Purification of hexane with effective extraction using ionic liquid as solvent

Ana B. Pereiro and Ana Rodriguez*

Received 13th August 2008, Accepted 6th January 2009
First published as an Advance Article on the web 5th February 2009
DOI: 10.1039/b814032d

The separation of hexane and ethanol is valuable but difficult due to the formation of an azeotropic mixture. This work demonstrates the ability of the ionic liquid (IL) 1-butyl-3-methylimidazolium methyl sulfate [BMIM][$MeSO_4$] to act as an extraction solvent in petrochemical processes for the removal of hexane from its mixture with ethanol. Knowledge of the phase behavior of the system is key in order to optimize the separation process. For this reason, the experimental liquid–liquid equilibrium (LLE) for the ternary system hexane + ethanol + [BMIM][$MeSO_4$] is investigated at 298.15 K. The separation sequence of the extraction process is checked by using conventional software for simulation. Experimental data are obtained in a laboratory-scale packed column extraction system for the separation of this azeotropic mixture by using [BMIM][$MeSO_4$]. It is concluded that this IL has the highest extraction efficiency.

Introduction

An increasing concern about the environment has recently directed the attention of the scientific community to novel processes based on greener technologies. The separation of azeotropic mixtures has conventionally been one of the most challenging tasks in industrial processes due to the fact that the separation of these azeotropes in a simple distillation is basically impossible. It is essential to separate these mixtures into special components so that the separated parts may be reused in production cycles.

The azeotrope ethanol with hexane is present in a growing number of processes aiming at the production of oxygenated additives for gasolines. Most of these processes, which are under development or have already reached the industrial production stage,[1] are created in order to achieve the reduction of lead in gasoline. Albeit extractive distillation is the most widely used process for the removal of the components in the azeotropic system, 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 ethanol with hexane as an alternative to azeotropic distillation,[2] a procedure which requires the use of considerable amounts of energy, volatile organic compounds, or high pressures.

Ionic liquids (ILs) are emerging as an appealing alternative in synthesis and extraction processes for the reduction of the amount of volatile organic solvents (VOSs) used in industry. ILs are receiving increasing attention due to notable properties such as negligible vapor pressure at room temperature, stable liquid phase over a wide temperature range, the possibility of designing the IL according to one's needs, high electrochemical stability, higher ionic conductivity in contrast with a regular solvent, non-flammability and non-odor.[3–5]

The separation of azeotropic mixtures is an engineering problem often solved by using extracting agents or entrainers. ILs due to a nonvolatile property have more advantages as entrainer than conventional organic compounds. Experimentally, ILs have exhibited the ability to separate azeotropic mixtures including ethanol + water[6,7] THF + water,[6–8] alcohols + alkanes mixtures,[9–11] aromatic + aliphatic mixtures,[12,13] ethyl acetate + alcohols,[14,15] ethyl acetate + hexane,[16] ketones + alkanes or alcohols mixtures,[17,18] and ethyl *tert*-butyl ether (ETBE) + ethanol.[19]

In this work, 1-butyl-3-methylimidazolium methyl sulfate [BMIM][$MeSO_4$] (Fig. 1) has been preliminarily selected according to its low melting point (well below room temperature), its relatively low viscosity (thus facilitating fluid flow and mass transfer), its low cost, its low toxicity and the fact that the anion [$MeSO_4$]$^-$ does not decompose in the presence of water[20] and at high temperatures[21] to bring about the corresponding acid.

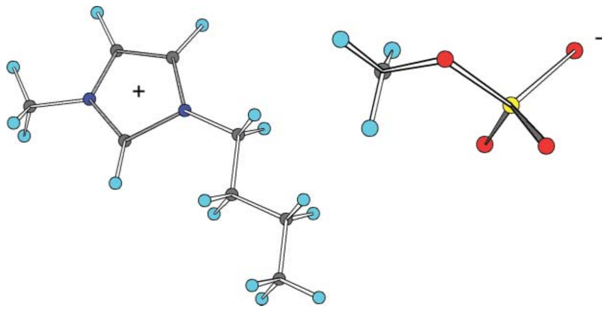

Fig. 1 Schematic 3D structure of [BMIM][$MeSO_4$].

