

# Applications of Ionic Liquids in Azeotropic Mixtures Separations

Ana B. Pereiro<sup>1,2</sup> and Ana Rodríguez<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, University of Vigo, 36310 Vigo,*

<sup>2</sup>*Present address: Instituto de Tecnología Química e Biológica, UNL,*

*Av. República 127 2780-157 Oeiras,*

<sup>1</sup>*Spain*

<sup>2</sup>*Portugal*

## 1. Introduction

The increasing concern about environmental issues, as well as the establishment of new regulations, has recently directed the attention of the scientific community to novel processes based on greener technologies. In many areas of industry, solvent mixtures accumulation occurs due to the hardness of recycling. The separation of these mixtures into the pure components is necessary so that they can be reused. However, most solvent mixtures contain azeotropes and thus, their separation by simple distillation becomes impossible.

Extractive distillation is the separation process most widely used to remove one of the components in the azeotropic system. In this process, the addition of a new solvent (entrainer) is used to interact more favourably with one component of the original mixture altering their relative volatilities. This obvious advantage is constrained to the high energy costs necessary to achieve a fluid phase system. Within this context, liquid-liquid separation, based on the immiscibility between two liquid phases at room temperature, emerges as a beneficial alternative to reduce the energy consumption and the environmental impact.

Ionic liquids (ILs) have become one of the growing “green” media for engineers not only due to their remarkable physicochemical properties but also for their recyclability. The most outstanding reason of interest in these neoteric solvents is their negligible vapor pressure at room temperature (Earle et al., 2006), which decreases the risk of worker exposure and the loss of solvent to the atmosphere. Moreover, ILs can be tailored for a specific application by accurately selecting the cation and the anion (Huddleston et al., 2001). This feature is very attractive for industry since fine-tuning of solvent properties permit the optimization of the chemical engineering needs in terms of efficiency and cost of the processes.

During the last years, ILs have exhibited the ability to separate azeotropes including ethanol + water (Jork et al., 2004; Seiler et al., 2004), tetrahydrofuran (THF) + water (Jork et al., 2004; Seiler et al., 2004; Hu et al., 2006), benzene + heptane (Letcher & Deenadayalu, 2003; Gonzalez et al., 2009), ethyl acetate + ethanol (Zhang et al., 2008), and ethyl tert-butyl ether

(ETBE) + ethanol (Arce et al., 2007). Although the increasing number of publications addressing azeotropic separations with ILs, these studies only analyze the liquid-liquid equilibria (LLE), vapor-liquid equilibria or simulation of the extractive distillation process.

The present work considers the use of ILs formed by 1-alkyl-3-methylimidazolium cation ( $[C_nMIM^+]$ ) and several anions as solvents in a bench-scale extraction process. One of the selected anions was hexafluorophosphate  $[PF_6^-]$  because it has been commonly investigated and considered historically one of the most important anion families; despite the fact that this anion can undergo hydrolysis producing hydrofluoric acid when in contact with water and at high temperatures (Swatloski et al., 2003; Najdanovic-Visak et al., 2002). Consequently, its industrial application has been restricted to those processes under water free conditions and moderate temperatures. Other anions chosen are methyl sulfate  $[MeSO_4^-]$  and ethyl sulfate  $[EtSO_4^-]$ , since they display the most promising potential for application in industrial processes (Holbrey et al., 2002) because they can be easily synthesized in an halide-free manner at reasonable cost, they are chemically and thermally stable, and they have low melting points and relatively low viscosities. Taking into account all these features, these ILs were considered good candidates to be tested as extracting solvents or entrainers in the separation of azeotropic mixtures.

In order to evaluate such a possibility, the liquid-liquid equilibria of different azeotropic mixtures with ionic liquids at 298.15 K and atmospheric pressure were accomplished. The experimental data were successfully correlated by applying the NRTL equation (Renon & Prausnitz, 1968), thus facilitating their implementation and use in computerized applications. The capacity of the selected ionic liquids as azeotrope breakers in liquid extraction processes was evaluated by means of the selectivity and the solute distribution ratio. This capacity was compared with other extracting solvents referred in literature.

From the analysis of all extraction capacities, the systems with the best results were selected to carry out the lab-scale extraction processes incorporating a solvent recycling stage. The operation conditions of the lab-scale extraction process were optimized by using HYSYS software. The optimized conditions were assessed in practice in a laboratory-scale packed column and the extraction efficiencies of the extraction processes in the packed column were calculated.

## 2. Experimental

### 2.1 Chemicals

1-Ethyl-3-methylimidazolium ethyl sulfate ( $[C_2MIM][EtSO_4]$ ) was purchased from Solvent Innovation with a purity  $\geq 99$  wt%. The others ionic liquids were synthesized according to procedure described in previous research (Pereiro et al., 2006a; Pereiro et al., 2007a; Pereiro et al., 2007b). NMR and positive FAB mass spectra were performed and the results are in agreement with literature. The ionic liquids were always used directly following the reduction of its water content to a mass fraction  $< 0.03\%$ , determined by Karl Fischer titration. Hexane (from Aldrich,  $\geq 99.0$  wt%), heptane (from Aldrich,  $\geq 99.0$  wt%), 2-butanone (from Merck, 99.5 wt%), 2-propanol (from Merck, 99.7 wt%), ethyl acetate (from Fluka, 99.8 wt%), cyclohexane (from Fluka, 99.8 wt%) and ethanol (from Merck,  $\geq 99.8$  wt%) were dried over 4 Å molecular sieves (supplied by Aldrich) for several weeks before use, and the purities were verified by means of gas chromatography.

## 2.2 Equipment and techniques

### 2.2.1 Experimental liquid- liquid equilibrium procedure

Ternary liquid-liquid equilibrium data were determined in a glass cell (Fig. 1a-b) containing a magnetic stirrer and thermostatted by a water jacket connected to a bath controlled to  $\pm 0.01$  K. The temperature in the cell was measured with an ASL F200 digital thermometer with an uncertainty of  $\pm 0.01$  K (Fig. 1c).

Two techniques were used to study the ternary liquid-liquid equilibrium. The first based on the experimental determination of the binodal curve, estimating the immiscible area. The second is grounded on the determination of the tie-lines, which calculates the composition of each layer.

The binodal curve was determined by adding known quantities of the three components corresponding to the immiscible area into the equilibrium cell. Then, we slowly added known quantities of solute maintaining the stirring until the “cloud point” disappears (Fig. 1a).

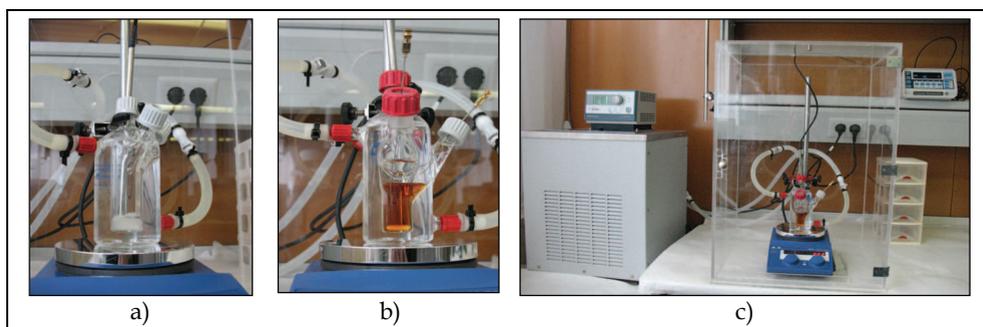


Fig. 1. (a)-(b) Liquid-liquid equilibria cells. (c) Experimental equipment used to determine of the liquid-liquid equilibria.

For the determination of the tie-lines, 30 ml of ternary mixture of known composition was added to the cell, the temperature was brought to  $298.15 \pm 0.01$  K, and the mixture was stirred vigorously for 1 h and left to settle for 4 h (Fig. 1b). Then, samples of both layers were taken with a syringe and the densities and refractive indices were determined. Lastly, the phase compositions were inferred by means of calibration curves which had been previously constructed at 298.15 K. These curves were obtained by fitting the composition on the binodal curve by means of refractive indices and densities at 298.15 K. The uncertainty of the phase composition is  $\pm 0.004$  in mass fraction. All weight measurements were performed in a Mettler AX-205 Delta Range balance with an uncertainty of  $\pm 10^{-4}$  mass fraction. Also, densities were measured with an Anton Paar DSA-48 digital vibrating tube densimeter with an uncertainty of  $\pm 2 \times 10^{-4}$  g cm<sup>-3</sup>. Finally, refractive indices were calculated via a Dr. Kernchen ABBEMAT WR automatic refractometer with an uncertainty of  $\pm 4 \times 10^{-5}$ .

