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Extraction of *n*-Alcohols from *n*-Heptane Using Ionic Liquids.

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ABSTRACT: In this work, the efficiency of three ionic liquids: 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium thiocyanate, and 1,3-dimethylimidazolium methylphosphonate to extract *n*-alcohols from an aliphatic compound was studied. Liquid−liquid equilibria (LLE) measurements of ternary mixtures containing 1-propanol, 1-butanol, or 1-pentanol with *n*-heptane and these ILs were carried out at 298.15 K in order to check the ability of these ILs to act as extractive solvents. Experimental data were successfully represented using the NRTL and UNIQUAC correlations.

INTRODUCTION

In the chemical industry, the separation and purification of the products, byproducts, and unreacted raw materials of a reaction mixture represent an important part of the unit cost. Distillation, which is the major separation and purification method, presents several drawbacks. It is an expensive unit operation in terms of capital and operating costs, requiring a large amount of energy and using volatile compounds. It is therefore desirable to design economically optimized separation processes that can save significant amounts of financial and energetic resources.[1,2]

For many years, as a result of the reduction of lead in gasoline, ternary ethers and alcohols have coexisted as additives for gasoline. Different azeotropic mixtures of alcohols and alkanes are present in various industrial processes.[3,4] The separation of nonideal mixtures especially azeotropic mixtures is very challenging. Extractive distillation is currently the mostly used process. However, liquid−liquid extraction represents a cost friendly alternative to extractive distillation. A liquid−liquid separation process is based on the immiscibility of the two liquid phases that exhibit preferential affinity or selectivity toward one or more components in the feed. This kind of process reduces the energy consumption and avoids the release of volatile solvent to the atmosphere.[5]

For this reason, the use of ionic liquids (ILs) for separation processes is promising because of their nonvolatile nature. For many applications, ILs have a number of advantages over conventional organic solvents determined by their chemical and physical properties. These liquids have good thermal stability and negligible vapor pressure. ILs are miscible with substances having a very wide range of polarities and they can simultaneously dissolve organic and inorganic substances. Physical properties of ILs can be modified and adjusted by employing different cation−anion combinations. These features offer opportunities for a large number of applications including catalysis, synthesis, gas separations, and liquid−liquid extractions.[6−8] Thermodynamic measurements such as activity coefficients at infinite dilution have proved that ILs are good candidates as alternative solvents in order to replace volatile organic compounds (VOCs) in separation processes. Indeed, the selectivities at infinite dilution for a specific separation using ILs are in most cases higher than with classically used solvents.[9] This is mainly due to the low miscibility of aliphatic compounds and the high solubility of polar compounds in ILs. It was recently shown that imidazolium based ionic liquids could be used in the liquid−liquid extraction of alcohol from aliphatic hydrocarbons.[4,5,8,10]

In our previous work,[9,11−14] we have contributed to developing a large databank of the thermodynamic properties of imidazolium based ionic liquids by determining activity coefficients at infinite dilution of organic compounds in ILs using inverse gas chromatography. Although researchers have an interest in ionic liquids, the physicochemical properties of pure ionic liquid and their mixtures, needed to design processes, is not available.

The aim of this study is to investigate the possible use of ILs as solvents for a separation problem frequently encountered in the chemical industry: {alcohol + aliphatic} mixtures. This work is focused on three ILs: 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4], 1,3-dimethylimidazolium methylphosphonate [DMIM][MP], and 1-butyl-3-methylimidazolium thiocyanate [BMIM][SCN]. These LLE measurement of ternary mixtures for nine systems were thus measured at 298.15 K and atmospheric pressure: {1-propanol + *n*-heptane + [BMIM][BF_4]}, {1-propanol + *n*-heptane + [DMIM][MP]}, {1-propanol + *n*-heptane + [BMIM][SCN]}, {1-butanol + *n*-heptane + [BMIM][BF_4]}, {1-butanol + *n*-heptane + [DMIM][MP]}, {1-butanol + *n*-heptane + [BMIM][SCN]}, {1-pentanol + *n*-heptane + [BMIM][BF_4]}, {1-pentanol + *n*-heptane + [DMIM][MP]}, and {1-pentanol + *n*-heptane + [BMIM][SCN]}. Experimental data were correlated using the NRTL and UNIQUAC activity coefficients models.