For all the reasons explained above, [BMIM][$MeSO_4$] seems to be a good candidate to be tested as an extracting solvent or entrainer in purifying of hexane from its mixture with ethanol. In order to evaluate such a possibility, in this work we carry out an equilibrium thermodynamic study of the ternary system hexane + ethanol + [BMIM][$MeSO_4$]. Its liquid–liquid equilibrium (LLE) at 298.15 K and atmospheric pressure are

---

Department of Chemical Engineering, University of Vigo, P. O. Box 36310, Vigo, Spain. E-mail: aroguez@uvigo.es; Fax: +34 986 81 23 80; Tel: +34 986 81 23 12

determined. The experimental data are successfully correlated, thus facilitating their implementation and use in computerized applications. The capacity of [BMIM][MeSO$_4$] as a solvent in liquid extraction processes is evaluated by using both the selectivity and the solute distribution ratio. This capacity is compared with the capacity of other ILs within the group of those based on the anion [PF$_6$]$^-$. A simulation of the extraction process is performed by using the HYSYS software with the aim of optimizing the operation conditions for continuous extraction of ethanol from the azeotropic mixture. The optimized conditions are assessed in practice in a laboratory-scale packed column and the extraction efficiency of the extraction process in the packed column is calculated.

Results and discussion

Liquid–liquid equilibrium

The composition of both phases in equilibrium was determined at 298.15 K for mixtures with different global composition in the heterogeneous region of the system hexane + ethanol + [BMIM][MeSO$_4$]. The results are reported in Table 1, alongside the corresponding values of solute distribution ratio (β_2) and selectivity (S), which are defined by the following expressions:

$$\beta_2 = \frac{w_2^{\text{IL-phase}}}{w_2^{\text{HC-phase}}} \tag{1}$$

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

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 solute distribution ratio gives an idea of the solvent capacity of the IL, since it is related to the amount of solvent required for the process. Selectivity provides a measurement of the separation power of the IL, consequently conditioning the number of equilibrium stages needed in the unit. Since it deploys high values of these parameters, as desired, [BMIM][MeSO$_4$] can be considered good in this extraction process.

Table 1 Composition of the experimental tie-line ends, solute distribution ratio (β_2) and selectivity (S) for the ternary system hexane + ethanol + [BMIM][MeSO$_4$] at 298.15 K. The mass fraction of hexane and ethanol are w_1 and w_2, respectively

Hydrocarbon-rich phase		Ionic liquid-rich phase			
$w_1^{\text{HC-phase}}$	$w_2^{\text{HC-phase}}$	$w_1^{\text{IL-phase}}$	$w_2^{\text{IL-phase}}$	β_2	S
0.994	0.005	0.013	0.030	5.51	432.0
0.994	0.006	0.016	0.045	7.64	482.1
0.993	0.007	0.020	0.070	10.27	523.0
0.992	0.008	0.024	0.123	15.98	651.7
0.991	0.009	0.033	0.156	18.28	553.9
0.988	0.012	0.040	0.213	17.62	437.3
0.987	0.012	0.048	0.282	23.31	483.2
0.979	0.019	0.076	0.334	17.89	231.0
0.962	0.035	0.101	0.381	11.01	105.0
0.951	0.044	0.128	0.409	9.30	68.9
0.934	0.060	0.160	0.441	7.31	42.6
0.905	0.088	0.199	0.466	5.27	24.0

The binodal curves of [BMIM][MeSO$_4$] with other ILs[10] are shown in Fig. 2. This figure indicates a clear visualization of the change in the size and shape of the immiscibility region. It can be observed that the immiscibility region decreases when the length of the alkyl chain in the imidazolium ring increases.

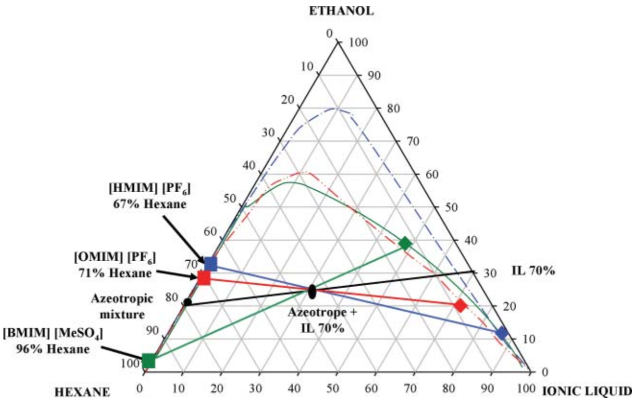

Fig. 2 Experimental binodal curves of the ternary systems hexane + ethanol + ionic liquid, where: (green solid line), [BMIM][MeSO$_4$]; (blue dash–dot line), [HMIM][PF$_6$]; (red dash–double dot line), [OMIM][PF$_6$] with the predictions of phase compositions when the azeotropic mixture ethanol + hexane and [BMIM][MeSO$_4$] containing 30% of ethanol (IL 70%) are mixed in solvent/feed ratio of 0.9, where: green ■, ◆, raffinate and extract of [BMIM][MeSO$_4$]; blue ■, ◆, raffinate and extract of [HMIM][PF$_6$]; red ■, ◆, raffinate and extract of [OMIM][PF$_6$].