### 2.2.2 Packed-column experiments

The practical performance of ionic liquids as azeotrope breakers in extraction processes was researched by using ionic liquids for continuous countercurrent separation of the azeotropic mixture in a  $54 \times 1585$  mm glass extraction column packed with  $8 \times 8$  mm Raschig rings to a height of 1475 mm (Fig. 2). The experiment was carried out at room temperature under

steady-state conditions. First, the azeotropic mixture and solvent streams were pumped in, the extract stream was pumped out (with FMI QV laboratory pumps) and the raffinate stream came out of the column under gravity. Then, samples from the top and bottom of the column were taken periodically and the composition was determined by analyzing their density and refractive index. At last, the ionic liquid was recovered from the extract stream and was recycled into the packed column after regeneration.

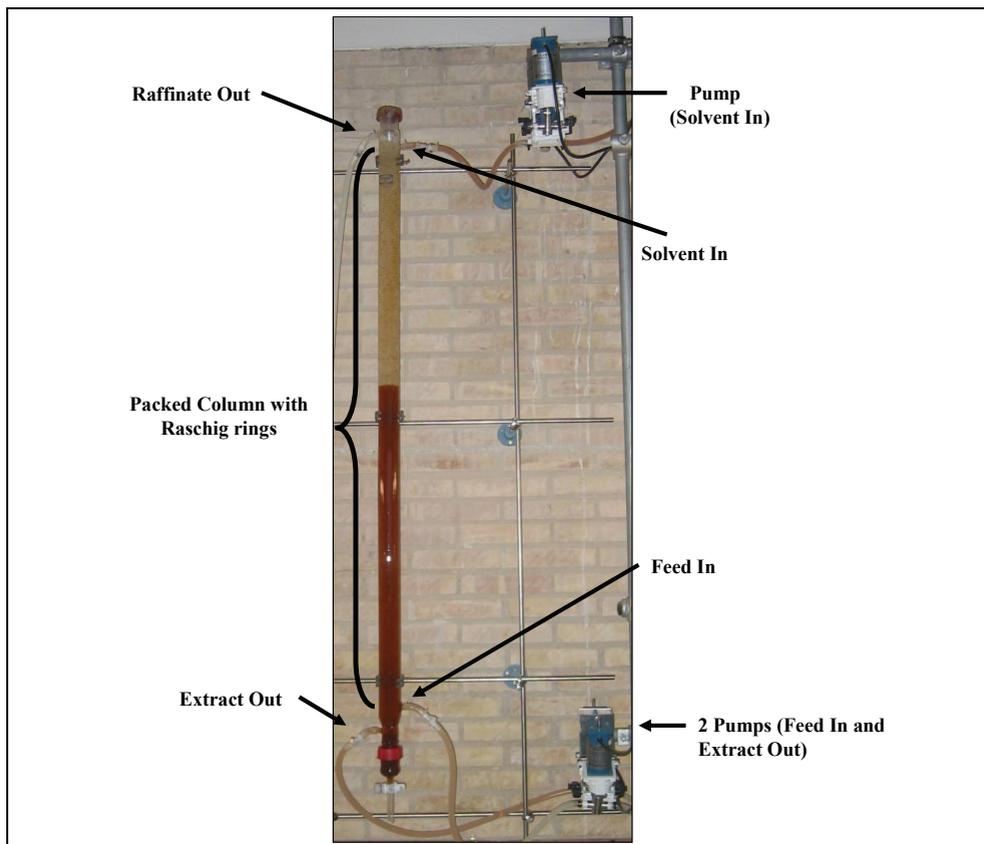


Fig. 2. Snapshot of the lab-scale packed countercurrent extraction column. The feed inlet, the raffinate and extract outlets are depicted, as well as the two pumps employed in the experimental set-up.

### 2.2.3 Regeneration of the Ionic Liquids

The ionic liquids used during these experiments were recovered and purified from the extract stream by removing the rest of its components in a Büchi R 3000 rotary evaporator with a vacuum controller. This operation is straightforward due to the fact that vapor pressure of ionic liquids is lower than the one of the rest of the components. The purity of the recovered ILs was verified by comparing its density at 298.15 K and NMR with the density and NMR of the freshly synthesized ones.

### 3. Results and discussion

#### 3.1 Liquid-liquid separation of the azeotropic mixtures

The implementation of a separation process requires the accurate knowledge and careful control of the thermodynamic properties of the mixture, especially the phase boundaries. In this study, ternary liquid-liquid equilibria of different azeotropic mixtures with ionic liquids as extraction agents (Table 1) were measured at 298.15 K and atmospheric pressure. The selected azeotropic mixtures are commonly used in different processes of coating industry, petrochemical and food industry. The separation of each azeotropic mixture is discussed in the following sections.

Azeotropic mixture	Ionic Liquids	Azeotropic mixture	Ionic Liquids
Ethanol + 2-Butanone	[C <sub>1</sub> MIM][MeSO <sub>4</sub> ]	Hexane+Ethanol	[C <sub>1</sub> MIM][MeSO <sub>4</sub> ]
	[C <sub>4</sub> MIM][PF <sub>6</sub> ]		[C <sub>4</sub> MIM][MeSO <sub>4</sub> ]
2-Propanol+2-Butanone	[C <sub>1</sub> MIM][MeSO <sub>4</sub> ]		[C <sub>2</sub> MIM][EtSO <sub>4</sub> ]
	[C <sub>4</sub> MIM][PF <sub>6</sub> ]		[C <sub>6</sub> MIM][PF <sub>6</sub> ]
2-Propanol+Ethyl acetate	[C <sub>1</sub> MIM][MeSO <sub>4</sub> ]		[C <sub>8</sub> MIM][PF <sub>6</sub> ]
	[C <sub>4</sub> MIM][PF <sub>6</sub> ]		[C <sub>1</sub> MIM][MeSO <sub>4</sub> ]
	[C <sub>6</sub> MIM][PF <sub>6</sub> ]	[C <sub>4</sub> MIM][MeSO <sub>4</sub> ]	
Hexane+Ethyl acetate	[C <sub>6</sub> MIM][PF <sub>6</sub> ]	[C <sub>2</sub> MIM][EtSO <sub>4</sub> ]	
	[C <sub>8</sub> MIM][PF <sub>6</sub> ]	[C <sub>6</sub> MIM][PF <sub>6</sub> ]	
Cyclohexane+2-Butanone	[C <sub>6</sub> MIM][PF <sub>6</sub> ]	[C <sub>8</sub> MIM][PF <sub>6</sub> ]	
	[C <sub>8</sub> MIM][PF <sub>6</sub> ]		

Table 1. Azeotropic mixture + ionic liquid systems analyzed by liquid-liquid equilibria at 298.15 K and atmospheric pressure.

Values of solute distribution ratio,  $\beta$ , and selectivity,  $S$ , are widely used parameters in assessing the solvent feasibility the in liquid-liquid extraction. The solute distribution ratio supplies the amount of ionic liquid required for the process, related to the capacity of the IL and the selectivity evaluate the efficiency of the ionic liquid used as solvent. These parameters are defined as follows:

$$\beta = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \quad (1)$$

$$S = \left( \frac{x_1^{\text{I}}}{x_1^{\text{II}}} \right) \cdot \left( \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \right) \quad (2)$$

where  $x$  is the mole fraction, subscripts 1 and 2 refer to inert and solute, respectively, and superscripts I and II indicate the organic (raffinate) and ionic liquid (extract) phases, respectively.

In order to perform simulation studies and process design, the experimental data were fitted with NRTL equation. The parameters were adjusted to minimize the difference between the experimental and calculated mole fraction defined as:

$$\text{O.F.} = \sum_{i=1}^n \left[ (x_{i1}^I - x_{i1}^I(\text{calc}))^2 + (x_{i2}^I - x_{i2}^I(\text{calc}))^2 + (x_{i1}^{II} - x_{i1}^{II}(\text{calc}))^2 + (x_{i2}^{II} - x_{i2}^{II}(\text{calc}))^2 \right] \quad (3)$$

where  $x_{i1}^I$ ,  $x_{i2}^I$ ,  $x_{i1}^{II}$ ,  $x_{i2}^{II}$  are the experimental mole fraction;  $x_{i1}^I(\text{calc})$ ,  $x_{i2}^I(\text{calc})$ ,  $x_{i1}^{II}(\text{calc})$  and  $x_{i2}^{II}(\text{calc})$  are the calculated mole fraction; and superscripts I and II indicate the organic (raffinate) and ionic liquid (extract) phases, respectively.

