



Effective extraction in packed column of ethanol from the azeotropic mixture ethanol + hexane with an ionic liquid as solvent

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ABSTRACT

Ionic liquids (ILs) are playing an increasingly important role in separation science. In this account, the application of ILs in all areas of separation including extraction, gas chromatography, and supported liquid membrane processes is highlighted. 1,3-Dimethylimidazolium methyl sulfate [MMIM] [MeSO₄] is suitable for use as solvent in the petrochemical extraction process for the removal of ethanol from its mixture with hexane. The knowledge of liquid–liquid equilibria (LLE) is essential for the design of the separation technique applied. For this reason, the experimental LLE for the ternary system hexane + ethanol + [MMIM] [MeSO₄] has been determined at 298.15 K. The solvent capacity of the [MMIM] [MeSO₄] is compared with other ILs. Extraction process with this solvent is simulated using conventional software and the obtained results are shown. Experimental data are obtained in a laboratory-scale packed column extraction system for the separation of this azeotropic mixture using [MMIM] [MeSO₄]. IL could be recycled and then the separating process reduces the energy consumption greatly.

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1. Introduction

The separation of hexane and ethanol is difficult due to the formation of an azeotropic mixture. The separation of this azeotrope in a simple distillation is impossible. 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 [1]. In these industrial processes, it is necessary that the separation of these azeotropic mixtures in their components and the separated parts can be reused in production cycles.

Extractive distillation is the most widely used process to remove the components in the azeotropic system, but this process needs energy to get a fluid phase system. Nevertheless, the liquid–liquid separation leads to an environmentally friendly extraction process of the azeotropic mixture hexane + ethanol as alternative to the azeotropic distillation [2], a procedure which requires the use of considerable amounts of energy, volatile organic compounds, or high pressures.

Ionic liquids (ILs) have received significant attention in recent years by the academic and industrial chemical community as green and potential environmentally friendly compounds. A major reason for the interest in ILs is their negligible vapor pressure at room temperature [3], which decreases the risk of worker exposure and

the loss of solvent to the atmosphere. Alkylsulfate imidazolium derivatives [4] are the most promising ILs to be applied in industrial processes. These ILs can be easily synthesized in an halide-free way at a reasonable cost, are chemically and thermally stable, and have low melting points and relatively low viscosity. These characteristics make ILs particularly attractive for separation processes, namely the one between hexane and ethanol azeotropic mixture. In this work we study the behaviour of 1,3-dimethylimidazolium methyl sulfate [MMIM] [MeSO₄] that is one of the cheapest of methyl sulfate imidazolium derivatives.

In order to continue our study of ILs and their physico-chemical properties [5–7], in this work, liquid extraction has been proposed as a promising recovery technique of ethanol from its azeotropic mixture with hexane. The separation process requires accurate knowledge and careful control of the phase boundaries. Taking into account this fact, ternary LLE of hexane + ethanol + [MMIM] [MeSO₄] are determined at 298.15 K and atmospheric pressure. Likewise, the experimental data are successfully correlated by applying the NRTL equation [8], thus facilitating their implementation and use in computerized applications. [MMIM] [MeSO₄] is evaluated using the selectivity, the solute distribution ratio and the extraction factor to investigate its capacity as solvent in liquid extraction process. This capacity is compared with other ILs [9]. A simulation of the extraction process is performed using the HYSYS software with the aim to optimize operation conditions for continuous extraction of ethanol from the azeotropic mixture. The optimized conditions are evaluated in practice in a laboratory-scale packed column.

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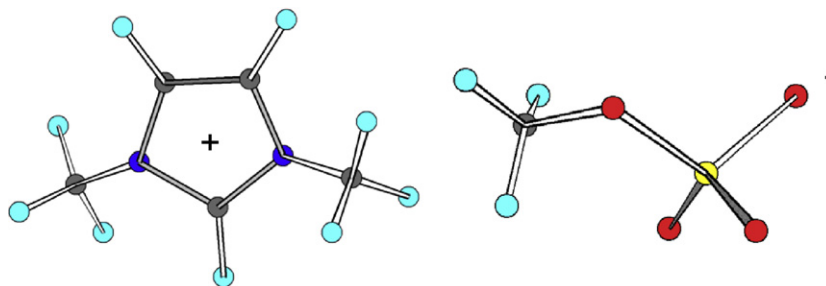


Fig. 1. Schematic structure in 3D of [MMIM] [MeSO₄].