EXPERIMENTAL PROCEDURES

Materials or Chemicals. *n*-Heptane was supplied by Aldrich with a quoted purity of 99.5%. 1-Propanol, 1-butanol, and 1-pentanol were purchased from Acros Organics, with purities of >99%. The ionic liquids investigated in this work were from Solvionic for 1-butyl-3-methylimidazolium tetrafluoroborate (99.5%) and 1,3-dimethylimidazolium methylphosphonate (98%). 1-Butyl-3-methylimidazolium thiocyanate was obtained from Fluka and was reported to have a purity >95%. The structures of ionic liquids as well as NMR

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Table 1. GC Operating Conditions for Composition Analysis

injector temperature	250 °C
carrier gas	helium
capillary column	WCOT Ulti-Metal coated with HT-SIMDIST-CB (10 m × 0.53 mm ×0.53 μm) with an empty precolumn.
flow rate	2 mL min^{-1}
column oven	70 °C → 125 °C (5 °C/min), 5 min
detector type	FID
detector temperature	250 °C

Table 2. Mole Fractions of Experimental Tie-Lines, Solute Distribution Ratios β, and Selectivity S for Ternary Systems {1-Propanol (1) + n-Heptane (2) + IL (3)} at T = 298.15 K

hydrocarbon-rich phase (I)			IL-rich phase (II)				
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}	β	S
{1-Propanol (1) + n-Heptane (2) + [BMIM][BF$_4$] (3)}							
0.002	0.998	0	0.243	0.017	0.740	131	7630
0.010	0.990	0	0.347	0.020	0.633	34.2	1700
0.026	0.974	0	0.401	0.022	0.577	15.5	693
0.039	0.961	0	0.437	0.022	0.541	11.2	481
0.047	0.953	0	0.452	0.022	0.526	9.54	405
0.053	0.947	0	0.474	0.023	0.502	9.01	365
0.058	0.942	0	0.608	0.024	0.368	10.5	411
0.065	0.935	0	0.725	0.024	0.251	11.2	444
{1-Propanol (1) + n-Heptane (2) + [BMIM][SCN] (3)}							
0.001	0.999	0.000	0.188	0.033	0.779	188	5657
0.013	0.987	0.000	0.326	0.033	0.641	25.1	748
0.015	0.985	0.000	0.434	0.049	0.517	29.5	588
0.030	0.970	0.000	0.529	0.070	0.401	17.8	247
0.081	0.919	0.000	0.643	0.108	0.250	7.96	67.8
0.118	0.883	0.000	0.653	0.121	0.226	5.38	39.1
0.119	0.881	0.000	0.685	0.190	0.125	5.75	26.6
0.130	0.870	0.000	0.677	0.256	0.067	5.22	17.8
{1-Propanol (1) + n-Heptane (2) + [DMIM][MP] (3)}							
0.002	0.999	0.000	0.173	0.005	0.822	115	21728
0.016	0.984	0.000	0.311	0.011	0.678	19.7	1713
0.022	0.978	0.000	0.444	0.022	0.534	20.6	907
0.031	0.969	0.000	0.558	0.034	0.408	18.1	523
0.036	0.964	0.000	0.640	0.063	0.297	17.6	271
0.038	0.962	0.000	0.683	0.075	0.242	17.9	232
0.054	0.946	0.000	0.709	0.121	0.170	13.0	102
0.080	0.920	0.000	0.698	0.165	0.137	8.77	49.1

Table 3. Mole Fractions of Experimental Tie-Lines, Solute Distribution Ratios β, and Selectivity S for Ternary Systems {1-Butanol (1) + n-Heptane (2) + IL (3)} at T = 298.15 K