The deviations were calculated by applying the following expression:

$$\sigma = \left( \frac{\sum_i (x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}})^2}{6k} \right)^{1/2} \quad (4)$$

where  $x$  is the mole fraction and the subscripts  $i$ ,  $l$  and  $m$  provide the component, the phase and the tie - line, respectively. The  $k$  value refers to the number of experimental tie-lines.

### 3.1.1 Separation of alcohols + 2-Butanone

Traditionally, 2-butanone has been used as a solvent in paints and resin adhesives. A mixture of different alcohols with this ketone that form azeotropes is a very common product. Given the wide diversity of alcohol + ketone mixtures, study of the binary mixtures ethanol or 2-propanol with 2-butanone has been considered (Pereiro & Rodriguez, 2007c; Pereiro & Rodriguez, 2007d).

At present, the separation of these azeotropic mixtures is made by azeotropic distillation (Berg, 1995; Berg, 1999) using as entrainers: amyl acetate, methyl formate, 2,2-dimethyl butane or 2,3-dimethyl butane for the azeotrope ethanol + 2-butanone; and 3-methylpentane, amyl ether or acetonitrile for the azeotrope 2-propanol + 2-butanone.

The evaluation of  $[\text{C}_4\text{MIM}][\text{PF}_6]$  and  $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  as potential solvents in liquid -liquid extraction for the recovery of alcohols from the azeotropes was carried out through the analysis of liquid-liquid equilibrium data. Binodal curves and the tie lines were obtained for the mixtures of ethanol + 2-butanone +  $[\text{C}_4\text{MIM}][\text{PF}_6]$ , 2-propanol + 2-butanone +  $[\text{C}_4\text{MIM}][\text{PF}_6]$ , 2-butanone + ethanol +  $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  and 2-butanone + 2-propanol +  $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  at 298.15 K and atmospheric pressure.

The values of the selectivity for the studied ternary systems as a function of the solute composition in the organic phase are plotted in Figure 3. A comparison with conventional organic extractive solvents (Katayama et al., 1998; Katayama & Amano, 2005) was made and also depicted in the Figure 3.

All the selectivity values for all areas of the binodal curves are higher than unity, from which it can be inferred that the extraction of the solute from the azeotropic system is indeed possible. A comparison between the selectivity values for the ternary systems shows that the  $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  obtains higher values than  $[\text{C}_4\text{MIM}][\text{PF}_6]$  for the ethanol + 2-butanone and the opposite behavior is observed for 2-propanol + 2-butanone. In Figure 3a, the selectivity values at low concentration of ethanol for the ethanol + 2-butanone separation are similar in the  $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  and glycerol and higher than they are in water and  $[\text{C}_4\text{MIM}][\text{PF}_6]$ . On the other hand, for 2-propanol + 2-butanone, the selectivity values of the  $[\text{C}_4\text{MIM}][\text{PF}_6]$  are higher than for the other solvents and ionic liquid.

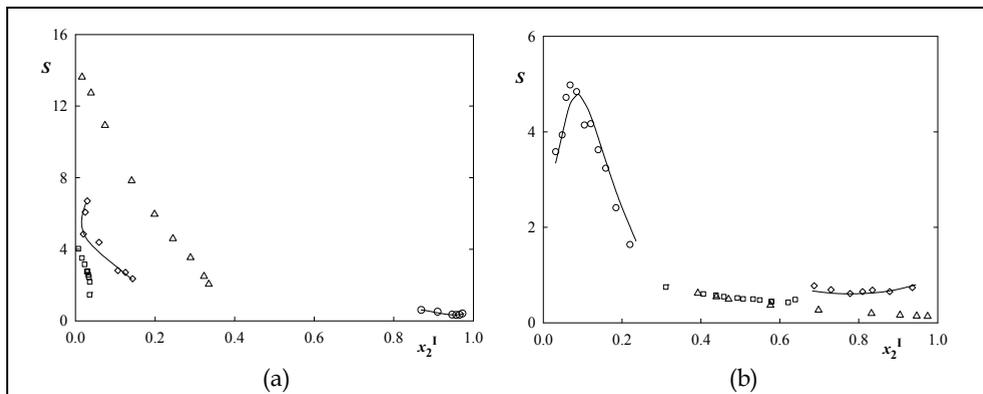


Fig. 3. Selectivity ( $S$ ) of the systems presenting azeotrope: (a) ethanol (1) + 2-butanone (2); (b) 2-propanol (1) + 2-butanone (2) where: O,  $[C_4MIM][PF_6]$  this work;  $\diamond$ ,  $[C_1MIM][MeSO_4]$  this work;  $\Delta$ , glycerol (Katayama et al., 1998);  $\square$ , water (Katayama & Amano, 2005); solid line, NRTL correlation as a function of the solute mole fraction (ethanol or 2-butanone) in the organic phases at 298.15 K.

### 3.1.2 Separation of 2-Propanol + Ethyl Acetate

The azeotropic mixture ethyl acetate + 2-propanol is present in the solvent extraction of edible oils (Bera et al., 2006). The liquid-liquid equilibrium data were obtained for the ternary mixtures of ethyl acetate + 2-propanol +  $[C_1MIM][MeSO_4]$ , 2-propanol + ethyl acetate +  $[C_4MIM][PF_6]$  and 2-propanol + ethyl acetate +  $[C_6MIM][PF_6]$  at 298.15 K and atmospheric pressure (Pereiro & Rodriguez, 2007e). The binodal curve for ternary mixture 2-propanol + ethyl acetate +  $[C_8MIM][PF_6]$  was also determined (Fig. 4).

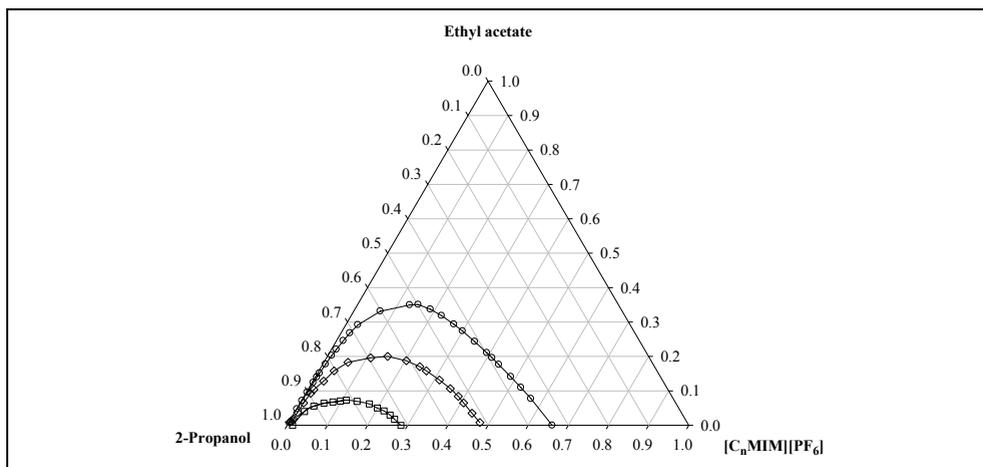


Fig. 4. Experimental binodal curves of the ternary systems 2-propanol (1) + ethyl acetate (2) +  $[C_nMIM][PF_6]$  (3) at 298.15 K, where: O,  $[C_4MIM][PF_6]$ ;  $\diamond$ ,  $[C_6MIM][PF_6]$ ; and  $\square$ ,  $[C_8MIM][PF_6]$ .

In Figure 4, it is observed how the immiscibility region decreases if the length of the alkyl chain in the imidazolium ring increases when the  $[C_nMIM][PF_6]$  was used as solvent in the liquid-liquid extraction.

The analysis of the LLE data (Pereiro & Rodriguez, 2007e) indicates that the alkyl chain length of the imidazolium ring plays a negative role in the capability of the  $[C_nMIM][PF_6]$  to purify the alcohol. This negative role may be caused mainly by the hydrophobic steric effect of the alkyl group which reduces the polar character of the secondary  $-OH$  group of 2-propanol. From the LLE data it is also verified that the use of  $[C_1MIM][MeSO_4]$  as solvent leads to higher values of solute distribution ratio and selectivity than the ionic liquids involving  $PF_6$  as the anion due to the fact that the  $MeSO_4$  ionic liquid contains just two  $-CH_3$  groups and the steric alkyl effect is reduced.

### 3.1.3 Separation of Hexane + Ethyl Acetate

The ILs  $[C_6MIM][PF_6]$  and  $[C_8MIM][PF_6]$  have been chosen for the separation of the azeotropic mixture hexane + ethyl acetate. This azeotrope is present in the process for purifying grafted polyolefins (Gupta & Carey, 2006), and its separation is made by azeotropic batch distillation (Rodriguez-Donis et al., 2005) with heterogeneous entrainers such as methanol, acetonitrile, water, and nitromethane. The evaluation of these two ILs as extraction solvents for the recovery of ethyl acetate from its mixture with hexane was carried out through the analysis of LLE (Pereiro & Rodriguez, 2008a).