2. Materials and methods

2.1. Materials

[MMIM] [MeSO₄] (as shown in Fig. 1) was synthesized as described in previous research [6]. NMR and positive FAB mass spectra were performed and the results are in close agreement with literature. This IL was always used directly following the reduction of its water content to a mass fraction <0.02% (as determined in a Karl Fischer 756 coulometer) by vacuum (0.2 Pa) at 343.15 K. The nominal purities of hexane (from Aldrich, >99.0%) and ethanol (from Merck, >99.8%) were verified by means of gas chromatography. Both solutes were dried over 3 Å molecular sieves before use.

2.2. Regeneration of the IL

[MMIM] [MeSO₄] was recovered and purified from the extract stream by removing the residual volatile compounds in a Büchi R 3000 rotary evaporator with a vacuum controller. This operation is straightforward due to the high vapor pressure of ethanol and hexane when compared with the almost null vapor pressure of the IL. After recovery of the IL, its purity was checked by comparison of its density at 298.15 K and NMR with the density and NMR of the freshly synthesized product.

2.3. Experimental LLE procedure

Ternary LLE data were determined in a glass cell containing a magnetic stirrer and was thermostatted by a water jacket connected to a bath controlled to ± 0.01 K. The temperature in the cell was measured with an ASL F200 digital thermometer with an uncertainty of ± 0.01 K. For the LLE measurements, 30 ml of ternary mixture of known composition was added to the cell, the 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 taken with a syringe and their densities and refractive indices were determined. Lastly, their 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 resulted in an estimation of ± 0.004 in mass fraction. All weighing was carried out 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 in the experimental measurements of ± 0.0002 g cm⁻³. A global uncertainty, taking into account all possible sources of error, was defined for the density as 0.2%. The purity of the sample, due to any possible contaminant or water, is the largest source of error in these measurements.

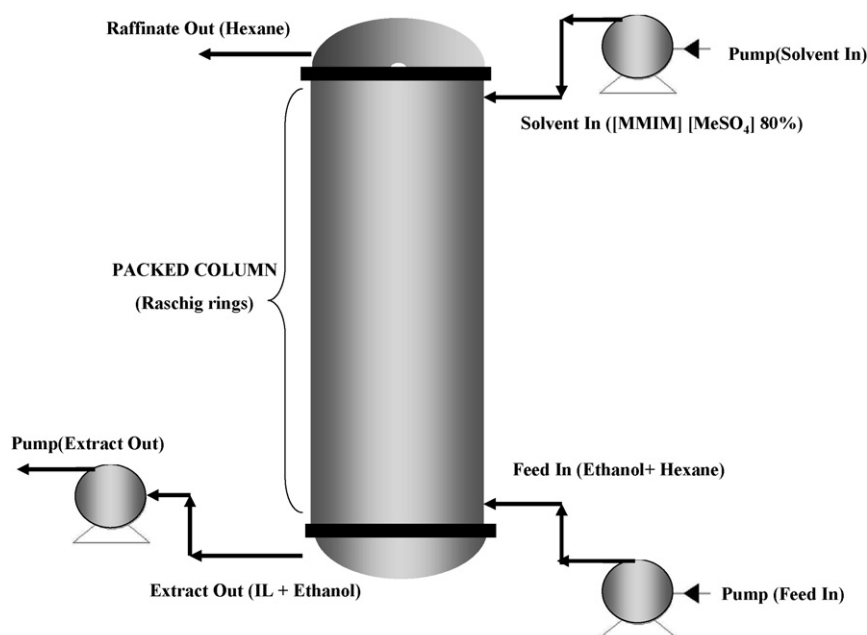


Fig. 2. The packed countercurrent extraction column.

