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Separation of Ethanol–Heptane Azeotropic Mixtures by Solvent Extraction with an Ionic Liquid

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Ionic liquids (ILs) are gaining attention as potential substitutes for classical organic solvents in extraction processes. This article reports the results of a study on the use of the IL 1,3-dimethylimidazolium methyl sulfate ([MMIM][MeSO₄]) as an extraction solvent in petrochemical processes for the removal of heptane from its mixtures with ethanol. The separation of heptane and ethanol is valuable but difficult because of the formation of an azeotropic mixture. Knowledge of the liquid–liquid equilibria (LLE) of this mixture is essential for the design of separation techniques. For this reason, the experimental LLE for the ternary system heptane + ethanol + [MMIM][MeSO₄] were investigated at 298.15 K. The solvent capacity of [MMIM][MeSO₄] was compared with those of other ILs. The extraction process derived from the use of this solvent was simulated using conventional software, and the obtained results are reported. Experimental data were obtained in a laboratory-scale packed-column extraction system for the separation of this azeotropic mixture using [MMIM][MeSO₄]. A comparison with the experimental column data for other ILs is included. Moreover, it is concluded that [MMIM][MeSO₄] has the highest extraction efficiency. Also, this IL can be recycled, meaning that the separation process results in a vast reduction of energy consumption.

1. Introduction

In many areas of industry, solvent mixtures usually accumulate because few are recycled. The separation of these mixtures into special components is necessary so that the separated parts can be reused in production cycles. However, most solvent mixtures contain azeotropic mixtures; thus, the separation of these azeotropes in a simple distillation becomes impossible.

As a result of the reduction of lead in gasoline, a growing number of processes in which alkanols and alkanes coexist to produce oxygenated additives for gasolines are under development or have already reached the industrial production stage.¹ Different azeotropes, e.g., heptane with ethanol, are present in these industrial processes. Extractive distillation is the most widely used process to remove the components in the azeotropic system. Yet, this process requires energy to obtain a fluid-phase system. On the other hand, liquid–liquid separation provides an environmentally friendly extraction process for the azeotropic mixture heptane + ethanol as an alternative to azeotropic distillation,² pervaporation,³ and reverse osmosis,⁴ because these procedures require the use of large amounts of energy, volatile organic compounds, or high pressures.

Ionic liquids (ILs) are molten salts that have received significant attention by the academic and industrial chemical community in recent years. They have come to be viewed as green and potentially environmentally friendly compounds. Their major characteristics include negligible vapor pressure at room temperature, stable liquid phase over a wide temperature range, high electrochemical stability, higher ionic conductivity than regular solvents, nonflammability, and lack of odor.^{5,6} ILs can be tailored for a specific application by accurately selecting the cation and anion.⁷ In other words, the solvent can be fine-tuned to optimize the chemical engineering and cost of the system.

Alkylsulfate imidazolium derivatives⁸ demonstrate the most promising potential for application in industrial processes 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. In this work, we study the behavior of an IL presenting a particularly attractive combination of these characteristics for the separation of heptane and ethanol, namely, 1,3-dimethylimidazolium methyl sulfate ([MMIM][MeSO₄]), which is one of the least expensive of the methyl sulfate imidazolium derivatives.

The separation process requires accurate knowledge and careful control of the thermodynamic properties of the mixture, especially the phase boundaries. In this article, ternary liquid–liquid equilibria (LLE) of heptane + ethanol + [MMIM][MeSO₄] were determined at 298.15 K and atmospheric pressure as a continuation of our study of azeotropic separation processes involving ILs as extraction agents.^{9–16} Likewise, the experimental data were successfully correlated by applying the NRTL equation,¹⁷ thus facilitating their implementation and use in computerized applications.

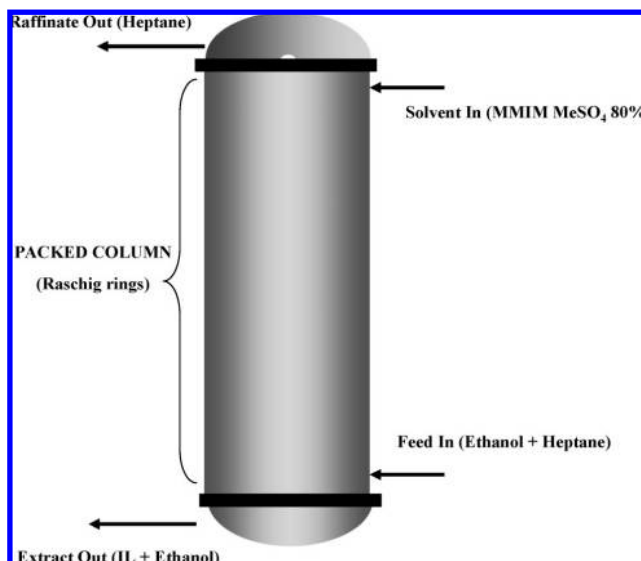


Figure 1. Packed countercurrent extraction column.