Correlation of LLE

As design of a separation process requires knowledge of the phase equilibria; the NRTL equation[22] is employed in order to correlate LLE data. Previous works confirm that the correlation equation is suitable to satisfactorily describe the phase equilibria involving electrolytes like ILs.[23–26] The parameters were adjusted to minimize the difference between the experimental and the calculated mole fraction defined as:

$$O.F. = \sum_{i=1}^{n}\left[\left(x_{1i}^{\text{HC-phase}} - x_{1i}^{\text{HC-phase}}(calc)\right)^2 + \left(x_{2i}^{\text{HC-phase}} - x_{2i}^{\text{HC-phase}}(calc)\right)^2\right] + \sum_{i=1}^{n}\left(\left(x_{1i}^{\text{IL-phase}} - x_{1i}^{\text{IL-phase}}(calc)\right)^2 + \left(x_{2i}^{\text{IL-phase}} - x_{2i}^{\text{IL-phase}}(calc)\right)^2\right) \tag{3}$$

where $x_{1i}^{\text{HC-phase}}$, $x_{2i}^{\text{HC-phase}}$, $x_{1i}^{\text{IL-phase}}$, $x_{2i}^{\text{IL-phase}}$ are the experimental mole fraction; $x_{1i}^{\text{HC-phase}}(calc)$, $x_{2i}^{\text{HC-phase}}(calc)$, $x_{1i}^{\text{IL-phase}}(calc)$ and $x_{2i}^{\text{IL-phase}}(calc)$ are the calculated mole fraction.

The fitting parameters are listed in Table 2. The deviation was calculated by applying the following expression:

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

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.

The value of σ provides a measure of the accuracy of the correlation, which is 0.024 in this case. A comparison

Table 2 Binary interaction parameters from the correlation of the LLE data of the ternary system hexane + ethanol + [BMIM][MeSO$_4$] by the NRTL equation

Components	Parameters ($\alpha = 0.19$)	
i, j	$g_{ij} - g_{jj}$ (J mol^{-1})	$g_{ji} - g_{ii}$ (J mol^{-1})
1, 2	373.77	7776.8
1, 3	6845.4	12649
2, 3	35506	−2415.0

between the experimental data and those obtained from the NRTL equation demonstrates that the NRTL equation maps the liquid–liquid behavior.

Selection of column operation conditions

Operating conditions for the 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 the purity of the solvent stream increase. Moreover, the cost of solvent recovery grows when the purity is as high as desired. This study has been carried out for solvent purities of 70–100%. All the solvent streams considered can result in theoretical raffinate purities > 90 wt% within solvent/feed ratios ranging lower than 1.5. Overlooking formal optimization, we have selected a solvent/feed ratio of 0.9 and a 70% pure solvent stream, both of which afford a theoretical raffinate purity of 96.2 wt%, to be used in further research.

Fig. 2 shows a comparison of the predictions of phase compositions when the azeotrope ethanol + hexane (in azeotropic composition) and [BMIM][MeSO$_4$] with a pure solvent stream of 70% are mixed in these selected operation conditions. The plotted data for the systems with other ILs are taken from previous work.[8] The corresponding separations are calculated from the tie-line data. A close look at this figure reveals that the [BMIM][MeSO$_4$] favors the separation of the azeotropic mixture ethanol + hexane. This conduct can also be found for other ternary systems in the literature.[27,28]

Simulation results

The performance of the process shown schematically in Fig. 3, where a liquid–liquid extractor with one equilibrium stage models the 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 the 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 Table 3, a raffinate with a purity of 97.8 wt% was achieved. Distillation of the extract stream afforded the recovery of 70:30 solvent (recycled to the first column). The ability of the [BMIM][MeSO$_4$] as an azeotrope breaker in liquid–liquid extraction processes for the separation of the mixture hexane + ethanol was proved.

