



Research article

Liquid-liquid extraction of phenolic compounds from water using ionic liquids: Literature review and new experimental data using [C₂mim]FSI

Olalla G. Sas, Irene Domínguez, Begoña González, Ángeles Domínguez*

Advanced Separation Processes Group, Department of Chemical Engineering, University of Vigo, Campus Lagoas-Marcosende, 36310 Vigo, Spain

ARTICLE INFO

Keywords:

Phenol
o-cresol
2-Chlorophenol
Resorcinol
Ionic liquids
FSI

ABSTRACT

In this work, the capability of the ionic liquid, 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide, [C₂mim]FSI, to extract o-cresol, 2-chlorophenol, resorcinol and phenol from water, reaching the legal limit of 1 mg L⁻¹ was analyzed. The extraction process was carried out for each one of these phenolic compounds varying the initial concentration in water from 3 mg L⁻¹ to 1000 mg L⁻¹, and for aqueous mixtures of the four phenolic compounds in the same concentration range. Because of the scarcity of physical properties of the [C₂mim]FSI, density, speed of sound, dynamic viscosity and refractive index were measured from 293.15 to 343.15 K at atmospheric pressure. From the experimental data, the thermal expansion coefficient and the isentropic compressibility for the pure ionic liquid were calculated. Even though [C₂mim]FSI is hydrophobic, it can solve small quantities of water that can hinder the recovery of the ionic liquid, consequently the solubility of water in the ionic liquid was determined at several temperatures and atmospheric pressure. In addition to experimental data, a literature review on the use of ionic liquids to extract phenolic compounds from water was performed.

1. Introduction

Phenolic compounds are pollutants present in wastewater from different kinds of industries, including oil refineries, coke plants, plastics, leather, chemical, paint and pharmaceutical industries (Saien et al., 2018) within a concentration range that can vary between a 0.1 and 3900 mg L⁻¹. Due to environmental restrictions, and according to the actual environmental regulations, these compounds must be removed before wastewater discharge. Organizations such as US Environmental Protection Agency (EPA) and European Union (EU), have included some of the phenolic compounds in their list as high priority pollutants (Brinda Lakshmi et al., 2013; Chen et al., 2012) and the EPA has fixed the threshold quantity (Chen et al., 2012) for phenolic compounds in wastewater in 1 mg L⁻¹.

Wastewater containing phenolic compounds can be treated by several methods such as biodegradation, thermal decomposition, distillation, adsorption over polymeric and inorganic adsorbents, membrane pervaporation, membrane-solvent extraction and liquid-liquid extraction with different solvents (Busca et al., 2008). However, many of these techniques present some drawbacks such as high energy consumption, long time required and relatively high cost of adsorbents. Among these methods, the extraction with solvents is considered one of the main methods in wastewater treatment due to the solubility of

phenolic compounds in several common solvents. In general, extraction with polar organic solvents, such as diisopropyl ether, methyl isobutyl ketone, ethylbenzene, cumene, di-isopropyl ether, isopropyl acetate, n-hexane, toluene, methyl-isobutyl ketone, benzene, n-octylpyrrolidone, ethyl acetate, cyclohexane, n-butyl acetate, n-hexyl acetate, n-pentylacetate, cyclohexyl acetate, acetate esters, and butyl acetate (Uslu et al., 2016; Palma et al., 2007; Pinto et al., 2005; Greminger et al., 1982) can be used for the separation of these components. Typical organic solvents used in this process are generally toxic, flammable and volatile, causing harmful environment effects. It is therefore necessary to find new solvents capable of replacing traditional organic solvents, reducing the environmental impact, the energy consumption and the installation and operational costs of the extraction process.

Over the last few years, ionic liquids (IL) have gained great attention as environmental friendly solvents due to some of their properties such as high thermal stability, negligible vapor pressure at moderate temperature and pressure, and their ability to solve a wide variety of materials (Wilkes, 2002), making them an alternative to conventional solvents in liquid-liquid extraction processes. Among other applications, ILs have been used to extract organic pollutants such as aromatic compounds and dyes from water (Ma and Hong, 2012).

Up to now most of the ILs studied for the extraction of phenolic compounds in water are BF₄⁻ and PF₆⁻-based ILs but they can present

* Corresponding author.