hydrocarbon-rich phase (I)			IL-rich phase (II)				
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}	β	S
{1-Butanol (1) + n-Heptane (2) + [BMIM][BF$_4$] (3)}							
0.027	0.973	0.000	0.236	0.021	0.743	8.88	416
0.076	0.924	0.000	0.343	0.027	0.630	4.50	155
0.114	0.886	0.000	0.425	0.044	0.532	3.71	75.5
0.170	0.830	0.000	0.473	0.072	0.456	2.66	30.8
0.242	0.758	0.000	0.522	0.101	0.377	2.16	16.2
0.283	0.717	0.000	0.610	0.158	0.232	2.15	9.7
0.329	0.672	0.000	0.630	0.184	0.186	1.92	7.01
{1-Butanol (1) + n-Heptane (2) + [BMIM][SCN] (3)}							
0.010	0.990	0.000	0.144	0.008	0.848	14.5	1774
0.043	0.957	0.000	0.275	0.021	0.704	6.44	291
0.093	0.907	0.000	0.392	0.038	0.570	4.21	101
0.153	0.847	0.000	0.493	0.065	0.442	3.22	42.0
0.169	0.831	0.000	0.529	0.090	0.381	3.12	28.7
0.267	0.733	0.000	0.594	0.146	0.260	2.23	11.2
0.284	0.716	0.000	0.598	0.172	0.230	2.11	8.8
{1-Butanol (1) + n-Heptane (2) + [DMIM][MP] (3)}							
0.004	0.997	0.000	0.177	0.006	0.817	50.7	8865
0.011	0.989	0.000	0.375	0.018	0.607	34.7	1862
0.021	0.980	0.000	0.547	0.042	0.411	26.7	618
0.030	0.970	0.000	0.648	0.075	0.276	23.3	301
0.034	0.966	0.000	0.695	0.122	0.183	20.4	161
0.051	0.949	0.000	0.727	0.240	0.033	14.3	56.5
0.081	0.919	0.000	0.684	0.301	0.015	8.43	25.7
0.096	0.904	0.000	0.702	0.276	0.023	7.28	23.8

spectra of pure IL are presented in a previous work.[15] Before measurements, the ionic liquids were purified by subjecting the liquid under vacuum for approximately 12 h to remove possible traces of solvents and moisture. Analysis for the water content for the ionic liquids using the Karl Fischer technique showed that water content was from 300 (1-butyl-3-methylimidazolium tetrafluoroborate) to 700 ppm.

Determination of Tie Lines of Ternary Mixtures. The LLE measurements of ternary mixtures have been performed in jacketed glass cells. The experimental set up consists of a cell with an internal volume of about 30 cm^3 kept at constant temperature of 298.15 K using a thermostatted bath. The temperature inside the cell is measured by a platinum resistance thermometer PT-100 with an accuracy of ±0.1 K. The ternary mixtures, with compositions inside the immiscible region of the system, are weighted using a METTLER analytical balance with a precision of ±0.0001 g. All of the mixtures were vigorously stirred using a Teflon coated magnet for 2 h to get a good contact between both phases and kept overnight in order to settle down.

Then, samples of both layers were taken from the cell using a syringe. The compositions of organic compounds such as n-heptane, 1-propanol, 1-butanol, or 1-pentanol were determined by gas chromatography. The GC operating conditions are given in Table 1. All GC analyses were repeated three times to check reproducibility. The sample concentration was given according to the area of each chromatograph peak and the calibration curve made prior for all of the solutes. For determination of the ionic liquid composition, density measurements of both phases were performed at 298.15 K with a vibrating tube densimeter (Anton Paar, model DMA601). The uncertainty in the measurements is $\pm 10^{-5}$ g cm^{-3}. The estimated uncertainty in the determination of mole fraction compositions is $\pm 1.10^{-3}$ for the hydrocarbon phase and $\pm 3.10^{-3}$ for the ionic liquid phase. NMR analysis of the

Table 4. Mole Fractions of Experimental Tie-Lines, Solute Distribution Ratios β, and Selectivity S for Ternary Systems {1-Pentanol (1) + n-Heptane (2) + IL (3)} at T = 298.15 K

hydrocarbon-rich phase (I)			IL-rich phase (II)				
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}	β	S
{1-Pentanol (1) + n-Heptane (2) + [BMIM][BF$_4$] (3)}							
0.023	0.977	0.000	0.299	0.036	0.665	13.1	356
0.038	0.962	0.000	0.429	0.074	0.497	11.3	147
0.060	0.940	0.000	0.526	0.119	0.355	9.90	85.6
0.108	0.893	0.000	0.642	0.207	0.151	5.97	25.7
0.130	0.870	0.000	0.661	0.244	0.096	5.08	18.1
0.181	0.819	0.000	0.674	0.273	0.053	3.73	11.2
{1-Pentanol (1) + n-Heptane (2) + [BMIM][SCN] (3)}							
0.006	0.994	0.000	0.301	0.029	0.670	47.8	1619
0.027	0.973	0.000	0.523	0.059	0.418	19.6	323
0.051	0.949	0.000	0.626	0.102	0.272	12.2	114
0.103	0.897	0.000	0.714	0.192	0.094	6.96	32.5
0.118	0.882	0.000	0.733	0.228	0.039	6.21	24.0
0.166	0.834	0.000	0.740	0.254	0.006	4.47	14.6
{1-Pentanol (1) + n-Heptane (2) + [DMIM][MP] (3)}							
0.002	0.998	0.000	0.295	0.012	0.693	173	14291
0.004	0.996	0.000	0.519	0.046	0.435	137	2956
0.006	0.995	0.000	0.587	0.102	0.311	107	1040
0.010	0.990	0.000	0.612	0.166	0.222	60.6	361
0.022	0.978	0.000	0.624	0.288	0.088	24.8	71.8