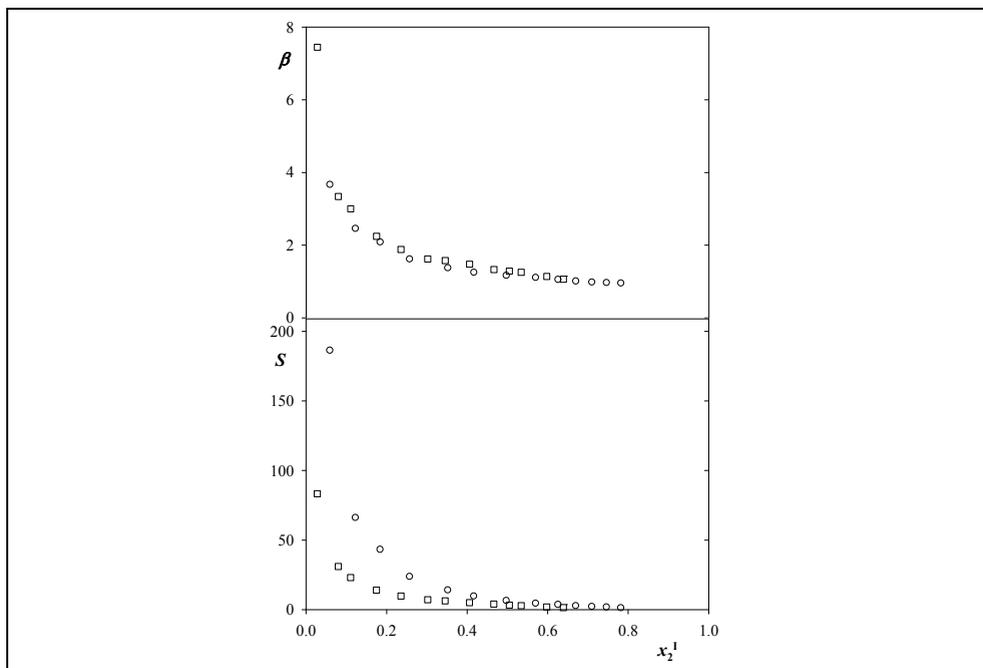


Fig. 5. Solute distribution ratio ( $\beta$ ) and selectivity ( $S$ ) of the systems presenting azeotrope hexane (1) + ethyl acetate (2) with: O,  $[C_6MIM][PF_6]$  and  $\square$ ,  $[C_8MIM][PF_6]$  versus ethyl acetate mole fraction in the organic phases at 298.15 K.

The solute distribution ratio (Eq. 1) provides the solvent capacity of the ionic liquid, related to the amount of ionic liquid required for the process. The selectivity (Eq. 2) is an important parameter to assess the efficiency of the ionic liquid used as solvent in the selective extraction of the solute from the azeotropic system. The values of the solute distribution ratio and selectivity for the studied ternary systems as a function of the solute composition in the organic phase are plotted in Figure 5.

A comparison between the selectivity values for the ternary systems shows that the  $[\text{C}_6\text{MIM}][\text{PF}_6]$  obtains better values than  $[\text{C}_8\text{MIM}][\text{PF}_6]$  for the removal of hexane from its azeotropic mixture with ethyl acetate.

### 3.1.4 Separation of Cyclohexane + 2-Butanone

The azeotropic mixture cyclohexane + 2-butanone occurs in the process for purifying grafted polyolefins (Gupta & Carey, 2006) and its separation is made by membrane in conjunction with a dephlegmation (Wijmans et al., 2005).

Liquid-liquid equilibrium data were obtained for the mixtures of cyclohexane + 2-butanone +  $[\text{C}_6\text{MIM}][\text{PF}_6]$  and cyclohexane + 2-butanone +  $[\text{C}_8\text{MIM}][\text{PF}_6]$  at 298.15 K and atmospheric pressure (Pereiro & Rodriguez, 2008b).

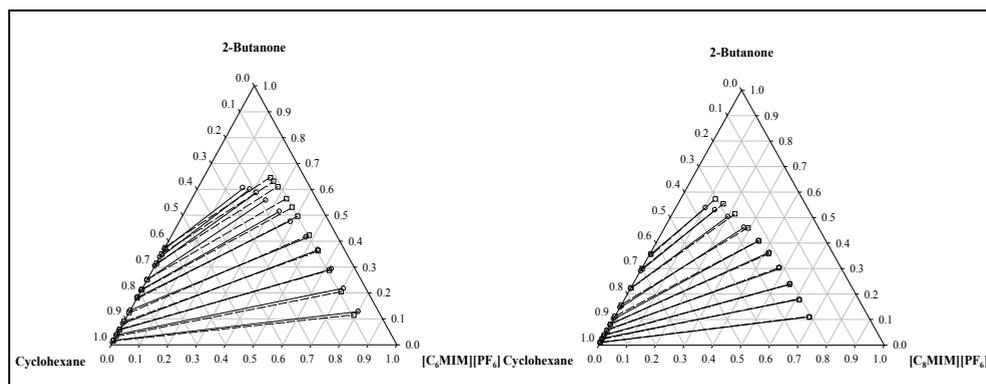


Fig. 6. Experimental tie-lines of the ternary systems at 298.15 K: (a) cyclohexane (1) + 2-butanone (2) +  $[\text{C}_6\text{MIM}][\text{PF}_6]$  (3); (b) cyclohexane (1) + 2-butanone (2) +  $[\text{C}_8\text{MIM}][\text{PF}_6]$  (3) where: O and solid line, experimental data; □ and dashed line, NRTL correlation.

The corresponding triangular diagrams with the experimental tie-lines for the studied systems are shown in Figure 6. An examination of this figure indicates a clear idea of the shape and the size of the immiscibility region of the systems. The positive slope shows that the solute goes preferentially to the solvent-rich phase. Another significant aspect is the fact that the ionic liquid does not enter in the organic-rich phase, *i.e.* the presence of  $[\text{C}_6\text{MIM}][\text{PF}_6]$  and  $[\text{C}_8\text{MIM}][\text{PF}_6]$  was not detected in the upper phase.

The use of  $[\text{C}_6\text{MIM}][\text{PF}_6]$  as solvent leads to higher values of selectivity (Pereiro & Rodriguez, 2008b) than the  $[\text{C}_8\text{MIM}][\text{PF}_6]$ , indicating that it would be a better choice as solvent for this azeotropic separation. The analysis of the data indicate that the increase of alkyl chain length of the imidazolium decreases the capability of the  $[\text{C}_n\text{MIM}][\text{PF}_6]$  to purify the cyclohexane from the azeotropic mixture.

### 3.1.5 Separation of Alkanes + Ethanol

As a result of the reduction of lead in gasoline, a growing number of processes in which alkanols and alkanes co-exist to produce oxygenated additives for gasolines are under development or have already reached the industrial production stage (Pucci, 1989). The azeotropic mixtures of either hexane or heptane with ethanol are chosen due to the difficulty that lies in separating them. The liquid-liquid separation leads to an environmentally friendly extraction process of these azeotropic mixtures as an alternative to azeotropic distillation (Laroche et al., 1991; Marwil, 1984), pervaporation (Okada & Matsuura, 1988) and reverse osmosis (Laatikainen & Lindstrom, 1986) which are procedures used for the separation of these azeotropes.

The  $[C_1MIM][MeSO_4]$ ,  $[C_4MIM][MeSO_4]$ ,  $[C_2MIM][EtSO_4]$ ,  $[C_6MIM][PF_6]$  and  $[C_8MIM][PF_6]$  ILs have been selected to act as azeotrope breakers for the alkanes + ethanol separation. Ternary liquid-liquid equilibria of these mixtures were determined at 298.15 K and atmospheric pressure (Pereiro et al., 2006b; Pereiro & Rodriguez, 2008c; Pereiro & Rodriguez, 2008d; Pereiro & Rodriguez, 2009a; Pereiro & Rodriguez, 2009b; Pereiro & Rodriguez, 2009c; Pereiro et al., 2010).