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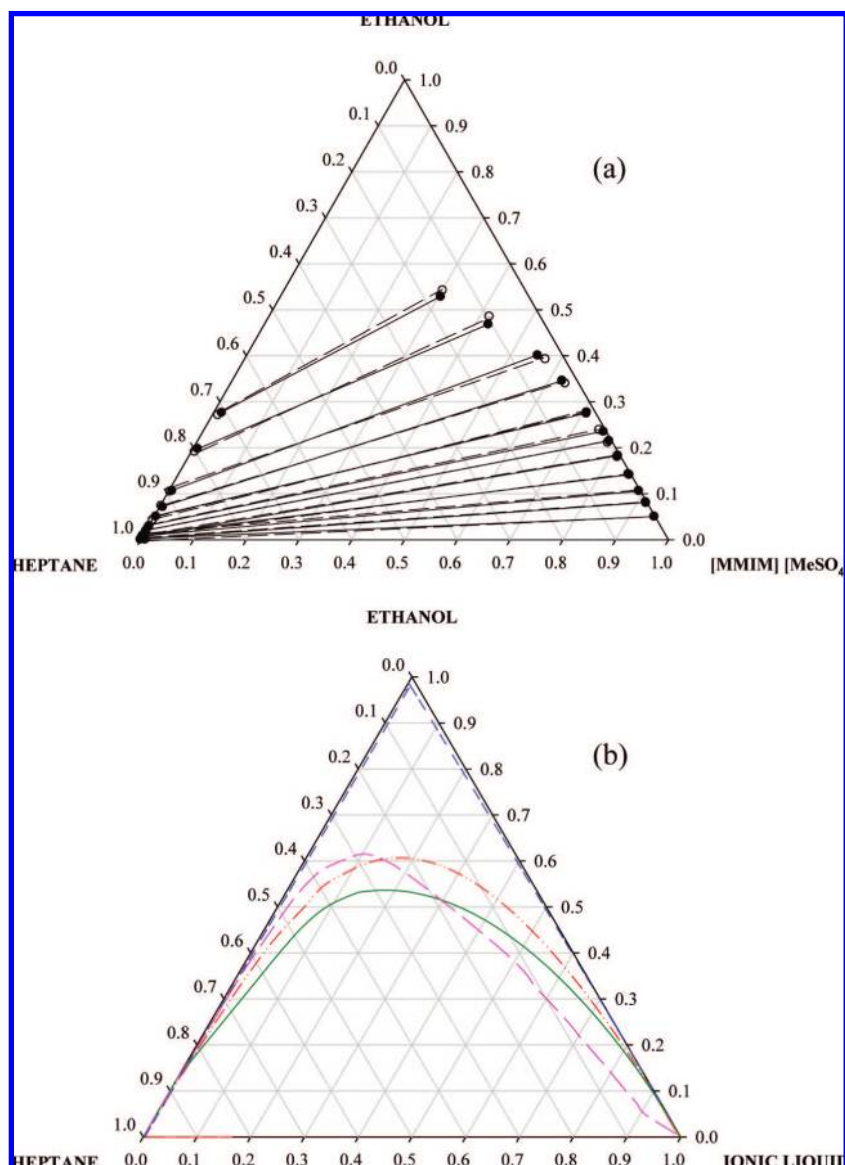


Figure 2. (a) Experimental LLE mass fraction tie lines of the ternary system heptane + ethanol + [MMIM][MeSO₄] at 298.15 K (●, solid lines) and tie lines according to the fitted NRTL equation (○, dashed lines). (b) Experimental binodal curves of the ternary systems heptane + ethanol + ionic liquid for different ionic liquids: (— · · —) [MMIM][MeSO₄], (—) [BMIM][MeSO₄], (---) 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF₆]), (— · —) 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF₆]).

[MMIM][MeSO₄] was evaluated in terms of the selectivity, solute distribution ratio, and extraction factor in order to investigate its capacity as a solvent in extraction processes. This capacity was compared with the capacities of other ILs. A simulation of the extraction process was performed using HYSYS software with the aim of optimizing operating conditions for continuous extraction of ethanol from the azeotropic mixture. The optimized conditions were evaluated in practice in a laboratory-scale packed column. The extraction efficiency of the [MMIM][MeSO₄] extraction process in the packed column was calculated and compared with the extraction efficiency of 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][MeSO₄]) under the same conditions, where the IL differs only in the alkyl chain on the imidazolium cation.

2. Experimental Methods

2.1. Materials. The nominal purities of heptane (Aldrich, ≥99.0 wt %) and ethanol (Merck, ≥99.8 wt %) were validated by means of gas chromatography. [MMIM][MeSO₄] was

synthesized as described in previous research.¹⁸ It resulted in NMR and positive FAB mass spectra in accordance with the literature. This IL was at all times employed immediately after the reduction of its water content to a mass fraction of <0.02% (as determined in a Karl Fischer 756 coulometer) by vacuum (2×10^{-1} Pa) at 343.15 K.

2.2. Regeneration of the IL. The removal of the other components in a Büchi R 3000 rotary evaporator with a vacuum controller allowed the recovery of [MMIM][MeSO₄] from the extract stream. The purity of this recovered compound was verified by contrasting its density at 298.15 K and NMR spectrum with the density and NMR spectrum of the freshly synthesized product.