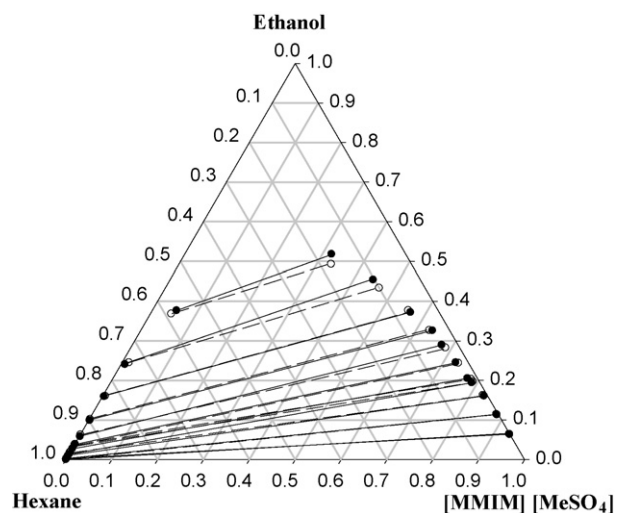


Fig. 3. Experimental LLE mass fraction tie-lines of the ternary system hexane + ethanol + [MMIM] [MeSO₄] at 298.15 K (●, solid lines), and tie-lines according to the fitted NRTL equation (○, dashed lines).

Finally, refractive indices were calculated via a Dr. Kernchen ABBEMAT WR automatic refractometer with an uncertainty of ± 0.00004 .

2.4. Packed column experiment

The practical performance of [MMIM] [MeSO₄] as a hexane+ethanol azeotrope breaker was investigated by using it for continuous countercurrent separation of the azeotropic mixture in a 54 mm × 1585 mm glass extraction column packed with 8 mm × 8 mm Raschig rings to a height of 1475 mm (as shown in Fig. 2). The experiment was carried out at room temperature under steady-state conditions with feed and solvent inflow rates of 1543 and 544 ml/h, respectively. First, the azeotropic mixture and solvent streams were pumped in, the extract stream was pumped out, all of them with FMI QV laboratory pumps. The raffinate stream came out of the column under gravity. Then, samples from the top and the bottom of the column were taken periodically for determination of their composition in relation to their density and refractive index. Lastly, [MMIM] [MeSO₄] was recovered on-line from the extract stream and was reused in the packed column.

Table 1
Composition of the experimental tie-lines, solute distribution ratio and selectivity for the ternary system hexane + ethanol + [MMIM] [MeSO₄] at 298.15 K.

Hydrocarbon-rich phase		Ionic liquid-rich phase		β_2	S
$w_1^{\text{HC-phase}}$	$w_2^{\text{HC-phase}}$	$w_1^{\text{IL-phase}}$	$w_2^{\text{IL-phase}}$		
0.999	0.000	0.001	0.063	118.68	167 156
0.996	0.003	0.003	0.113	32.97	9 426.9
0.990	0.010	0.008	0.161	16.10	2 035.1
0.986	0.013	0.018	0.194	14.61	814.80
0.971	0.028	0.022	0.205	7.36	328.57
0.960	0.039	0.027	0.245	6.29	221.94
0.940	0.058	0.035	0.289	4.99	132.16
0.898	0.099	0.038	0.326	3.29	78.49
0.837	0.159	0.063	0.372	2.34	31.24
0.751	0.240	0.103	0.454	1.89	13.80
0.570	0.376	0.162	0.518	1.38	4.85