Table 3 Properties of the main streams in the extraction of ethanol from its azeotropic mixture with hexane using [BMIM][MeSO$_4$] as solvent by means of HYSIS software

Stream name	Solvent	Feed	Raffinate	Extract	Alcohol
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)	7.52	12.55	7.107	12.96	5.44
Mass flow (kg/h)	0.8076	0.9156	0.6028	1.1204	0.3128
Liquid volume flow (ml/h)	770.7	1333.4	905.6	1198.5	427.8
Component mass fraction					
Hexane	0	0.7916	0.9777	0.1209	0.4289
Ethanol	0.3000	0.2084	0.0021	0.3757	0.5711
[BMIM][MeSO$_4$]	0.7000	0	0.0021	0.5034	0

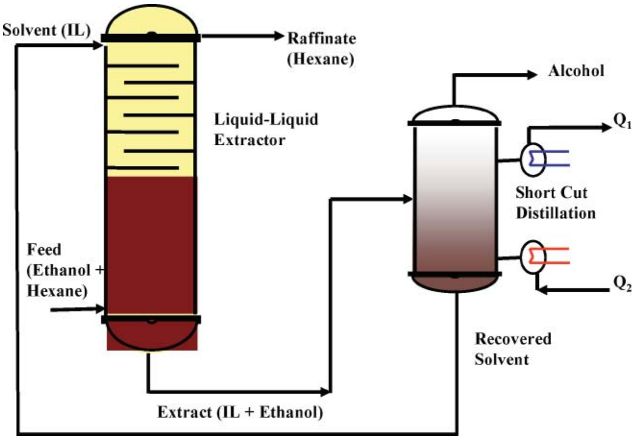

Fig. 3 Extraction process flow sheet in the separation of the azeotropic mixture ethanol + hexane using [BMIM][MeSO$_4$] as solvent.

Results of packed column experiment

Fig. 4 plots the evolution of the hexane content of raffinate, observed in a packed column countercurrent extraction experiment, carried out under operating conditions approximating those prescribed by the simulation results. In addition, Fig. 5 shows times, raffinate purity and the extract mass composition stabilized. The performance of the experimental column exceeded theoretical (96.2 wt.%) and simulation-based (97.8 wt.%)

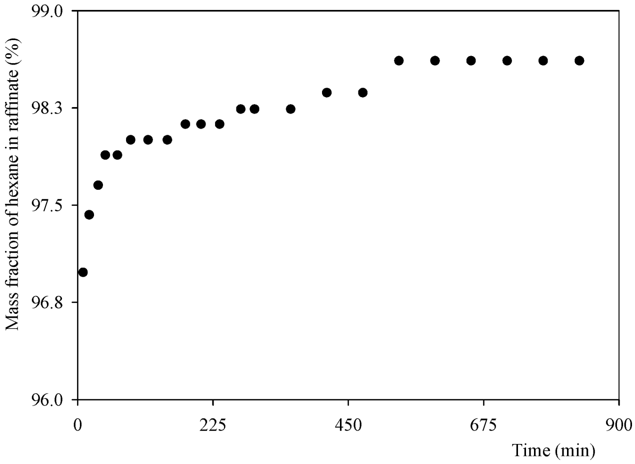

Fig. 4 Time dependence of the mass fractions of hexane in raffinate following start-up of the extraction column using [BMIM][MeSO$_4$] as solvent.