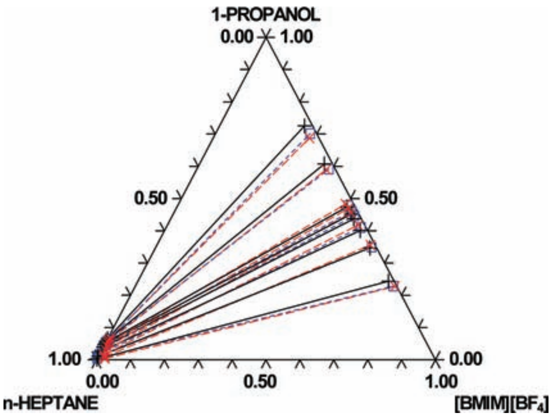

Figure 1. Tie lines for ternary mixture {1-propanol + n-heptane + [BMIM][BF$_4$]} at 298.15 K. Experimental data: + and —, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

hydrocarbon rich phase was also performed to check its possible contamination with ionic liquid.

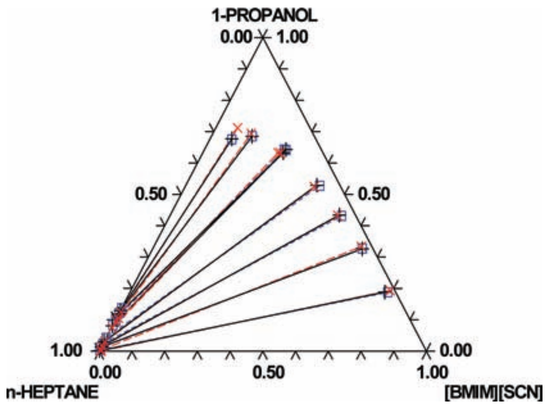

Figure 2. Tie lines for ternary mixture {1-propanol + n-heptane + [BMIM][SCN]} at 298.15 K. . Experimental data: + and —, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

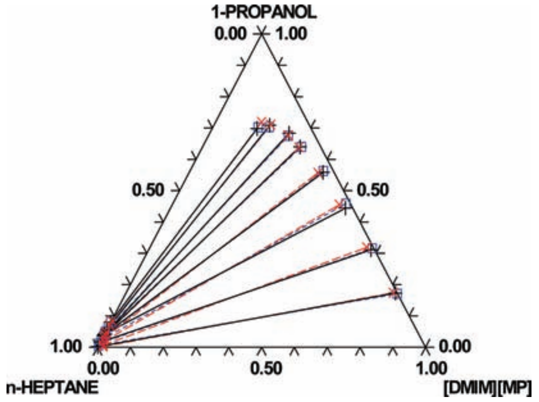

Figure 3. Tie lines for ternary mixture {1-propanol + n-heptane + [DMIM][MP]} at 298.15 K. Experimental data: + and —, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

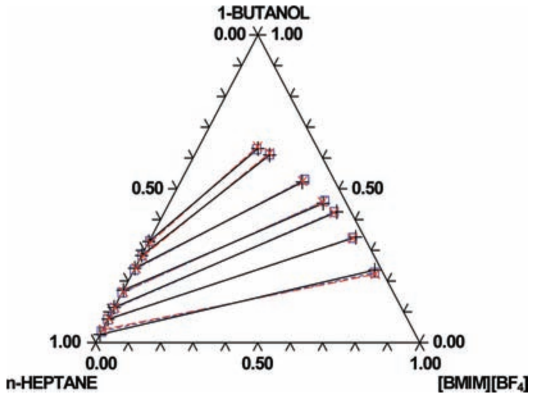

Figure 4. Tie lines for ternary mixture {1-butanol + n-heptane + [BMIM][BF$_4$]} at 298.15 K. Experimental data: + and —, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