E-mail address: admiguez@uvigo.es (Á. Domínguez).

thermal and chemical decomposition and BF_4^- -based ionic liquids are not stable in water because they can hydrolyze (Freire et al., 2010).

The IL selected in this work was 1-ethyl-3-methylimidazolium bis (fluorosulfonyl)imide, $[\text{C}_2\text{mim}]\text{FSI}$, because of its low viscosity, that makes it easy to handle, its relatively low price and the fact that the environmental impact should be low since its solubility in water is negligible.

To our knowledge, there is little information about this IL in literature, only one publication (Seki et al., 2012) reporting densities and refractive indices of $[\text{C}_2\text{mim}]\text{FSI}$ and a few publications about its use as electrolyte (Menne et al., 2015; Shkrob et al., 2014) were found. In order to design an industrial process using this IL, it is essential to have enough information about its physical properties because they are necessary for the design of the separation units involving heat and mass transfer. Moreover, the knowledge of these properties is also crucial to develop theoretical models, which are a powerful tool to predict the behavior of these pure compounds and their mixtures.

Accordingly, experimental densities, speeds of sound, dynamic viscosities and refractive indices of the pure 1-ethyl-3-methylimidazolium bis (fluorosulfonyl)imide ionic liquid, $[\text{C}_2\text{mim}]\text{FSI}$, were measured from 293.15 to 343.15 K at atmospheric pressure. From density and speed of sound, the thermal expansion coefficient and the isentropic compressibility, which allow us to know the volume change of a liquid when there is a variation of temperature or pressure respectively, were calculated.

Another factor to consider is the amount of water that can be solved in the IL because, despite the fact that this IL is hydrophobic and the solubility of $[\text{C}_2\text{mim}]\text{FSI}$ in water is negligible, some water can be solved in the IL. For that reason the maximum water content of $[\text{C}_2\text{mim}]\text{FSI}$ at temperatures from 293.15 to 328.15 K and at atmospheric pressure was measured.

Liquid-liquid extraction is widely used for the separation of low concentration compounds present in a mixture, therefore the ability of $[\text{C}_2\text{mim}]\text{FSI}$ to remove some phenolic compounds from water reaching the legal concentration limit of 1 mg L^{-1} was evaluated. The selected phenolic compounds were phenol, 2-chlorophenol, o-cresol and resorcinol with concentrations of 3, 5, 10, 50, 100 and 1000 mg L^{-1} . The extraction process was previously optimized attending to: IL to aqueous solution ratio, stirring time, settling time, pH and temperature. The equilibrium concentration of the phenolic compounds in water was determined by the 4-amineantipyrine analytical method (Rice et al., 2012).

The presence of more than one phenolic compounds in water may lead to a variation in the extraction yield. Hence, in this work the ability of the IL to remove phenolic compounds in a multicomponent system {o-cresol + 2-chlorophenol + resorcinol + phenol + water} at 298.15 K and atmospheric pressure was also carried out.

A literature review shows that there are not experimental data concerning the use of $[\text{C}_2\text{mim}]\text{FSI}$ in the extraction of phenolic compounds, however other ILs have been used for this purpose, so a literature review about the different kind of ILs studied and the main conclusions obtained from these works is considered below.

2. ILs as separation agents for the extraction of phenolic compounds from water

2.1. Partition coefficients, $K_{\text{IL}/\text{W}}$, of phenolic compounds in IL/water systems

Solute distribution between two immiscible or partially immiscible solvents depends on many factors, such as temperature, initial solute concentration and solvents ratio, however, the determination of partition coefficients at given conditions allows a comparison among the behavior of different ILs or phenolic compounds.

In order to evaluate the capability of 1-butyl-3-methyl imidazolium hexafluorophosphate $[\text{C}_4\text{mim}][\text{PF}_6]$ ionic liquid to extract phenolic

compounds from water (Inoue et al., 2007), the partition coefficients of phenol, o-cresol, m-cresol, p-cresol, 3,5-xyleneol and α -naphthol in the $[\text{C}_4\text{mim}][\text{PF}_6]$ /water two-phase system was determined. They found that $K_{\text{IL}/\text{W}}$ of phenol, cresol isomers and α -naphthol are almost independent of their initial concentration in water (from $10 \times 10^{-4} \text{ M}$ to $40 \times 10^{-4} \text{ M}$ approximately) while the partition coefficients of 3,5-xyleneol increase with increasing its initial concentration in water. The difference in $K_{\text{IL}/\text{W}}$ among the cresol isomers is not very large: o-cresol < m-cresol \approx p-cresol and the partition coefficient values of the studied compounds increase in the following order: phenol < cresol isomers < 3,5-xyleneol < α -naphthol. Additionally, the $K_{\text{IL}/\text{W}}$ values for these phenolic compounds in the $[\text{C}_4\text{mim}][\text{PF}_6]$ /water are lower than those in the 1-octanol-water system even though they follow the same trend.