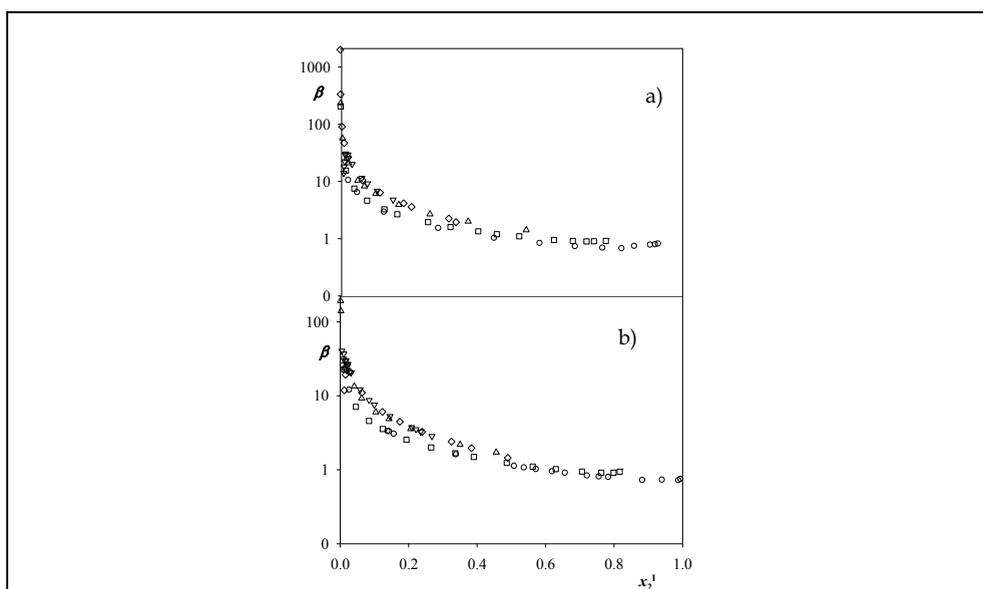


Fig. 7. Solute distribution ratio ( $\beta$ ) of the systems presenting azeotrope: (a) hexane (1) + ethanol (2); (b) heptane (1) + ethanol (2) where:  $\circ$ ,  $[C_6MIM][PF_6]$ ;  $\square$ ,  $[C_8MIM][PF_6]$ ;  $\triangle$ ,  $[C_1MIM][MeSO_4]$ ;  $\nabla$ ,  $[C_4MIM][MeSO_4]$ ; and  $\diamond$ ,  $[C_2MIM][EtSO_4]$  as a function of the solute mole fraction (ethanol) in the organic phase at 298.15 K.

The corresponding values for the solute distribution ratio of the studied ternary systems are plotted in Figure 7 as a function of the ethanol mass fraction in the organic-rich phase. High values of these parameters are desired and all ionic liquids are suitable for extraction processes. Although, by analysing the selectivity values (Pereiro & Rodriguez, 2009c) we can conclude that shorter alkyl chain on the imidazolium cation increases selectivity, being favourable for alkane/ethanol separation.

### 3.2 Lab-Scale extraction process

From the analysis of all extraction capacities, the systems composed by alkanes (hexane or heptane) + ethanol + ionic liquids with the methyl sulfate anion ( $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  and  $[\text{C}_4\text{MIM}][\text{MeSO}_4]$ ) were selected to carry out the lab-scale extraction process incorporating a solvent recycling stage (Pereiro & Rodriguez, 2008d; Pereiro & Rodriguez, 2009a; Pereiro & Rodriguez, 2009b; Pereiro & Rodriguez, 2009c). The use of alkylsulfate ILs as azeotrope breakers amplifies the selectivities and solute distribution ratio, encouraging us to test these ILs in our lab-scale extraction process.

#### 3.2.1 Selection of column operation conditions

Operating conditions for simulations and packed column experiments were selected in order to lessen cost while respecting the requirement of an elevated purity of the raffinate. Both cost and purity rise when the solvent/feed flow ratio in the column and/or the purity of the solvent stream increase. Moreover, the cost of solvent recovery grows when the purity is as high as desired. For that reason, this study has been carried out for solvent purities (ILs) of 70–100%. The restrictions applied on solvent stream were raffinate purities >85 wt% and solvent/feed ratio lower than 2.

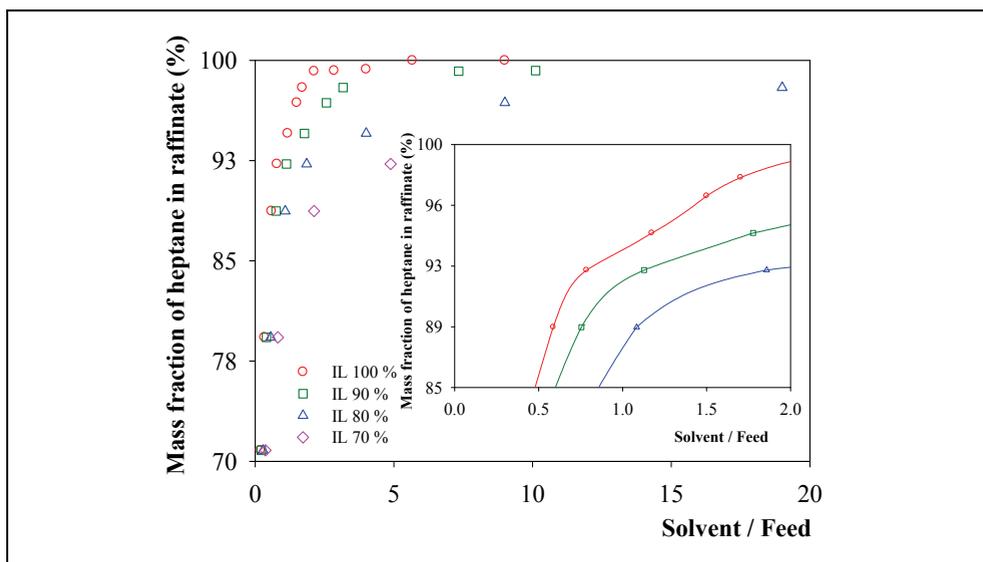


Fig. 8. Effect of solvent purity ( $[\text{C}_1\text{MIM}][\text{MeSO}_4]$ ) on the raffinate purity for the ternary system heptane + ethanol +  $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  at 298.15 K.

Figure 8 shows plots of raffinate purity alongside solvent/feed ratio calculated from the experimental tie line data for the ternary system heptane + ethanol +  $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  as illustrated in Figure 9, where is showed an example of a tie-line. Each point in Figure 8 corresponds to the crossing between the tie-line and the line that combine the feed (azeotrope) with solvent stream (IL stream with different purities). More details on this procedure can be found elsewhere (Pereiro & Rodriguez, 2008d).

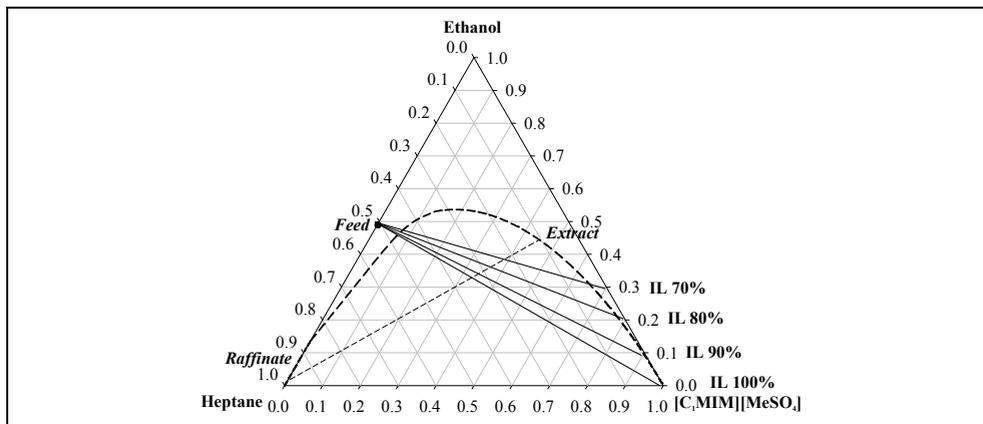


Fig. 9. Ternary diagram depicting the phase compositions for the *Raffinate* and *Extract* streams when an azeotropic mixture of heptane and ethanol (*Feed*) is mixed with  $[C_1MIM][MeSO_4]$  containing: 0% (100% IL), 10% (90% IL), 20% (80% IL), or 30% (70% IL) of ethanol in ratios corresponding to the crossing with the tie-line (dashed line).

### 3.2.2 Simulation results

The design of the extraction process was accomplished via HYSYS v.3.2 (Aspen Technology Inc., Cambridge, MA, USA) with the NRTL equation fitted to experimental tie-line data. The simulation model is illustrated schematically in Figure 10, where a liquid-liquid extractor with one equilibrium stage models the packed column and a short-cut distillation process models solvent recovery. As simulation constraints, the solvent and feed compositions were kept constant (in the region of the chosen theoretical operation conditions, as mentioned in the above sub-section), and the flow rates were optimized in order to maximize raffinate purity.