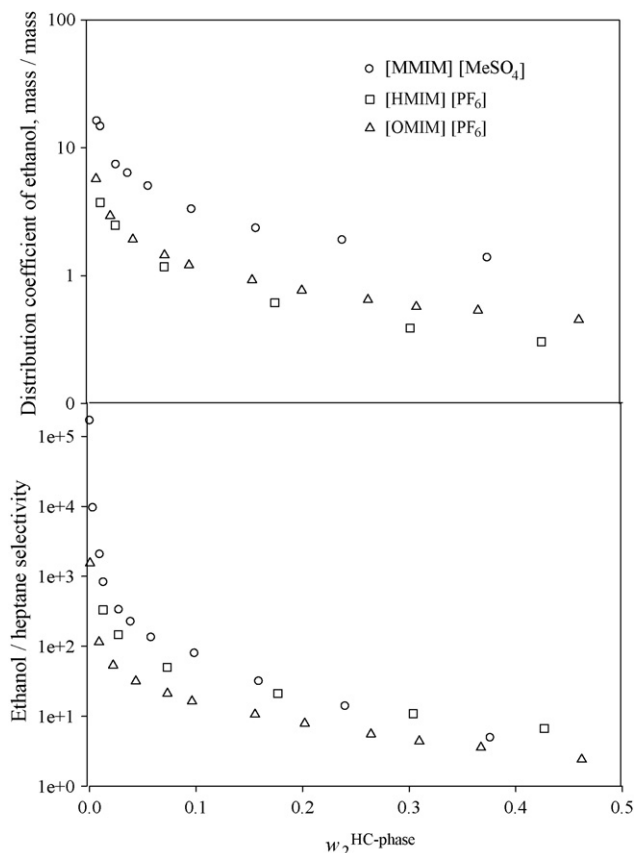


Fig. 4. Solute distribution ratio and selectivity with mass fraction of the system presenting azeotrope ethanol + hexane at 298.15 K.

3. Results and discussion

3.1. Liquid–liquid equilibrium

The triangular diagram with the tie-lines for the hexane+ethanol+[MMIM] [MeSO₄] is plotted in Fig. 3. The experimental data show that [MMIM] [MeSO₄] and hexane are practically immiscible. Together with the LLE data, Table 1 includes the corresponding values for the ethanol mass distribution ratio, β_2 , and the selectivity, S, which are widely used parameters in assessing the feasibility of utilizing the solvent in liquid–liquid extraction. These

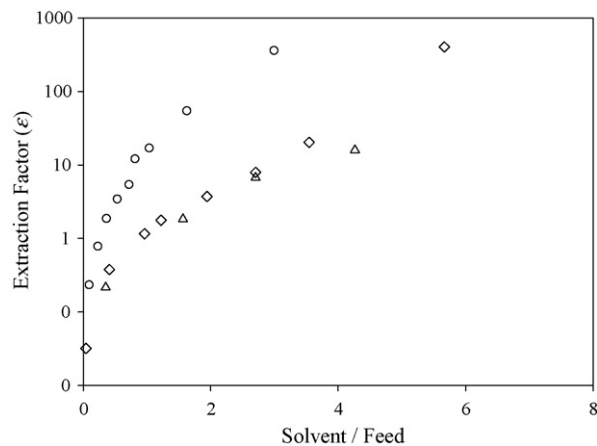


Fig. 5. Extraction factors plotted with solvent/feed ratio for the ternary systems: hexane + ethanol + IL, where (○) [MMIM] [MeSO₄]; (Δ) [HMIM] [PF₆]; (◇) [OMIM] [PF₆].

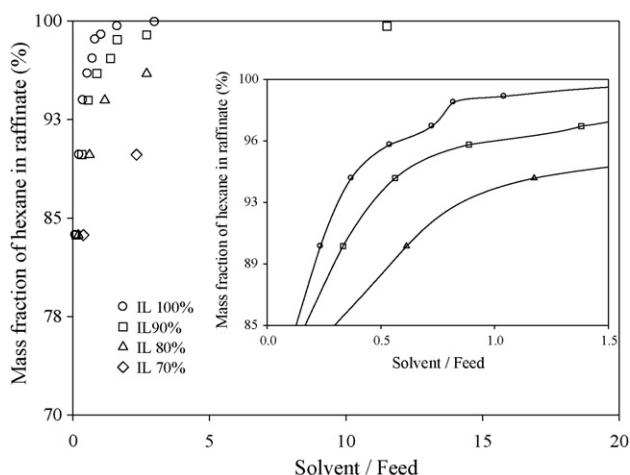


Fig. 6. Effect of solvent purity (IL) on the dependence of raffinate purity on solvent/feed ratio for the ternary system hexane+ethanol+[MMIM][MeSO₄] at 298.15 K (lines merely aids to identification).