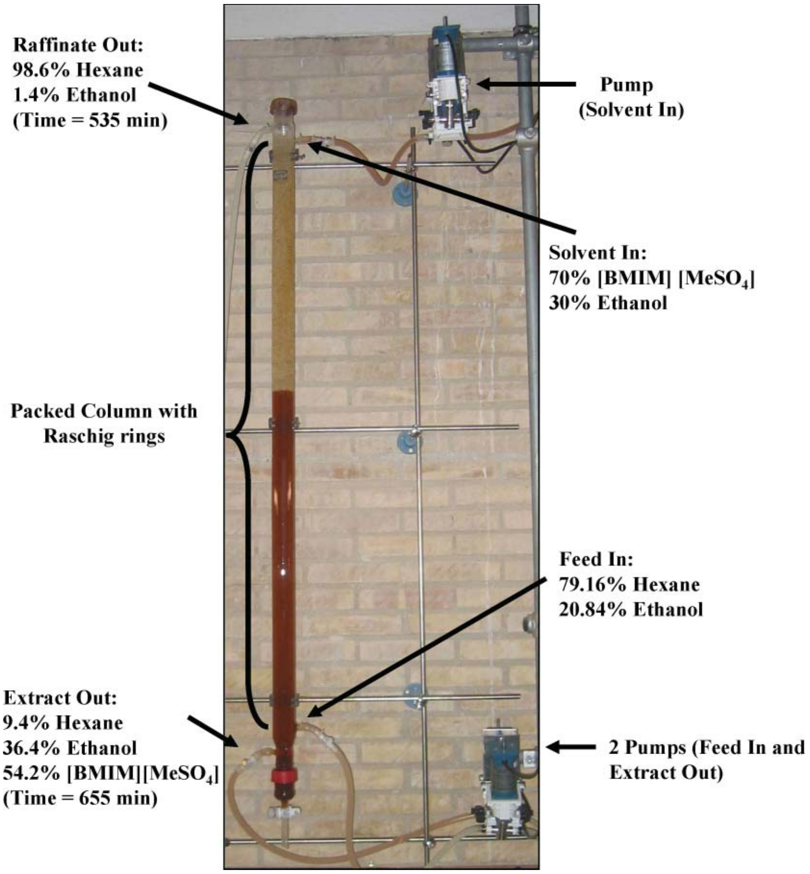

Fig. 5 The packed countercurrent extraction column with the experimental data in the steady state of extraction process.

expectations, undoubtedly because of superior mixing between feed and solvent. The extraction of hexane with a purity of 98.6 wt.% was feasible by using a packed extraction column and [BMIM][$MeSO_4$] as solvent.

The extraction efficiency, E, was calculated in order to study the extraction process in the packed column. This parameter points toward the ability of [BMIM][$MeSO_4$] to remove ethanol from the azeotropic mixture of ethanol and hexane in the extraction column. This parameter is defined as follows:

$$E = \frac{w_1^F - w_1^R}{w_1^F - w_1^{Eq}} \tag{5}$$

where w is the mass fraction, subscript 1 indicates the hexane and F, R and Eq provide the feed stream, the raffinate stream and one equilibrium stage, respectively. The extraction efficiency for [BMIM][$MeSO_4$] is 1.14 in the separation of the azeotrope ethanol with hexane.

Experimental methods

Materials

The synthesis of [BMIM][$MeSO_4$] was carried out as described in previous research.[29] It gave NMR and positive FAB mass spectra as a result, in keeping with the 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 (2×10^{-1} Pa) at 343.15 K. The nominal purities of hexane (from Aldrich, ≥ 99.0 wt%) and ethanol (from Merck, ≥ 99.8 wt%) were verified by means of gas chromatography.

Regeneration of the IL

The [BMIM][$MeSO_4$] used during this experiment was 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 is lower than the one of the rest of the components. The purity of this recovered compound was verified by comparing its density at 298.15 K and NMR with the density and NMR of the freshly synthesized product.

Experimental LLE procedure

Ternary LLE data were determined in a glass cell containing a magnetic stirrer and 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 after the determination of the binodal curve. Known masses of the three components were added slowly until one phase was obtained and then the binodal curve composition was detected visually. Forty miscible samples were prepared by mass near to the binodal curve and the density and refractive index were measured at 298.15 K to guarantee that the ternary physical properties were described properly. The calibration curves were obtained by fitting the composition on these samples 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 weight measurements were performed 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}. Finally, refractive indices were calculated *via* a Dr. Kernchen ABBEMAT WR automatic refractometer with an uncertainty of $\pm 4 \times 10^{-5}$.

Packed column experiment

The practical performance of [BMIM][$MeSO_4$] as a hexane + ethanol azeotrope breaker was researched 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 (Fig. 5). 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 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 for the determination of their composition in relation to their density and refractive index. Lastly, [BMIM][$MeSO_4$] was recovered on-line from the extract stream and was recycled into the packed column.

Conclusions

The use of [BMIM][$MeSO_4$] as solvent for the separation of the azeotropic mixture ethanol with hexane by liquid–liquid extraction was analyzed. Experimental determination of LLE data for the ternary system hexane + ethanol + [BMIM][$MeSO_4$] at 298.15 K allowed the NRTL equation to be fitted and afforded the corresponding distribution ratios and selectivities for the extraction of ethanol from azeotropic hexane + ethanol mixtures. The phase diagram of [BMIM][$MeSO_4$] was compared with the phase diagram of [CnMIM][PF_6] when both are used as solvent. [BMIM][$MeSO_4$] substantiates the best results in the separation of the azeotrope ethanol + hexane.