2.3. Experimental LLE Procedure. Ternary LLE data were determined in a glass cell containing a magnetic stirrer that was thermostatted by a water jacket connected to a bath controlled to ± 0.01 K. An ASL F200 digital thermometer with an uncertainty of ± 0.01 K was employed to measure the temperature in the cell. For the LLE measurements, 30 mL of ternary mixture of known composition was added to the cell, the

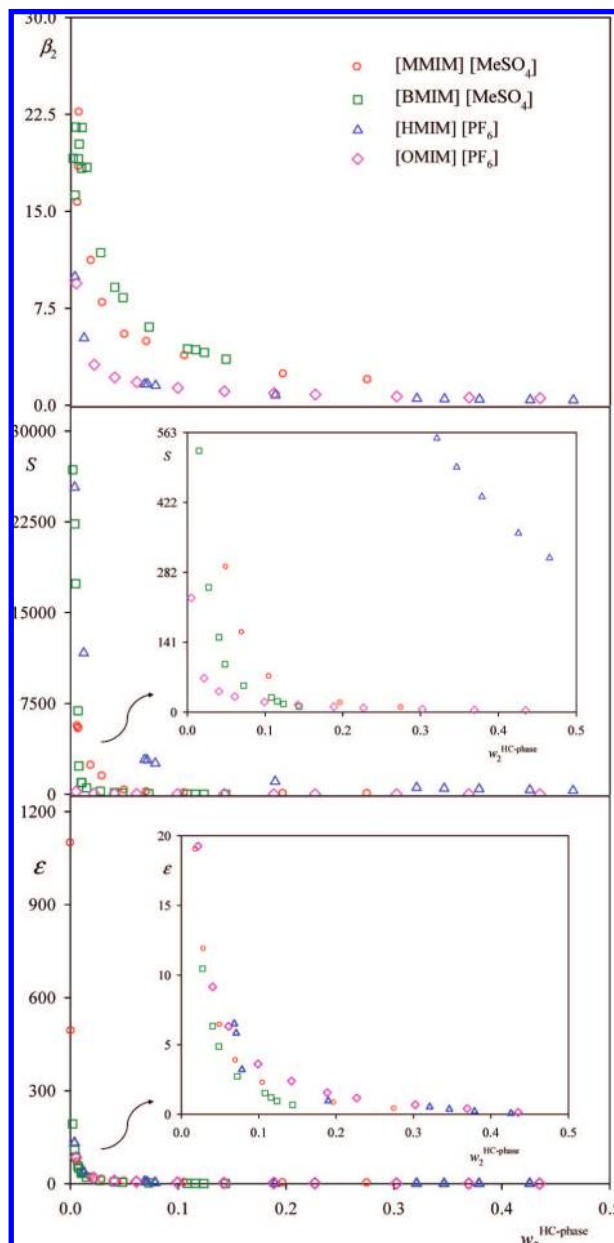


Figure 3. Plots of solute distribution ratio (β_2), selectivity (S), and extraction factor (ϵ) against mass fraction for the systems presenting ethanol + heptane azeotropes at 298.15 K.

Table 1. Parameters^a for the NRTL Equation Fitted to the Experimental Data for the Ternary System at 298.15 K

| components (i, j) | $g_{ij} - g_{ji}$ (J mol ⁻¹) | $g_{ji} - g_{ii}$ (J mol ⁻¹) |
|-----------------------|--|--|
| 1,2 | 6157.5 | -1238.3 |
| 1,3 | 11397 | 2074.9 |
| 2,3 | -6028.9 | -16320 |

^a $\alpha = 0.19$.

temperature was brought to 298.15 ± 0.01 K, and the mixture was mixed vigorously for 1 h and left to settle for 4 h. Then, samples of both layers were obtained with a syringe, and their densities and refractive indices were determined. Last, their compositions were inferred by means of calibration curves at 298.15 K that had been constructed beforehand. These curves were obtained by fitting the composition on the binodal curve by the use of refractive indices and densities at 298.15 K. The uncertainty of the phase composition resulted in an estimation of ± 0.004 in mass fraction. All weight measurements were

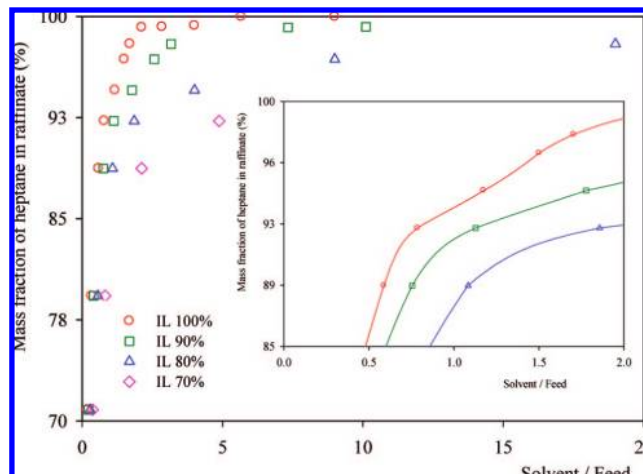


Figure 4. Effect of solvent (IL) purity on the dependence of the raffinate purity on the solvent/feed ratio, for the ternary system heptane + ethanol + [MMIM][MeSO₄] at 298.15 K. (Lines are merely aids to identification.)

carried out in a Mettler AX-205 Delta Range scale 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⁻³, and refractive indices were calculated via a Dr. Kernchen ABBE-MAT WR automatic refractometer with an uncertainty of $\pm (4 \times 10^{-5})$.