parameters are defined as follows:

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

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

In these equations, w is the mass fraction; subscripts 1 and 2 indicate the hexane and the ethanol, respectively; and HC-phase and IL-phase indicate the hydrocarbon (top phase) and IL (bottom phase) rich phase, respectively. The corresponding values for the solute distribution ratio and selectivity for the studied ternary system are plotted in Fig. 4 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 a previous work [9]. High values of these parameters are desired and all ILs are suitable for extraction processes. Comparison of the experiments with different ILs leads to the conclusion that a shorter alkyl chain on the imidazolium

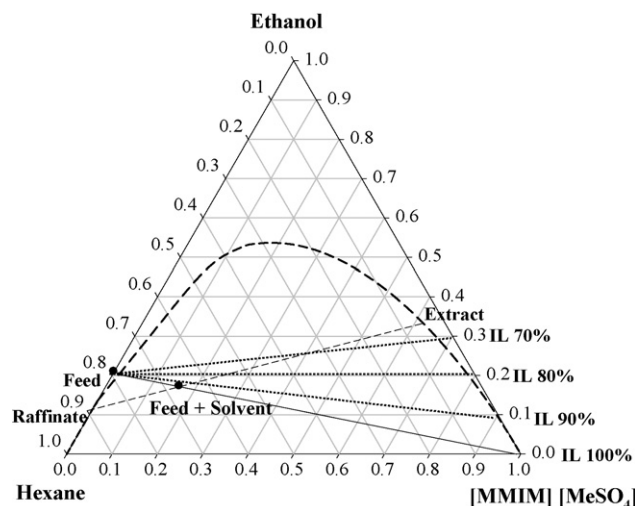


Fig. 7. Ternary diagram of the prediction of phase compositions when an azeotropic mixture of ethanol and hexane (feed) and [MMIM][MeSO₄] containing 0% (IL 100%), 10% (IL 90%), 20% (IL 80%) or 30% (IL 70%) of ethanol are mixed in ratios corresponding to the point labeled (Feed + Solvent).

cation increases selectivity, being favorable for hexane/ethanol separation.

An important characteristic that the IL should have to be a good extraction solvent is a high extraction factor, ε , which is defined:

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

where β_2 is ethanol mass distribution ratio, Solv and F are the solvent and feed ratios, respectively. Fig. 5 shows that in terms of the extraction factor, ε , the ILs with the anion methyl sulfate perform better at all solvent/feed ratios than do ILs based in the anion hexafluorophosphate.

3.1.1. Correlation of LLE

In order to perform simulation studies and process design, the experimental data are fitted with NRTL equation. Previous works confirm that the correlation equation is able to describe the phase

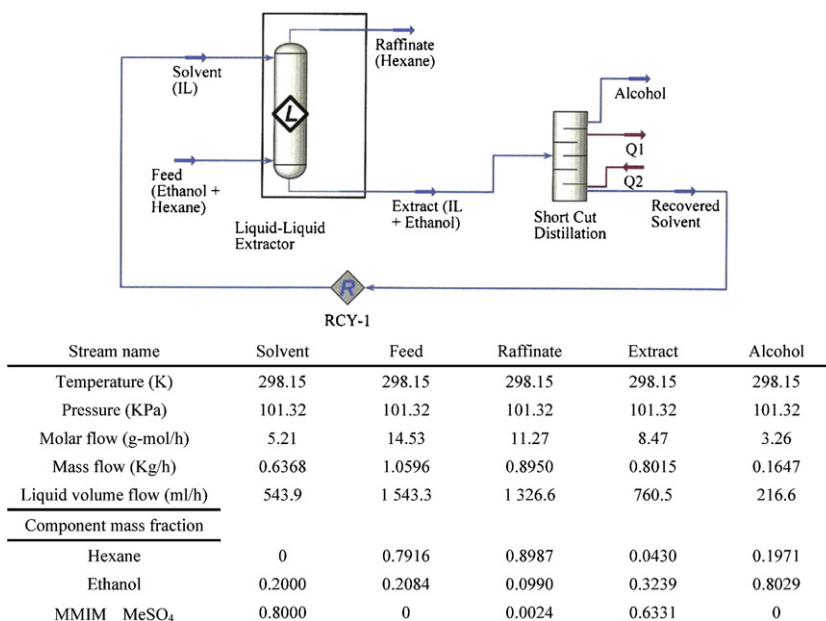


Fig. 8. Process flow sheet and properties of the main streams in the extraction of ethanol from its azeotropic mixture with hexane using [MMIM][MeSO₄] as solvent.