RESULTS AND DISCUSSION

The experimental LLE data of the nine ternary systems mentioned above were determined. Tables 2−4 list the compositions of the experimental tie-lines for the nine investigated ternary systems at 298.15 K. The phase diagrams of these systems are shown in Figures 1−9. All the observed diagrams show a behavior that corresponds to a type II according to the Treybal classification with two of their binary systems exhibiting partial immiscibility.[15]

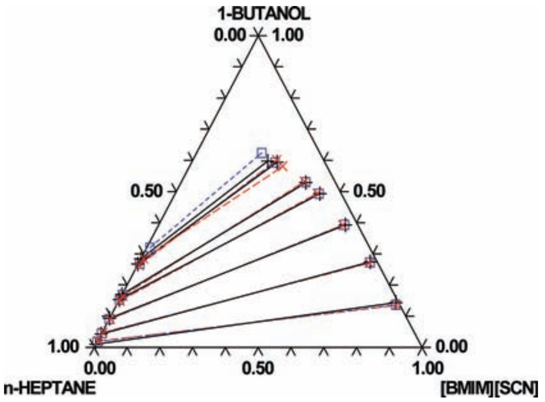

Figure 5. Tie lines for ternary mixture {1-butanol + *n*-heptane + [BMIM][SCN]} at 298.15 K. . Experimental data: + and —, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

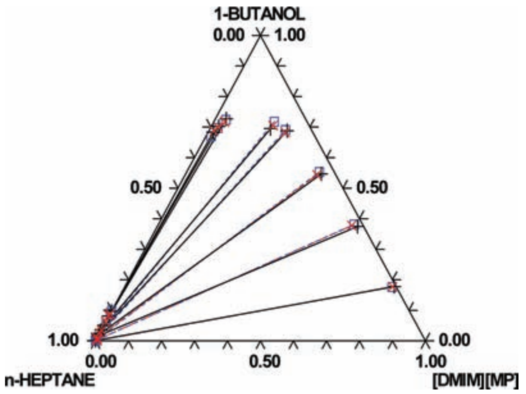

Figure 6. Tie lines for ternary mixture {1-butanol + *n*-heptane + [DMIM][MP]} at 298.15 K. Experimental data: + and —, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

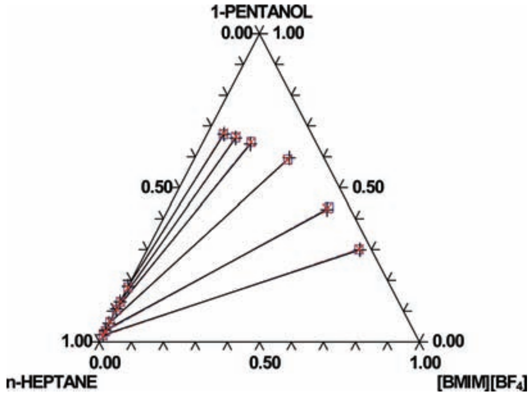

Figure 7. Tie lines for ternary mixture {1-pentanol + *n*-heptane + [BMIM][BF_4]} at 298.15 K. Experimental data: + and —, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

Values of solute distribution ratio β and selectivity S are also reported in the Tables 2−4. These parameters were calculated from experimental data in order to evaluate solvent extraction capacity according to eqs 1 and 2

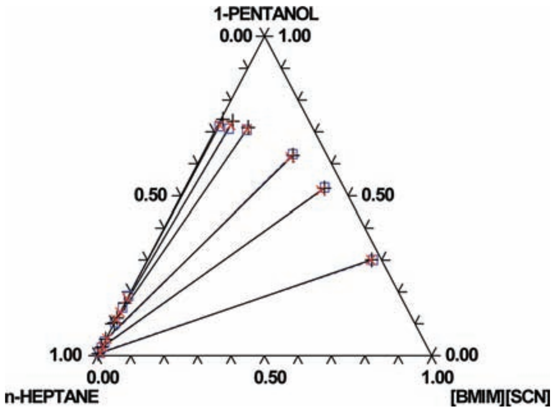

Figure 8. Tie lines for ternary mixture {1-pentanol + *n*-heptane + [BMIM][SCN]} at 298.15 K. . Experimental data: + and —, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