2.4. Packed-Column Experiments. The functional performance of [MMIM][MeSO₄] as a heptane + ethanol azeotrope breaker was tested by using it for continuous countercurrent separation of the azeotropic mixture in a 54×1585 mm glass extraction column packed with 8×8 mm Raschig rings to a height of 1475 mm (Figure 1). The experiments were carried out at room temperature under steady-state conditions with feed and solvent inflow rates of 1216 and 857 mL/h, respectively. First, the azeotropic mixture and solvent streams were pumped in, and the extract stream was pumped out with FMI QV laboratory pumps; the raffinate stream came out of the column at the top, and no pump was used. Then, samples from the top and bottom of the column were extracted at regular intervals for the determination of their composition according to their density and refractive index. Finally, [MMIM][MeSO₄] was retrieved online from the extract stream and was recycled into the packed column.

3. Results and Discussion

3.1. Liquid–Liquid Equilibrium. A triangular diagram with tie lines for heptane + ethanol + [MMIM][MeSO₄] is plotted in Figure 2a. The experimental data show that [MMIM][MeSO₄] and heptane are practically immiscible. A comparison of the binodal curves of [MMIM][MeSO₄] with those for other ILs^{13,16} is shown in Figure 2b. This figure provides a clear visualization of the change in the size and shape of the immiscibility region as a result of the increase in the length of the hydrocarbon side chain of the solvent cation and the change of the anion in the IL. It can be observed that the immiscibility region decreases when the length of the alkyl chain in the imidazolium ring increases. The difference between the solubilities is higher when hexafluorophosphate rather than methyl sulfate is used as the anion.

The ethanol mass distribution ratio (β_2), the selectivity (S), and the extraction factor (ϵ) are important parameters in

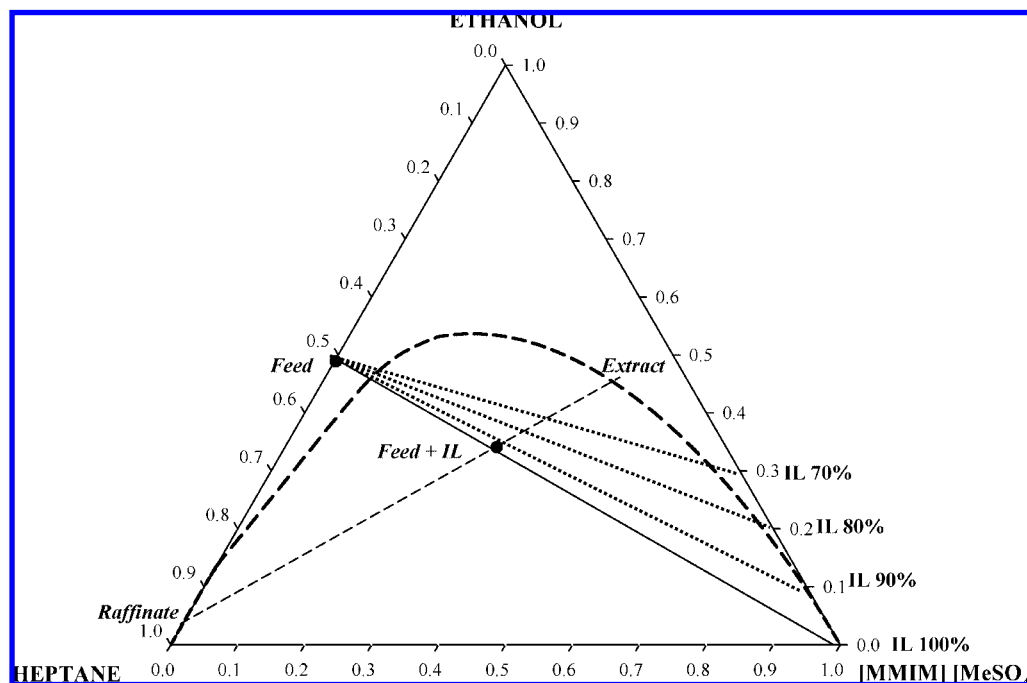


Figure 5. Ternary diagram for the prediction of phase compositions when an azeotropic mixture of heptane and ethanol (Feed) plus [MMIM][MeSO₄] containing 0% (100% IL), 10% (90% IL), 20% (80% IL), or 30% (70% IL) ethanol are mixed in ratios corresponding to the point labeled Feed + IL.