Table 2
NRTL equation parameters fitted to the experimental data for the ternary system at 298.15 K.

Components i, j	Parameters ($\alpha = 0.19$) $g_{ij} - g_{ji}$ (J mol ⁻¹)	$g_{ji} - g_{ii}$ (J mol ⁻¹)
1, 2	3,090.2	-5167.9
1, 3	29,197	15,196
2, 3	-14,837	-7,540.0

equilibria involving electrolytes like ILs [10–13] satisfactorily. The parameters were adjusted to minimize the difference between the experimental and calculated mole fraction defined as:

$$O.F. = \sum_{i=1}^n \left[(x_{1i}^{HC-phase} - x_{1i}^{HC-phase}(calc))^2 + (x_{2i}^{HC-phase} - x_{2i}^{HC-phase}(calc))^2 \right] + \sum_{i=1}^n \left[(x_{1i}^{IL-phase} - x_{1i}^{IL-phase}(calc))^2 + (x_{2i}^{IL-phase} - x_{2i}^{IL-phase}(calc))^2 \right] \quad (4)$$

where $x_{1i}^{HC-phase}$, $x_{2i}^{HC-phase}$, $x_{1i}^{IL-phase}$, $x_{2i}^{IL-phase}$ are the experimental mole fraction; $x_{1i}^{HC-phase}(calc)$, $x_{2i}^{HC-phase}(calc)$, $x_{1i}^{IL-phase}(calc)$ and $x_{2i}^{IL-phase}(calc)$ are the calculated mole fraction. The fitting parameters are listed in Table 2. The deviation was calculated by applying the following expression:

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

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.

The value of σ provides a measure of the accuracy of the correlation, in this case is 0.007. A comparison between the experimental data and those obtained from the NRTL equation is shown in Fig. 3 where the NRTL equation intends to map the liquid–liquid behaviour of the azeotropic mixture.

3.2. Column operation conditions

Operating conditions for the simulation and for the 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. For solvent purities between 70 and 100%, Fig. 6 shows plots of raffinate purity as a function of solvent/feed ratio calculated from the experimental tie-line data as illustrated in Fig. 7, where raffinate is the composition of the raffinate obtained from the Feed + Solvent stream composition when the feed is the azeotropic hexane–ethanol mixture and the IL is pure. All solvent streams considered may result in the-

Table 3
Comparison of experimental data in the steady state for extraction process with theoretical data for the separation of azeotropic mixture ethanol + hexane.

	Raffinate			Extract		
	% $w_1^{HC-phase}$	% $w_2^{HC-phase}$	% $w_3^{HC-phase}$	% $w_1^{IL-phase}$	% $w_2^{IL-phase}$	% $w_3^{IL-phase}$
[MMIM] [MeSO ₄]						
$t = 305$ min	98.5	1.5	0.0	$t = 485$ min	6.2	36.8
1 equilibrium stage	89.8	9.9	0.3	1 equilibrium stage	3.7	32.6
					57.0	63.7