Katsuta et al. (2011) determined the partition coefficients of phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,3-dichlorophenol, 3,5-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, and 2,4,6-trinitrophenol in several IL/water systems. The ILs selected were 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide $[\text{C}_4\text{mim}][\text{NTf}_2]$, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide $[\text{C}_4\text{C}_1\text{Pyr}][\text{NTf}_2]$, 1-butyl-3-methylimidazolium hexafluorophosphate $[\text{C}_4\text{mim}][\text{PF}_6]$, 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide $[\text{C}_8\text{mim}][\text{NTf}_2]$, and 1-methyl-3-octylimidazolium tetrafluoroborate $[\text{C}_8\text{mim}][\text{BF}_4]$. Some interesting conclusions were drawn from the results: i) the partition coefficients in a given IL/water system increase when the number of chlorine atoms or nitro groups in the phenol molecule increases ii) The differences in cation structure of the studied ILs have little influence on $K_{\text{IL}/\text{W}}$ iii) The difference in the anion between $[\text{C}_4\text{mim}][\text{NTf}_2]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ has a small effect on $K_{\text{IL}/\text{W}}$, however, the $K_{\text{IL}/\text{W}}$ values in the $[\text{C}_8\text{mim}][\text{BF}_4]$ /water system are significantly higher than in the $[\text{C}_8\text{mim}][\text{NTf}_2]$ /water system.

With the aim of determining the influence of the substituent position in the phenolic ring, the partition coefficients of 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, 4-propylphenol and 2,3,5-trimethylphenol in the $[\text{C}_4\text{mim}][\text{PF}_6]$ /water system were measured (Shymoyama et al., 2010). For ethylphenol isomers, the partition coefficients of 3-ethylphenol and 4-ethylphenol are almost the same and lower than those for 2-ethylphenol. The $K_{\text{IL}/\text{W}}$ values for 2,3,5-trimethylphenol are higher than those for 4-propylphenol. The effect of the isomers was explained from the profiles of the surface charge densities of CH and OH groups calculated by COSMO-SAC (Conductor-like Screening Model – Surface Activity Coefficient) method.

2.2. Phenolic compounds extraction using hydrophobic ionic liquids

Several ILs have been tested as separation agents for the extraction of different phenolic compounds, most of them with the NTf_2^- , PF_6^- or BF_4^- anions due to their hydrophobic characteristics. Regarding to the cation, imidazolium based ILs have been the most widely used.

The first study found in literature (Vidal et al., 2004) investigated the ability of the $[\text{C}_8\text{mim}][\text{BF}_4]$, $[\text{C}_{10}\text{mim}][\text{BF}_4]$, $[\text{C}_6\text{mim}][\text{PF}_6]$ and $[\text{C}_8\text{mim}][\text{PF}_6]$ to extract phenol, tyrosol and p-hydroxybenzoic acid. The results indicate that ILs containing the BF_4^- anion are more efficient in the extraction of all the phenolic compounds and that the effect of temperature is not significant in the studied range from 288.15 K to 313.15 K.

$[\text{C}_4\text{mim}][\text{PF}_6]$ was used for the extraction of phenol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 2,4,6-trinitrophenol, 1-naphthol, 2-naphthol, 4-chlorophenol, catechol and resorcinol from water (Khachatryan et al., 2005) at $295.15 \pm 2 \text{ K}$, obtaining an extraction yield over than 90% for nitrophenols, naphthols and 4-chlorophenol. The analysis of the influence of the pH on the extraction shows that the solution pH should be lower than pKa to get a good recovery, nevertheless, in the case of 1-naphthol and 4-chlorophenol, the extraction is

Download English Version:

<https://daneshyari.com/en/article/11028776>

Download Persian Version:

<https://daneshyari.com/article/11028776>

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