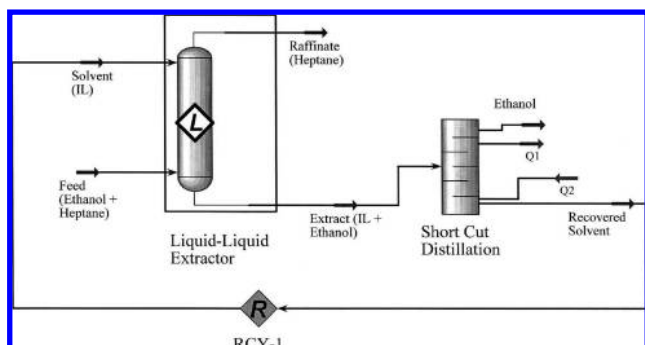


Figure 6. Extraction process flow sheet in the separation of the azeotropic mixture ethanol + heptane using [MMIM][MeSO₄] as a solvent.

Table 2. Properties of the Main Streams in the Extraction of Ethanol from Its Azeotropic Mixture with Heptane Using [MMIM][MeSO₄] as a Solvent

| | solvent | feed | raffinate | extract | ethanol |
|----------------------------|---------|--------|-----------|---------|---------|
| temperature (K) | 298.15 | 298.15 | 298.15 | 298.15 | 298.15 |
| pressure (kPa) | 101.32 | 101.32 | 101.32 | 101.32 | 101.32 |
| molar flow (g-mol/h) | 8.22 | 13.99 | 5.17 | 17.03 | 8.81 |
| mass flow (kg/h) | 1.0039 | 0.8944 | 0.4590 | 1.4393 | 0.4354 |
| liquid volume flow (mL/h) | 857.3 | 1216.0 | 656.8 | 1416.5 | 559.2 |
| component mass fraction | | | | | |
| heptane | 0 | 0.5172 | 0.8845 | 0.0395 | 0.1263 |
| ethanol | 0.2000 | 0.4828 | 0.1121 | 0.4038 | 0.8737 |
| [MMIM][MeSO ₄] | 0.8000 | 0 | 0.0038 | 0.5568 | 0 |

assessing the feasibility of use of a solvent in liquid-liquid extraction. These parameters are defined as follows:

$$\beta_2 = \frac{w_2^{\text{IL phase}}}{w_2^{\text{HC phase}}} \quad (1)$$

$$S = \left(\frac{w_1^{\text{HC phase}}}{w_1^{\text{IL phase}}} \right) \left(\frac{w_2^{\text{IL phase}}}{w_2^{\text{HC phase}}} \right) \quad (2)$$

$$\varepsilon = \frac{\beta_2 \text{Solv}}{F} \quad (3)$$

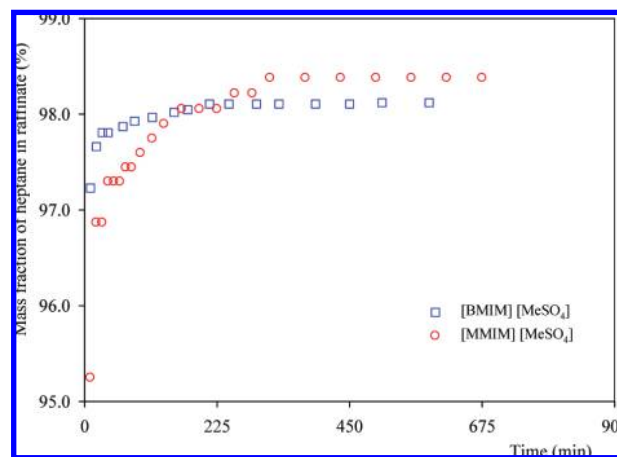


Figure 7. Time dependence of the mass fractions of heptane in the raffinate following startup of the extraction column of Figure 1 for (○) [MMIM][MeSO₄] and (□) [BMIM][MeSO₄].

The corresponding values for the solute distribution ratio, selectivity, and extraction factor for the studied ternary system are plotted in Figure 3 as a function of the solute mass fraction in the hydrocarbon-rich phase. The plotted data for the systems with other ILs were obtained from previous works.^{13,16} All ILs can be considered good, given that, as generally desired, they all give high values for the three parameters plotted. Although [HMIM][PF₆] shows a much higher selectivity than the other ILs, the ternary system heptane + ethanol + [HMIM][PF₆] presents solutropic behavior. This fact makes the use of this IL inadvisable.

Comparison of the experiments with the different ILs leads to the conclusion that a shorter alkyl chain on the imidazolium ion is favorable for heptane/ethanol selectivities. This behavior was also found for other ternary systems in the literature.^{19,20}

3.2. Correlation of LLE. To carry out simulation studies and process design, the experimental data were integrated by means of the NRTL equation. Previous works^{21–24} confirm that

Table 3. Comparison of Experimental Data in the Steady State for the Extraction Process with Theoretical Data for the Ternary System at 298.15 K

| | raffinate | | | | extract | | |
|----------------------------|------------------------------|------------------------------|------------------------------|-----------------------|------------------------------|------------------------------|------------------------------|
| | $w_1^{\text{HC phase}} (\%)$ | $w_2^{\text{HC phase}} (\%)$ | $w_3^{\text{HC phase}} (\%)$ | | $w_1^{\text{IL phase}} (\%)$ | $w_2^{\text{IL phase}} (\%)$ | $w_3^{\text{IL phase}} (\%)$ |
| [MMIM][MeSO ₄] | | | | | | | |
| $t = 315$ 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 |
| [BMIM][MeSO ₄] | | | | | | | |
| $t = 535$ min | 98.1 | 1.9 | 0.0 | $t = 655$ min | 11.8 | 46.0 | 42.2 |
| one equilibrium stage | 92.8 | 7.2 | 0.0 | one equilibrium stage | 10.5 | 44.0 | 45.5 |

the correlation equation is able to satisfactorily describe phase equilibria including electrolytes such as ionic liquids.

