present work. One of the proposed treatments is centrifugation, which recovers successfully hydrophobic ILs [32]. In another interesting report by Lee et al. [33], a magnetic field was used to recover an IL with a strong magnetic response. Membrane filtration has been used to retain contaminants that ILs may have; the advantage of this method is that in comparison with the others, it does not require auxiliary substances and can be used with a wide variety of ILs [34,35]. Another treatment was carried out with the help of a rotary evaporator and then vacuum, resulting in a quite efficient tool to recover and purify ILs containing sulfur compounds. The operation was based on the IL vapor pressure, which is lower than that of the rest of the components [36]. The recovery of ILs containing sulfur compounds in their structure has also been achieved. In this case, the pH change was used to promote the precipitation of pollutants, which are filtered in order to get the base IL; it is worth highlighting that for this treatment, it is necessary to regenerate the anionic part [37].

Finally, the addition of a phase has also been applied, where salting out is used in the recovery process, which consists of adding an electrolyte such as a solid or a saturated aqueous solution, which when put in contact removes some water, forming a second phase that can be removed by settling or evaporation. In some cases, a potassium phosphate electrolyte, carbon dioxide and kosmotropic salts (those that contribute to the stability of molecular interactions) have been used [38–40].

According to the aforementioned, in the present work, two goals were set. The first one was to propose a new methodology for recovering and purifying ammonium-based ILs applying the addition-phase method. The second one was to find a mechanism to explain the extraction of metallic cations from aqueous solutions. The ILs with trioctylmethyl ammonium camphorate (CTMA) and dodecanedioate (DTMA) structures used for running the experiments were synthesized free of halides, fluorides or cyanides [41,42] in order to comply with an environmentally-frien-

dly-chemistry commitment. In order to do so, our ILs were considered similar to surfactants, which are less pollutant [43,44].

The extraction process was carried out with the two ILs mentioned above, selected from a previous work [31] that encouraged us to keep evaluating these promising compounds. Each IL was evaluated in five continuous cycles with three metals, where the corresponding aqueous solutions were prepared under neutral pH conditions at 30 °C. The recovery process was based on ionic liquid properties such as polarity and miscibility.

2. Experimental

2.1. Materials

The reagents were: camphoric acid (99%), dodecanedioic acid (99%), cadmium (II) chloride (99%), copper (II) sulfate (99%), and lead (II) acetate trihydrate (99%), which were purchased from Aldrich and used as received. Ethanol and acetone were reagent grade.

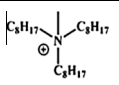
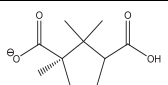
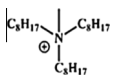
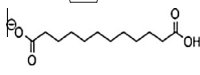
2.2. IL synthesis procedure and characterization

The ILs (Table 1) were synthesized in one step, starting from methyltrioctylammonium methylcarbonate as feedstock. The synthesis procedure of this compound was described previously [31].

In this first step, anionic exchanges of the methyl carbonate ion by the corresponding carboxylate anions were performed as shown in Fig. 1.

The ILs 1–2 were synthesized by following a general procedure: Camphoric or dodecanedioic acids (15 mmol) were dissolved in 50 mL of methanol and 30 mL of methanol solution containing 15 mmol of the IL feedstock (trioctylmethyl ammonium methyl carbonate) were added to the mixture. The reaction occurred with the release of gas. The reaction was kept under constant stirring for 30 min at 40 °C. After reaction completion, the solvents were removed by vacuum evaporation and the product was dried under vacuum.

Table 1
Structures and names of the synthesized ILs.

IL number	Short name	Name	Cation	Anion	Molecular weight (g/mol)	Yield (%)
1	CTMA	Trioctylmethyl ammonium camphorate			567.93	81
2	TMA	Trioctylmethyl ammonium dodecanedioate			598	76

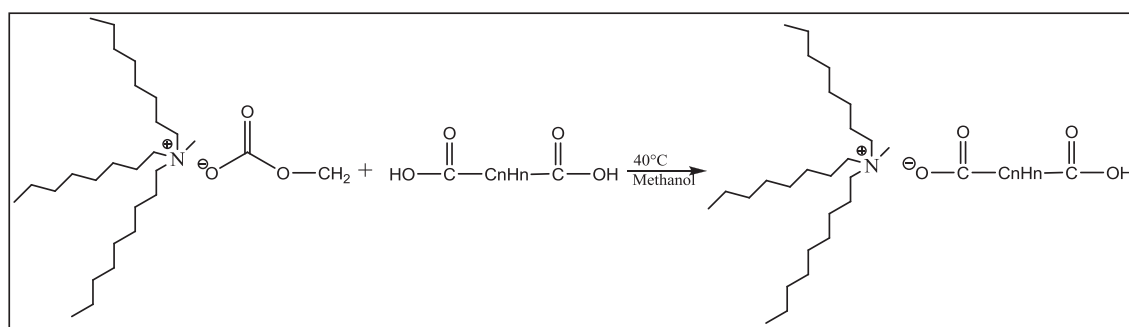


Fig. 1. Synthesis of CTMA or DTMA.

Download English Version:

<https://daneshyari.com/en/article/640281>

Download Persian Version:

<https://daneshyari.com/article/640281>

[Daneshyari.com](https://daneshyari.com)