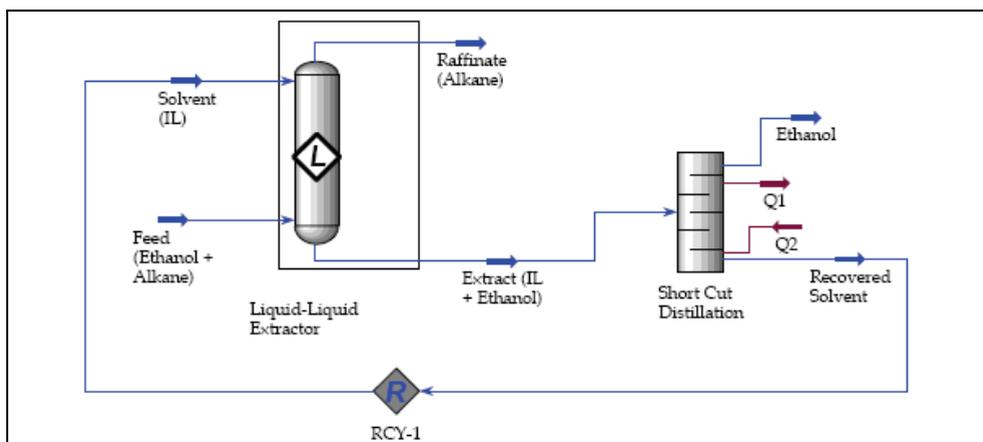


Fig. 10. Flowsheet simulation for the extraction process of ethanol + alkanes azeotropic mixtures using ionic liquid as solvent.

The ability of ionic liquids to act as azeotrope breakers in liquid-liquid extraction processes for the separation of the mixture ethanol + alkanes has been clearly proven by the performed simulations.

### 3.2.3 Results of packed-column experiments

The evolution of the alkane content observed in raffinate stream of the countercurrent column extraction experiment, carried out under operating conditions attained from the simulation results, is plotted in Figure 11. The amount of time needed to attain steady state, raffinate purity and the extract mass composition under steady state are outlined in Table 2.

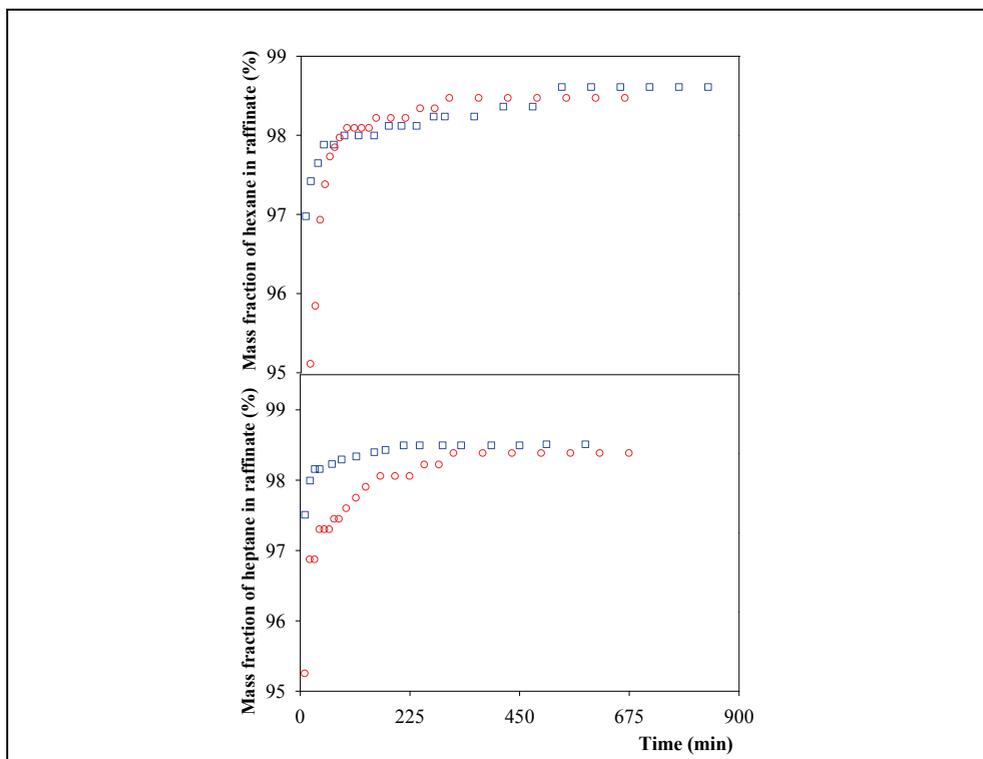


Fig. 11. Time dependence of the mass fractions of heptane in raffinate following start-up of the extraction column of Fig. 2 for:  $\circ$ ,  $[\text{C}_1\text{MIM}][\text{MeSO}_4]$ ; and  $\square$ ,  $[\text{C}_4\text{MIM}][\text{MeSO}_4]$ .

The extraction of alkane with a purity  $\geq 98$  wt. % was feasible by using the packed extraction column and the above mentioned ILs ( $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  and  $[\text{C}_4\text{MIM}][\text{MeSO}_4]$ ) as solvent. A comparison between packed column experimental data and theoretical data from experimental tie-lines is also depicted in Table 2. The performance of the experimental column exceeds the theoretical (from LLE) and simulation-based expectations, certainly due to the superior mixing between the feed and the solvent.

Figure 12 compares the compositions of the initial feed and the two outlet streams of the countercurrent packed column for the two ionic liquids ( $[\text{C}_1\text{MIM}][\text{MeSO}_4]$  and

[C<sub>4</sub>MIM][MeSO<sub>4</sub>]). The results indicate clearly that the [C<sub>1</sub>MIM][MeSO<sub>4</sub>] has a lower amount of alkane in the extract stream.

	Raffinate				Extract		
	% w <sub>1</sub> <sup>I</sup>	% w <sub>2</sub> <sup>I</sup>	% w <sub>3</sub> <sup>I</sup>		% w <sub>1</sub> <sup>II</sup>	% w <sub>2</sub> <sup>II</sup>	% w <sub>3</sub> <sup>II</sup>
Hexane + Ethanol + [C <sub>1</sub> MIM][MeSO <sub>4</sub> ]							
t = 305 min	98.5	1.5	0.0	t = 485 min	6.2	36.8	57.0
one equilibrium stage	89.8	9.9	0.3	one equilibrium stage	3.7	32.6	63.7
Hexane + Ethanol + [C <sub>4</sub> MIM][MeSO <sub>4</sub> ]							
t = 535 min	98.6	1.4	0.0	t = 655 min	9.4	36.4	54.2
one equilibrium stage	96.2	3.5	0.3	one equilibrium stage	10.0	38.1	51.9
Heptane + Ethanol + [C <sub>1</sub> MIM][MeSO <sub>4</sub> ]							
t = 315 min	98.4	1.6	0.0	t = 495 min	3.6	38.4	58.0
one equilibrium stage	88.7	10.6	0.7	one equilibrium stage	4.7	40.1	55.2
Heptane + Ethanol + [C <sub>4</sub> MIM][MeSO <sub>4</sub> ]							
t = 4 min	98.1	1.9	0.0	t = 8 min	11.9	46.0	42.1
one equilibrium stage	92.8	7.2	0.0	one equilibrium stage	10.5	44.0	45.5

Table 2. Comparison of experimental data under steady state for the extraction processes with theoretical data (from tie-lines) for the studied ternary systems.

In order to contrast the two ionic liquids for extraction processes in the packed column, the extraction efficiency,  $E$ , was calculated. This parameter indicates the ability of extraction solvent ([C<sub>1</sub>MIM][MeSO<sub>4</sub>] and [C<sub>4</sub>MIM][MeSO<sub>4</sub>]) to remove solute (ethanol) from the azeotropic mixtures (ethanol + alkanes) in the extraction column. This parameter is defined as follows:

$$E = \frac{w_1^F - w_1^R}{w_1^F - w_1^{Eq}} \quad (5)$$

where  $w$  is the mass fraction, subscript 1 refer to inert component (alkane) and superscripts F, R and Eq indicate the feed stream, raffinate stream and one equilibrium stage (theoretical data), respectively.

Azeotropic mixture	[C <sub>1</sub> MIM][MeSO <sub>4</sub> ]	[C <sub>4</sub> MIM][MeSO <sub>4</sub> ]
Hexane+Ethanol	1.81	1.14
Heptane+Ethanol	1.26	1.13

Table 3. Extraction efficiencies for the separation of the azeotrope alkanes + ethanol in the packed column.