The parameters were adjusted to minimize the difference between the experimental and calculated mole fractions defined as

$$\text{OF} = \sum_{i=1}^n \{ [x_{1i}^{\text{HC phase}} - x_{1i}^{\text{HC phase}}(\text{calc})]^2 + [x_{2i}^{\text{HC phase}} - x_{2i}^{\text{HC phase}}(\text{calc})]^2 \} + \sum_{i=1}^n \{ [x_{1i}^{\text{IL phase}} - x_{1i}^{\text{IL phase}}(\text{calc})]^2 + [x_{2i}^{\text{IL phase}} - x_{2i}^{\text{IL phase}}(\text{calc})]^2 \} \quad (4)$$

Table 1 provides a list of the fitting parameters. The deviation was calculated by applying the expression

$$\sigma = \left[\frac{\sum_i (x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}})^2}{6k} \right]^{1/2} \quad (5)$$

The value of σ provides a measure of the accuracy of the correlation, which is 0.009 in this case. Figure 2a shows a comparison between the experimental data and those previously obtained from the NRTL equation; the NRTL equation is used to plot the liquid–liquid behavior of azeotropic mixtures.

3.3. Selection of Column Operating Conditions. Operating conditions for the simulation and packed-column experiment were chosen in order to minimize cost while respecting the need of an elevated purity of the raffinate. Both cost and purity rise when the solvent/feed flow ratio and the purity of the solvent stream increase. Furthermore, the cost of solvent recovery rises when the desired purity is superior ($\geq 98\%$). For solvent purities of 70–100%, Figure 4 shows plots of raffinate purity alongside solvent/feed ratio calculated from the experimental tie line data as illustrated in Figure 5, where Raffinate is the composition of the raffinate obtained from the Feed + IL stream composition

when the feed is the azeotropic heptane–ethanol mixture and the IL is pure. All solvent streams considered may result in theoretical raffinate purities >85 wt % within solvent/feed ratios ranging lower than 2. Not aiming at formal optimization, we have chosen a solvent/feed ratio of 1.1 and an 80% pure solvent stream, both of which afford a theoretical raffinate purity of 88.7 wt %, to be employed in further research.

3.4. Simulation Results. Figure 6 schematically illustrates the performance of the process. A liquid–liquid extractor with one equilibrium stage models the packed column in Figure 1. Also, solvent recovery is modeled by a short-cut distillation process. This process was optimized in the region of the chosen theoretical operating conditions via HYSYS v.3.2 (from Aspen Technology Inc., Cambridge, MA, USA) with NRTL equation fitted to the experimental tie line data. The solvent and feed compositions were kept invariable and flow rates were optimized to maximize raffinate purity. Table 2 lists the solvent and feed flow rates used in order to achieve a raffinate with a purity of 88.5 wt %. Distillation of the extract stream, which is about 56% [MMIM][MeSO₄], 40% ethanol and 4% heptane, affords the recovery of 80:20 solvent (recycled to the first column) and a mixture containing 87.4 wt % of ethanol. The ability of the IL as an azeotrope breaker in liquid–liquid extraction processes for the separation of the mixture heptane + ethanol has been attested.

3.5. Results of Packed-Column Experiments. The evolution of the heptane content of the raffinate observed in a packed-column countercurrent extraction experiment carried out under operating conditions approximating those prescribed by the simulation results is plotted in Figure 7. Times, raffinate purities, and stabilized extract mass compositions are shown in Table 3. The extraction of heptane with a purity of 98.4 wt % was feasible using a packed extraction column and [MMIM][MeSO₄] as the solvent. The experimental data for the ternary system heptane + ethanol + [BMIM][MeSO₄] listed in Table 3 were taken from a previous work.¹³ A comparison between the packed-column experimental data and the theoretical data from experimental tie lines is also shown in Table 3. The performance of the experimental column thus exceeds the theoretical and simulation-based expectations, certainly because of superior mixing between the feed and the solvent. Figure 8 shows a comparison between the compositions of the heptane + ethanol mixture in the initial feed and the streams obtained in the packed column with the two ILs. The results indicate that [MMIM][MeSO₄] has a lower amount of heptane in the extract stream.