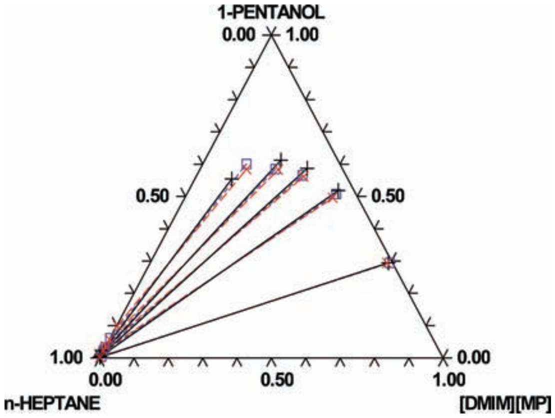

Figure 9. Tie lines for ternary mixture {1-pentanol + n-heptane + [DMIM][MP]} at 298.15 K. Experimental data: + and _, NRTL correlation × and --- (red symbols), UNIQUAC correlation ☐ and ——- (blue symbols).

$$\beta = \frac{x_1^{\mathrm{II}}}{x_1^{\mathrm{I}}} \qquad (1)$$

$$S = \frac{x_1^{\mathrm{II}} x_2^{\mathrm{I}}}{x_1^{\mathrm{I}} x_2^{\mathrm{II}}} \qquad (2)$$

where x is the mole fraction, subscripts 1 and 2 refer to solute (alcohol) and to hydrocarbon (*n*-heptane), respectively, and superscripts I and II indicate the hydrocarbon-rich phase and the IL-rich phase, respectively. In order to have an adequate separation, values of solute distribution ratios have to be higher than the unit.

The evolution of the solute distribution ratio and selectivities for each system {*n*-alcohol + *n*-heptane} as a function of the mole fraction of the solute are plotted in Figures 10−12. For all of the studied systems, the ionic liquids show distribution ratio largely higher than 1, which indicates a very high alcohol solubility in these ionic liquids. The *n*-heptane/alcohol selectivities are relatively high and similar for all the ionic liquids. The three ionic liquids could be considered as

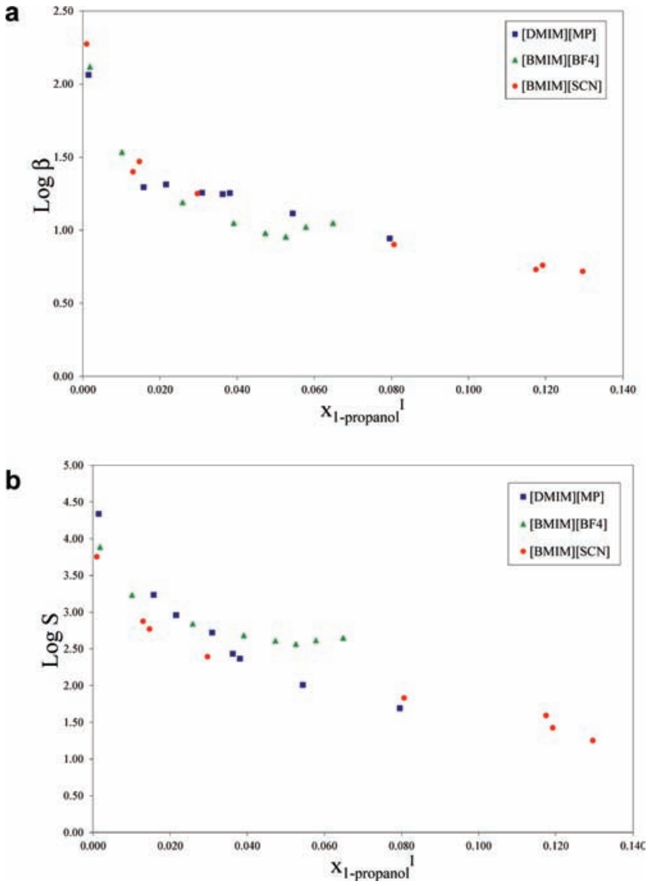

Figure 10. Evolution of 1-propanol distribution ratio β (a) and selectivities (b) as function of mole fraction of 1-propanol in the hydrocarbon-rich phase for the three ionic liquids.

extractive solvents for the *n*-heptane/alcohol separation. Nevertheless, according to the high values of β obtained with [DMIM][MP], this ionic liquid should be preferred, particularly for the extraction of 1-butanol or 1-pentanol.