In the separations of the azeotropes alkanes (hexane and heptane) + ethanol, the extraction efficiencies are listed in Table 3. The values obtained for [C<sub>1</sub>MIM][MeSO<sub>4</sub>] are better in comparison with those for [C<sub>4</sub>MIM][MeSO<sub>4</sub>]. Moreover, [C<sub>1</sub>MIM][MeSO<sub>4</sub>] has both lower viscosity and synthesized cost.

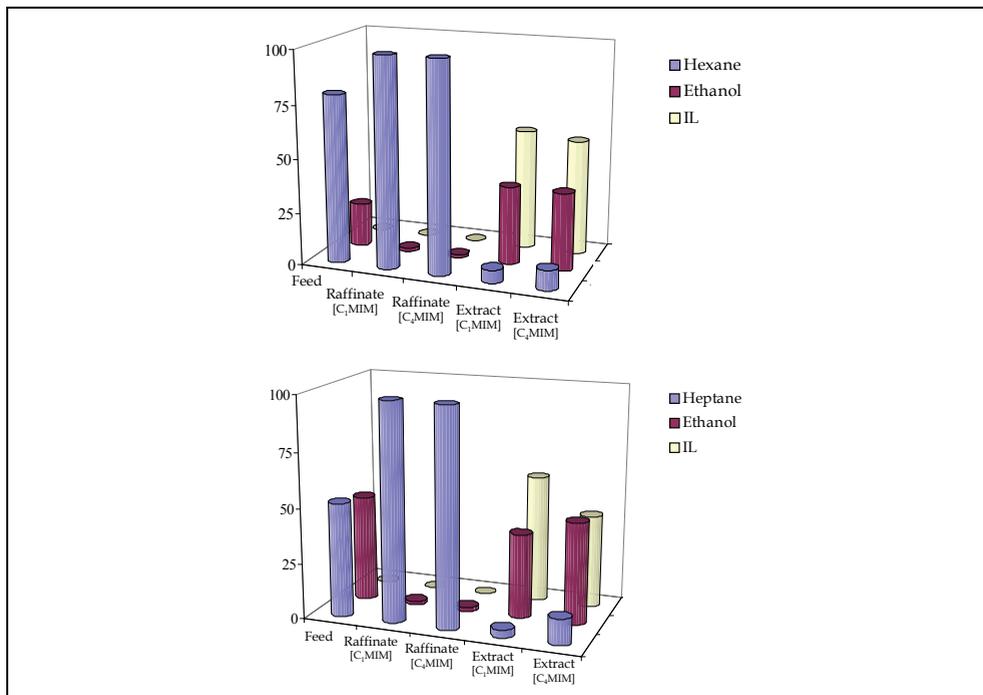


Fig. 12. Mass composition (%) of the feed, raffinate and extract streams of the packed column (Figure 2) under steady state conditions for  $[C_1MIM][MeSO_4]$  and  $[C_4MIM][MeSO_4]$ .

#### 4. Conclusion

The ability of different ILs as solvents for the separation of azeotropes by liquid-liquid extraction was demonstrated. The first approach for designing any extraction process should be addressed on the basis of several points: i) determination of LLE data for the ternary systems azeotropic mixtures + ILs, ii) correlation of the experimental data by means of theoretical equations, iii) evaluation of the extraction capacity with decisive parameters such as the solute distribution ratios and selectivities, iv) computational simulation to optimize the operating conditions, v) experimental lab-scale extraction process.

The alkyl sulfate-based ILs are the most promising alternative as solvents in the separation of the azeotropes studied in this work. The increase of the alkyl side chain length of the imidazolium ring plays a negative role in the extraction capability of the ionic liquids.

The extraction processes for the separation of the azeotropes ethanol plus alkanes were carried out with methyl sulfate-based ILs ( $[C_1MIM][MeSO_4]$  and  $[C_4MIM][MeSO_4]$ ). As it was proposed, the LLE data enabled the identification of theoretically appropriate operating conditions for countercurrent continuous extraction process at room-temperature including a solvent recycling stage. The operation conditions were subsequently optimized by simulation techniques. Experiments with a laboratory-scale packed column under steady-state conditions achieved a raffinate purity of over 98 wt %. The lab-scale experiments also confirmed the possibility of ready online recovery of selected ILs.

To contrast the different extraction processes in the packed column, the extraction efficiency was calculated. The values acquired for [C<sub>1</sub>MIM][MeSO<sub>4</sub>] are better than those for [C<sub>4</sub>MIM][MeSO<sub>4</sub>]. Moreover, [C<sub>1</sub>MIM][MeSO<sub>4</sub>] is considered the best candidate due to its lower viscosity and cost. If the raffinate purity of alkane obtained in the extraction process is taken into account, scaling up for industrial application seems viable. Some likely issues to be addressed in the near future include the scaling-up of the process in a pilot plant, to check the viability of the industrial application.

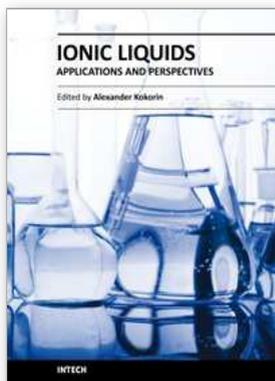
The use of ILs as azeotrope breakers should reduce the effects of the conventional solvents (VOCs) in the global climate change. This approach is an excellent opportunity to achieve the enhanced goals on reducing emissions of greenhouse gases established in the last United Nations Climate Conference (COP15).

## 5. References

- Arce, A.; Rodriguez, H.; Soto, A. (2007). Use of a green and cheap ionic liquid to purify gasoline octane boosters. *Green Chem.*, 9, 3, March 2007 247–253, 1463-9262
- Bera, D.; Lahiri, D.; De Leonardis, A.; De, K. B.; Nag, A. (2006). A Novel Azeotropic Mixture for Solvent Extraction of Edible Oils. *Agricultural Engineering International: the CIGR Ejournal.*, Manuscript FP 06 005, 8, April 2006 1–6, 1682-1130
- Berg, Lloyd. (1995). Separation of 2-butanone from isopropanol by azeotropic distillation. *U.S. Patent* 5423954, June 1995
- Berg, Lloyd. (1999). Separation of methyl ethyl ketone from ethanol by azeotropic distillation. *U.S. Patent* 5868907, February 1999
- Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. (2006). The distillation and volatility of ionic liquids. *Nature*, 439, 7078, February 2006 831–834, 0028-0836
- Gonzalez, E. J.; Calvar, N.; Gonzalez, B.; Dominguez, A. (2009). (Liquid plus liquid) equilibria for ternary mixtures of (alkane plus benzene plus [EMpy] [ESO<sub>4</sub>]) at several temperatures and atmospheric pressure. *J. Chem. Thermodyn.*, 41, 11, November 2009 1215-1221, 0021-9614
- Gupta, V. P.; Carey, E. P. (2006). Extraction of Impurities from Grafted Polyolefins. *U.S. Patent* 7060787, June 2006
- Holbrey, J. D.; Reichert, W. M.; Swatoski, R. P.; Broker, G. A.; Pitner, W. R.; Seddon, K. R.; Rogers, R. D. (2002). Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions. *Green Chem.* 4, 5, October 2002, 407–413, 1463-9262
- Hu, X.; Yu, J.; Liu, H. (2006). Separation of THF and water by room temperature ionic liquids. *Water Sci. Tech.*, 53, 11, 2006 245–249, 0273-1223
- Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.*, 3, 4, August 2001 156–164, 1463-9262
- Jork, C.; Seiler, M.; Beste, Y.-A.; Arlt, W. (2004). Influence of ionic liquids on the phase behavior of aqueous azeotropic systems. *J. Chem. Eng. Data*, 49, 4, July-August 2004 852–857, 0021-9568
- Katayama, H.; Hayakawa, T.; Kobayashi, T. (1998). Liquid-liquid equilibria of three ternary systems: 2-propanone-glycerol-methanol, 2-butanone-glycerol-ethanol, and 2-