To contrast the two extraction processes in the packed column, the extraction efficiency, E , was calculated. This parameter indicates the ability of the IL, i.e., [MMIM][MeSO₄] or [BMIM][MeSO₄], to remove ethanol from the azeotropic mixture of ethanol and heptane in the extraction column. This parameter is defined as follows:

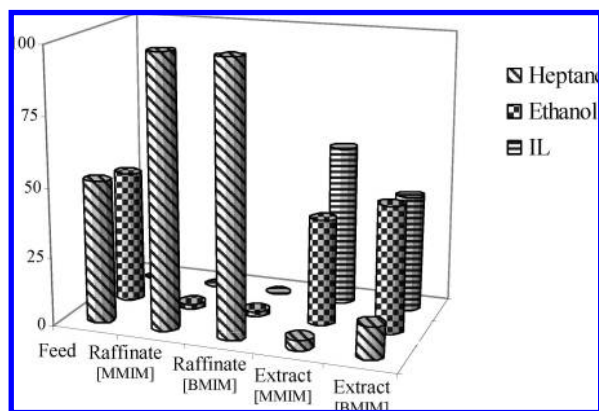


Figure 8. Mass compositions (%) of the feed, raffinate, and extract for the packed column of Figure 1 in the steady state for [MMIM][MeSO₄] and [BMIM][MeSO₄].

$$E = \frac{w_1^F - w_1^R}{w_1^F - w_1^{\text{Eq}}} \quad (6)$$

In the separation of the ethanol + heptane azeotrope, the extraction efficiency for [MMIM][MeSO₄] is 1.26, and that for [BMIM][MeSO₄] is 1.13. The values obtained for [MMIM]-[MeSO₄] are better than those for [BMIM][MeSO₄]. Moreover, [MMIM][MeSO₄] has both a lower viscosity and a lower cost than [BMIM][MeSO₄].

4. Conclusions

In this work, the experimental determination of LLE data for the ternary system heptane + ethanol + [MMIM][MeSO₄] at 298.15 K allowed the NRTL equation to be fitted. It also afforded the corresponding distribution ratios, selectivities, and extraction factors for the extraction of ethanol from azeotropic heptane + ethanol mixtures using [MMIM][MeSO₄]. These parameters were compared with those for [BMIM][MeSO₄], [HMIM][PF₆], and [OMIM][PF₆]. In general, ILs with the anion methyl sulfate show the best results. Moreover, these ILs do not degrade in the presence of water²⁵ or at high temperatures.²⁶ Such conditions can lead to the formation of HF in other ILs. This fact has weakened the use of the ILs based on the hexafluorophosphate anion.

The LLE data enabled the identification of theoretically appropriate operating conditions for a room-temperature countercurrent continuous extraction process including a solvent recycling stage; these conditions were optimized by simulation techniques. Experiments with a laboratory-scale packed column under steady-state conditions close to the simulated optimum achieved a raffinate purity of over 98.4 wt % and thus confirmed the possibility of ready online recovery of [MMIM][MeSO₄]. These results were compared with experimental data obtained with [BMIM][MeSO₄] as the solvent in terms of extraction efficiency. This parameter indicates that [MMIM][MeSO₄] would be a better choice as the solvent in this separation process. If the raffinate purity of heptane obtained in the extraction process is taken into account, scaling up for industrial applications seems feasible.

Acknowledgment

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Supporting Information Available: Comparison of the physical properties of the pure components at 298.15 K with recent literature values and composition of the tie lines end together with the values of solute distribution ratio and selectivity for the ternary mixture heptane + ethanol + [MMIM][MeSO₄] at 298.15 K and atmospheric pressure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Nomenclature

α = NRTL nonrandomness parameter
 β_2 = solute (ethanol) distribution ratio
 ε = extraction factor
 E = extraction efficiency
 F = feed ratio
 g_{ji} , g_{ii} = NRTL parameters
 k = number of experimental tie lines
 OF = objective function
 S = selectivity

$Solv$ = solvent ratio

σ = deviation

w = mass fraction

x = mole fraction

$x_{1i}^{\text{HC phase}}$, $x_{2i}^{\text{HC phase}}$, $x_{1i}^{\text{IL phase}}$, $x_{2i}^{\text{IL phase}}$ = experimental mole fractions

$x_{1i}^{\text{HC phase}}(\text{calc})$, $x_{2i}^{\text{HC phase}}(\text{calc})$, $x_{1i}^{\text{IL phase}}(\text{calc})$, $x_{2i}^{\text{IL phase}}(\text{calc})$ = calculated mole fractions

Superscripts

calc = calculated

exp = experimental

Eq = one equilibrium stage

F = feed stream

HC phase = hydrocarbon-rich phase

IL phase = ionic-liquid-rich phase

R = raffinate stream

Subscripts

i = component i

i, j = NRTL parameter indices

l = phase

m = tie line

1 = inert (heptane)

2 = solute (ethanol)