An extraction process was carried out with [BMIM][$MeSO_4$]. The LLE data were used for the identification of theoretically appropriate operating conditions for a room-temperature countercurrent continuous extraction process including a solvent recycling stage. The extraction process with this solvent was simulated by using conventional software. An experiment with a laboratory-scale packed column under steady-state conditions close to the simulated optimum achieved a raffinate purity of over 98.6 wt%. It also confirmed the possibility of ready on-line recovery of [BMIM][$MeSO_4$]. The extraction efficiency of this extraction process was calculated and the results indicate that the [BMIM][$MeSO_4$] would be a suitable alternative as solvent in this separation process. If the raffinate purity of hexane obtained in the extraction process is taken into account, scaling up for industrial application seems viable.

Acknowledgements

We would like to thank the Ministerio de Educación y Ciencia (Spain) for the financial support through Project CTQ 2004–00454.

References

1 A. Pucci, *Pure Appl. Chem.*, 1989, **61**, 1363–1372.
2 S. J. Marwil, Separation of hydrocarbon and alcohol azeotropic mixtures by distillation with anhydrous ammonia. *US Pat.*, 4 437 941, 1984.
3 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.
4 A. G. Fadeev and M. M. Meagher, *Chem. Commun.*, 2001, 295–296.
5 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156–164.
6 C. Jork, M. Seiler, Y.-A. Beste and W. Arlt, *J. Chem. Eng. Data*, 2004, **49**, 852–857.
7 M. Seiler, C. Jork, A. Kavarnou, W. Arlt and R. Hirsch, *AIChE J.*, 2004, **50**, 2439–2454.
8 X. Hu, J. Yu and H. Liu, *Water Sci. Tech.*, 2006, **53**, 245–249.
9 A. B. Pereiro, E. Tojo, A. Rodriguez, J. Canosa and J. Tojo, *Green Chem.*, 2006, **8**, 307–310.
10 A. B. Pereiro and A. Rodriguez, *Fluid Phase Equilib.*, 2008, **270**, 23–29.
11 A. B. Pereiro and A. Rodriguez, *Sep. Purif. Technol.*, 2008, **62**, 733–738.
12 G. W. Meindersma, A. Podt and A. B. de Haan, *Fuel Proc. Technol.*, 2005, **87**, 59–70.
13 G. W. Meindersma and A. B. de Haan, *Chem. Eng. Res. Des.*, 2008, **86**, 745–752.
14 A. B. Pereiro and A. Rodriguez, *J. Chem. Thermodyn.*, 2007, **39**, 1608–1613.
15 L. Zhang, Y. F. Deng, C. B. Li and Ji. Chen, *Ind. Eng. Chem. Res.*, 2008, **47**, 1995–2001.
16 A. B. Pereiro and A. Rodriguez, *J. Chem. Eng. Data*, 2008, **53**, 1360–1366.
17 A. B. Pereiro and A. Rodriguez, *J. Chem. Eng. Data*, 2007, **52**, 2138–2142.
18 A. B. Pereiro and A. Rodriguez, *J. Chem. Thermodyn.*, 2008, **40**, 1282–1289.
19 A. Arce, H. Rodriguez and A. Soto, *Green Chem.*, 2007, **9**, 247–253.
20 R. P. Swatloski, J. D. Rogers and R. D. Rogers, *Green Chem.*, 2003, **5**, 361–363.
21 V. Najdanovic-Visak, J. M. S. S. Esperanca, L. P. N. Rebelo, M. Nunes da Ponte, H. J. R. Guedes, K. R. Seddon and J. Szydlowski, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1701–1703.
22 H. Renon and J. M. Prausnitz, *AIChE J.*, 1968, **14**, 135–144.
23 G. W. Meindersma, A. Podt and A. B. De Haan, *J. Chem. Eng. Data*, 2006, **51**, 1814–1819.
24 T. M. Letcher and P. Reddy, *J. Chem. Thermodyn.*, 2005, **37**, 415–421.
25 X. Hu, J. Yu and H. Liu, *J. Chem. Eng. Data*, 2006, **51**, 691–695.
26 A. Arce, M. J. Earle, H. Rodríguez and K. R. Seddon, *Green Chem.*, 2007, **9**, 70–74.
27 A. Arce, M. J. Earle, H. Rodríguez and K. R. Seddon, *J. Phys. Chem. B*, 2007, **111**, 4732–4736.
28 G. W. Meindersma, A. Podt, M. B. Klaren and A. B. De Haan, *Chem. Eng. Commun.*, 2006, **193**, 1384–1396.
29 A. B. Pereiro, P. Verdía, E. Tojo and A. Rodriguez, *J. Chem. Eng. Data*, 2007, **52**, 377–380.