- butanone-glycerol-2-propanol in the range of 283.15 to 303.15 K. *Fluid Phase Equilib.*, 144, 1-2, February 1998 157-167, 0378-3812
- Katayama, H.; Amano, K. (2005). Liquid-liquid equilibria of three ternary systems: Water plus 2-butanone plus aliphatic alcohols (Ethanol, 2-propanol and 1-propanol). *J. Chem. Eng. Japan*, 38, 7, July 2005 459-464, 0021-9592
- Laatikainen, M.; Lindstrom, M. (1986). Separation of methanol-ethanol and ethanol-normal-heptane mixtures by reverse-osmosis and pervaporation. *Acta Polytech Scandinavica Chem. Tech. Metall. Series*, 175, 1986 1-61, 1239-0518
- Laroche, L.; Bekiaris, N.; Andersen, H. W.; Morari, M. (1991). Homogeneous azeotropic distillation - comparing entrainers. *Can. J. Chem. Eng.*, 69, 6, December 1991 1302-1319, 0008-4034
- Letcher, T. M.; Deenadayalu, N. (2003). Ternary liquid-liquid equilibria for mixtures of 1-methyl-3-octyl-imidazolium chloride plus benzene plus an alkane at T-298.2 K and 1 atm. *J. Chem. Thermodyn.*, 35, 1, January 2003 67-76, 0021-9614
- Marwil, S. J. (1984). Separation of hydrocarbon and alcohol azeotropic mixtures by distillation with anhydrous ammonia. *U.S. Patent* 4437941, March 1984
- Najdanovic-Visak, V.; Esperanca, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydłowski, J. (2002). Phase Behaviour of Room Temperature Ionic Liquid Solutions: an Unusually Large Co-Solvent Effect in (Water + Ethanol). *Phys. Chem. Chem. Phys.*, 4, 10, 2002 1701-1703, 1463-9076
- Okada, T.; Matsuura, T. (1988). A study on the pervaporation of ethyl alcohol/heptane mixtures by porous cellulose membranes. *Proc. Int. Conf. Pervaporation Processes Chem. Ind.* 3, pp. 224-230
- Pereiro, A. B.; Santamarta, F.; Tojo, E.; Rodriguez, A.; Tojo, J. (2006a). Temperature dependence of physical properties of ionic liquid 1,3-dimethylimidazolium methyl sulfate. *J. Chem. Eng. Data*, 51, 3, May 2006 952-954, 0021-9568
- Pereiro, A. B.; Tojo, E.; Rodriguez, A.; Canosa, J.; Tojo, J. (2006b). HMImPF<sub>6</sub> ionic liquid that separates the azeotropic mixture ethanol + heptane. *Green Chem.*, 8, 3, March 2006 307-310, 1463-9262
- Pereiro, A. B.; Legido, J. L.; Rodriguez, A. (2007a). Physical properties of ionic liquids based on 1-alkyl-3-methylimidazolium cation and hexafluorophosphate as anion and temperature dependence. *J. Chem. Thermodyn.*, 39, 8, August 2007 1168-1175, 0021-9614
- Pereiro, A. B.; Verdia, P.; Tojo, E.; Rodriguez, A. (2007b). Physical properties of 1-butyl-3-methylimidazolium methyl sulfate as a function of temperature. *J. Chem. Eng. Data*, 52, 2, March-April 2007 377-380, 0021-9568
- Pereiro, A. B.; Rodriguez, A. (2007c). Ternary Liquid-Liquid Equilibria Ethanol + 2-Butanone + 1-Butyl-3-Methylimidazolium Hexafluorophosphate, 2-Propanol + 2-Butanone + 1-Butyl-3-Methylimidazolium Hexafluorophosphate, and 2-Butanone + 2-Propanol + 1,3-Dimethylimidazolium Methyl Sulfate at 298.15 K. *J. Chem. Eng. Data*, 52, 6, November 2007 2138-2142, 0021-9568
- Pereiro, A. B.; Canosa, J.; Rodriguez, A. (2007d). Liquid-liquid equilibria of 1,3-dimethylimidazolium methyl sulfate with ketones, dialkyl carbonates and acetates. *Fluid Phase Equilib.*, 254, 1-2, June 2007 150-157, 0378-3812

- Pereiro, A. B.; Rodriguez, A. (2007e). Ternary (liquid + liquid) equilibria of the azeotrope (ethyl acetate + 2 - propanol) with different ionic liquids at T = 298.15 K. *J. Chem. Thermodyn.*, 39, 12, December 2007 1608-1613, 0021-9614
- Pereiro, A. B.; Rodriguez, A. (2008a). Phase Equilibria of the Azeotropic Mixture Hexane + Ethyl Acetate with Ionic Liquids at 298.15 K. *J. Chem. Eng. Data*, 53, 6, June 2008 1360-1366, 0021-9568
- Pereiro, A. B.; Rodriguez, A. (2008b). Measurement and correlation of liquid - liquid equilibria of the azeotrope (cyclohexane + 2 - butanone) with different ionic liquids at T = 298.15 K. *J. Chem. Thermodyn.*, 40, 8, August 2008 1282-1289, 0021-9614
- Pereiro, A. B.; Rodriguez, A. (2008c). A study on the liquid-liquid equilibria of 1-alkyl-3-methylimidazolium hexafluorophosphate with ethanol and alkanes. *Fluid Phase Equilib.*, 270, 1-2, August 2008 23-29, 0378-3812
- Pereiro, A. B.; Rodriguez, A. (2008d). Azeotrope-breaking using [BMIM] [MeSO<sub>4</sub>] ionic liquid in an extraction column. *Sep. Purif. Technol.*, 62, 3, September 2008 733-738, 1383-5866
- Pereiro, A. B.; Rodriguez, A. (2009a). Separation of Ethanol-Heptane Azeotropic Mixtures by Solvent Extraction with an Ionic Liquid. *Ind. Eng. Chem. Res.*, 48, 3, February 2009 1579-1585, 0888-5885
- Pereiro, A. B.; Rodriguez, A. (2009b). Purification of hexane with effective extraction using ionic liquid as solvent. *Green Chem.*, 11, 3, March 2009 346-350, 1463-9262
- Pereiro, A. B.; Rodriguez, A. (2009c). Effective extraction in packed column of ethanol from the azeotropic mixture ethanol + hexane with an ionic liquid as solvent. *Chem. Eng. J.*, 153, 1-3, November 2009 80-85, 1385-8947
- Pereiro, A. B.; Deive, F. J.; Esperança, J. M. S. S.; Rodriguez, A. (2010). Alkylsulfate-based ionic liquids to separate azeotropic mixtures. *Fluid Phase Equilib.*, 291, 1, April 2010 13-17, 0378-3812
- Renon, H.; Prausnitz, J. M. (1968). Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.*, 14, 1, 1968 135-144, 0001-1541
- Pucci, A. (1989). Phase-equilibria of alkanol alkane mixtures in new oil and gas process-development. *Pure Appl. Chem.*, 61, 8, August 1989 1363-1372, 0033-4545
- Rodriguez-Donis, I.; Acosta-Esquivarosa, J.; Gerbaud, V.; Pardillo-Fondevila, E.; Joulia, X. (2005). Separation of n-hexane-ethyl acetate mixtures by azeotropic batch distillation with heterogeneous entrainers. *Chem. Eng. Process.*, 44, 1, January 2005 131-137, 0255-2701
- Seiler, M.; Jork, C.; Kavarnou, A.; Arlt, W.; Hirsch, R. (2004). Separation of azeotropic mixtures using hyperbranched polymers or ionic liquids. *AIChE J.*, 50, 10, October 2004 2439-2454, 0001-1541
- Swatloski, R. P.; Rogers, J. D.; Rogers, R. D. (2003). Ionic Liquids are not always Green: Hydrolysis of 1-Butyl-3-methylimidazolium Hexafluorophosphate. *Green Chem.*, 5, 4, August 2003 361-363, 1463-9262
- Wijmans, J. G.; Baker, R. W.; Mairal, A. P. (2005). Separation of organic mixtures using gas separation or pervaporation and dephlegmation. *U.S. Patent* 6899743, May 2005
- Zhang, D. L.; Deng, Y. F.; Li, C. B.; Chen, J. (2008). Separation of ethyl acetate-ethanol azeotropic mixture using hydrophilic ionic liquids. *Ind. Eng. Chem. Res.*, 47, 6, March 2008 1995-2001, 0888-5885



## **Ionic Liquids: Applications and Perspectives**

Edited by Prof. Alexander Kokorin

ISBN 978-953-307-248-7

Hard cover, 674 pages

**Publisher** InTech

**Published online** 21, February, 2011

**Published in print edition** February, 2011

This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Ana B. Pereiro and Ana Rodríguez (2011). Applications of Ionic Liquids in Azeotropic Mixtures Separations, *Ionic Liquids: Applications and Perspectives*, Prof. Alexander Kokorin (Ed.), ISBN: 978-953-307-248-7, InTech, Available from: <http://www.intechopen.com/books/ionic-liquids-applications-and-perspectives/applications-of-ionic-liquids-in-azeotropic-mixtures-separations>

# **INTECH**

open science | open minds

### **InTech Europe**

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
[www.intechopen.com](http://www.intechopen.com)

### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](#), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.