Literature Cited

- (1) Pucci, A. Phase equilibria of alkanol/alkane mixtures in new oil and gas process development. *Pure Appl. Chem.* **1989**, *61*, 1363.
- (2) Laroche, L.; Bekiaris, N.; Andersen, H. W.; Morari, M. Homogeneous azeotropic distillation—Comparing entrainers. *Can. J. Chem. Eng.* **1991**, *69*, 1302.
- (3) Okada, T.; Matsuura, T. A study on the pervaporation of ethyl alcohol/heptane mixtures by porous cellulose membranes. *Proc. Int. Conf. Pervaporation Processes Chem. Ind., 3rd* **1988**, 224.
- (4) Laatikainen, M.; Lindstrom, M. Separation of methanol—ethanol and ethanol—*n*-heptane mixtures by reverse osmosis and pervaporation. *Acta Polytech. Scand., Chem. Tech. Metall. Ser.* **1986**, 175, 61.
- (5) Huddleston, J. G.; Willauer, H. D.; Swatoski, R. P.; Visser, A. E.; Rogers, R. D. Room temperature ionic liquids as novel media for “clean” liquid—liquid extraction. *Chem. Commun.* **1998**, 16, 1765.
- (6) Fadeev, A.; Meagher, M. M. Opportunities for ionic liquids in recovery of biofuels. *Chem. Commun.* **2001**, 3, 295.
- (7) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, 3, 156.
- (8) Holbrey, J. D.; Reichert, W. M.; Swatoski, R. P.; Broker, G. A.; Pitner, W. R.; Seddon, K. R.; Rogers, R. D. Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-Dialkylimidazolium salts containing methyl- and ethyl-sulfate anions. *Green Chem.* **2002**, 4, 407.
- (9) Pereiro, A. B.; Tojo, E.; Rodriguez, A.; Canosa, J.; Tojo, J. HMImPF₆ ionic liquid that separates the azeotropic mixture ethanol + heptane. *Green Chem.* **2006**, 8, 307.
- (10) Pereiro, A. B.; Canosa, J.; Rodriguez, A. Liquid—liquid equilibria of 1,3-dimethylimidazolium methyl sulfate with ketones, dialkyl carbonates and acetates. *Fluid Phase Equilib.* **2007**, 254, 150.
- (11) Pereiro, A. B.; Rodriguez, A. Ternary (liquid + liquid) equilibria of the azeotrope (ethyl acetate + 2-propanol) with different ionic liquids at $T = 298.15$ K. *J. Chem. Thermodyn.* **2007**, 39, 1608.
- (12) Pereiro, A. B.; Rodriguez, A. 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* **2007**, 52, 2138.
- (13) Pereiro, A. B.; Rodriguez, A. Azeotrope-breaking using [BMIM]-[MeSO₄] ionic liquid in a extraction column. *Sep. Purif. Technol.* **2008**, 62, 735.
- (14) Pereiro, A. B.; Rodriguez, A. Phase Equilibria of the Azeotropic Mixture Hexane + Ethyl Acetate with Ionic Liquids at 298.15 K. *J. Chem. Eng. Data* **2008**, 53, 1360.

- (15) Pereiro, A. B.; Rodriguez, A. 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.* **2008**, *40*, 1282.
- (16) Pereiro, A. B.; Rodriguez, A. A study on the liquid–liquid equilibria of 1-alkyl-3-methylimidazolium hexafluorophosphate with ethanol and alkanes. *Fluid Phase Equilib.* **2008**, *270*, 23.
- (17) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *270*, 23.
- (18) Pereiro, A. B.; Santamarta, F.; Tojo, E.; Rodriguez, A.; Tojo, J. Temperature Dependence of Physical Properties of Ionic Liquid 1,3-Dimethylimidazolium Methyl Sulfate. *J. Chem. Eng. Data* **2006**, *51*, 952.
- (19) Arce, A.; Earle, M. J.; Rodriguez, H.; Seddon, K. R. J. Separation of Benzene and Hexane by Solvent Extraction with 1-Alkyl-3-methylimidazolium Bis{(trifluoromethyl)sulfonyl}amide Ionic Liquids: Effect of the Alkyl-Substituent Length. *Phys. Chem. B* **2007**, *111*, 4732.
- (20) Meindersma, G. W.; Podt, A.; Klaren, M. B.; De Haan, A. B. Separation of aromatic and aliphatic hydrocarbons with ionic liquids. *Chem. Eng. Comm.* **2006**, *193*, 1384.
- (21) Meindersma, G. W.; Podt, A.; De Haan, A. B. Ternary liquid–liquid equilibria for mixtures of an aromatic + an aliphatic hydrocarbon + 4-methyl-*n*-butylpyridinium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1814.
- (22) Letcher, T. M.; Reddy, P. Ternary liquid + liquid equilibria for mixtures of 1-hexyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate + benzene + an alkane at $T = 298.2$ K and $P = 0.1$ MPa. *J. Chem. Thermodyn.* **2005**, *37*, 415.
- (23) Hu, X.; Yu, J.; Liu, H. Liquid–liquid equilibria of the system 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate or 1-(2-hydroxyethyl)-2,3-dimethylimidazolium tetrafluoroborate + water + 1-butanol at 293.15 K. *J. Chem. Eng. Data* **2006**, *51*, 691.
- (24) Arce, A.; Earle, M. J.; Rodriguez, H.; Seddon, K. R. Separation of aromatic hydrocarbons from alkanes using the ionic liquid 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide. *Green Chem.* **2007**, *9*, 70.
- (25) Swatloski, R. P.; Rogers, J. D.; Rogers, R. D. Ionic liquids are not always green: Hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem.* **2003**, *5*, 361.
- (26) 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. Phase behaviour of room temperature ionic liquid solutions: an unusually large co-solvent effect in (water + ethanol). *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701.

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