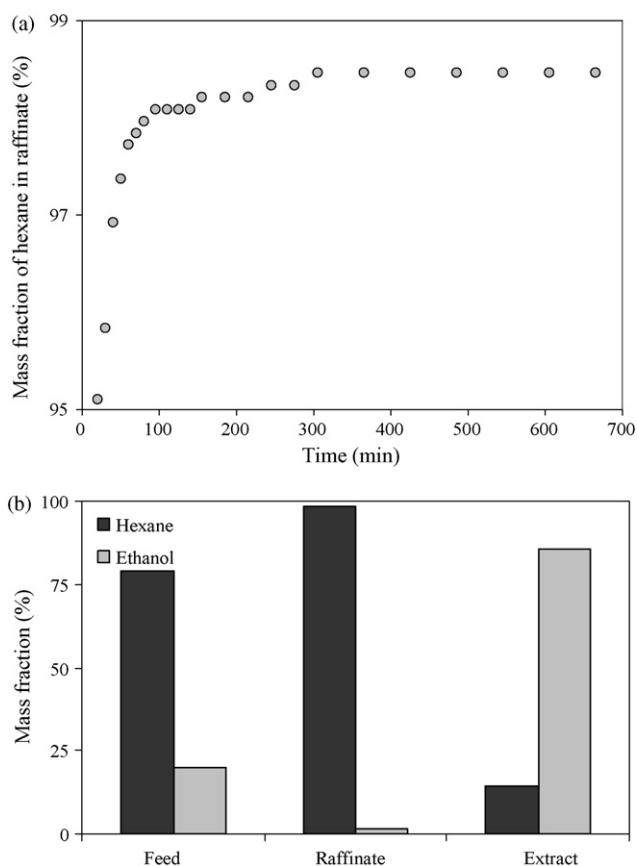


Fig. 9. (a) Time dependence of the mass fractions of hexane in raffinate following start-up of the extraction column for (●) [MMIM] [MeSO₄]. (b) Hexane and ethanol contents of the feed, raffinate and extract of the packed column in the steady state for [MMIM] [MeSO₄].

oretical raffinate purities >85% within solvent/feed ratios ranging lower than 1.5. We have chosen a solvent/feed ratio of 0.6 and 80% pure solvent stream, both of which afford a theoretical raffinate purity of 89.9%, to be employed in further research. These conditions were chosen without performing any optimization of the process.

3.2.1. Simulation results

The performance of the process shown schematically in Fig. 8, where a liquid–liquid extractor with an equilibrium stage models packed column and a short-cut distillation process models solvent recovery, was optimized in the neighborhood 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 constant, and flow rates were optimized in order to maximize raffinate purity. With the solvent and feed flow rates listed in Fig. 8, a raffinate with a purity of 89.9% was achieved. Distillation of the extract stream afforded the recovery of 80:20 solvent (recycled to the first column). The ability of the [MMIM] [MeSO₄]

as an azeotrope breaker in liquid–liquid extraction processes for the separation of the mixture hexane + ethanol showed promising data.

3.2.2. Results of packed column experiment

The evolution of the hexane content on 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 Fig. 9a. Times, raffinate purity and the extract mass composition stabilized are shown in Table 3. The extraction of hexane with a purity of 98.5% was feasible by using a packed extraction column and [MMIM] [MeSO₄] as solvent. Fig. 9b shows a comparison between the compositions of the mixture hexane + ethanol in the initial feed and the streams obtained in the packed column with the IL.

4. Conclusions

[MMIM] [MeSO₄] is suitable for use as solvent in the extraction process for the removal of ethanol from its azeotropic mixtures with hexane. Experimental determination of LLE data for the ternary system hexane + ethanol + [MMIM] [MeSO₄] at 298.15 K allowed NRTL equation to be fitted and afforded the corresponding distribution ratios and selectivities, and also extraction factors for the separation of ethanol from azeotropic hexane + ethanol mixture using [MMIM] [MeSO₄]. These parameters have been compared with [HMIM] [PF₆] and [OMIM] [PF₆]. In general, the IL with the anion methyl sulfate has the best results. Besides, these [MeSO₄]⁻ based ILs are considered more stable in the presence of water and at high temperatures than [PF₆]⁻ or [BF₄]⁻ based ones [14,15].

The LLE data allowed the identification of theoretically appropriate operating conditions for a room-temperature countercurrent continuous extraction process including a solvent recycling stage, and these conditions were optimized by simulation techniques. An experiment with a laboratory-scale packed column under steady-state conditions close to the simulated optimum achieved a raffinate purity of over 98.5% and confirmed the possibility of ready on-line recovery of [MMIM] [MeSO₄]. According to the purity of hexane in the raffinate stream obtained in the extraction process, scaling up for industrial application seems feasible.

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