The LLE data of the investigated ternary systems were correlated using the non-random two-liquid equation (NRTL) proposed by Renon and Prausnitz[16] and the universal quasi-chemical (UNIQUAC) theory developed by Abrams and Prausnitz.[17]

NRTL Model. For the NRTL model, the activity coefficient γ_i, for any component i in the ternary system, is given by

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right) \tag{3}$$

with $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$, $\tau_{ji} = (g_{ji} - g_{ii})/(RT) = \Delta g_{ji}/(RT)$ and $\alpha_{ji} = \alpha_{ji} = \alpha$ where g is an energy parameter characterizing the interaction of species i and j, x_i is the mole fraction of component i, and α the nonrandomness parameter. Although α can be treated as an adjustable parameter, in this study α was set equal to 0.3 according to the literature.[18]

UNIQUAC Model. For the UNIQUAC model, the activity coefficient γ_i, for any component i in the ternary system, is given by

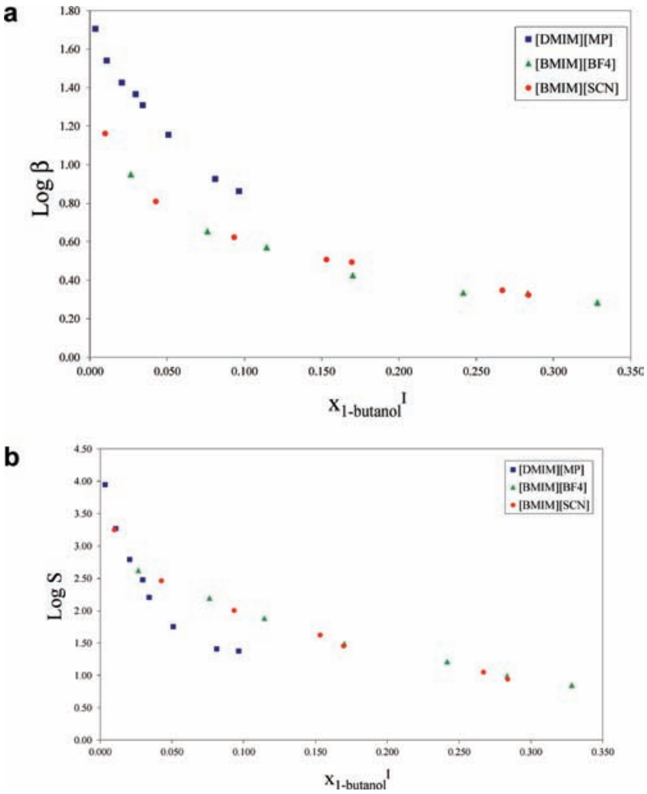

Figure 11. Evolution of 1-butanol distribution ratio β (a) and selectivities (b) as function of mole fraction of 1-butanol in the hydrocarbon-rich phase for the three ionic liquids.

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{m} x_j l_j - q_i \ln(\theta_i \tau_{ji}) + q_i - q_i \sum_{j=1}^{m} \frac{\theta_j \tau_{ji}}{\sum_{k=1}^{m} \theta_k \tau_{kj}} \tag{4}$$

where $\Phi_i = (r_i x_i)/(\sum_{j=1}^{m} r_j x_j)$, $\theta_i = (q_i x_i)/(\sum_{j=1}^{m} q_j x_j)$, $l_j = (z/2)(r_j - q_j) - (r_j - 1)$ and $\tau_{ji} = \exp(-\Delta u_{ij}/(RT))$

Here, the lattice coordination number z is assumed to be equal to 10, r_i and q_i are respectively a relative volume and surface area of the pure component i. Parameters r_i and q_i are respectively relative to molecular van der Waals volumes and molecular surface areas. They are calculated as the sum of the group volume and group area parameters R_k and Q_k

$$r_i = \sum_k \upsilon_k^i R_k \quad \text{and} \quad q_i = \sum_k \upsilon_k^i Q_k \tag{5}$$

where υ_k^i is the number of groups of type k in molecule i. The group parameters R_k and Q_k are obtained from van der Waals group volumes and surface areas, and V_k and A_k are taken from the UNIFAC group contributions[19]

$$R_k = \frac{V_k}{15.17} \quad \text{and} \quad Q_k = \frac{A_k}{2.5 \times 10^9} \tag{6}$$

The values of 15.17 and 2.5×10^9 are respectively the standard segment volume and standard segment area of a methylene group. Values of r and q used in the UNIQUAC equation are listed in Table 5.

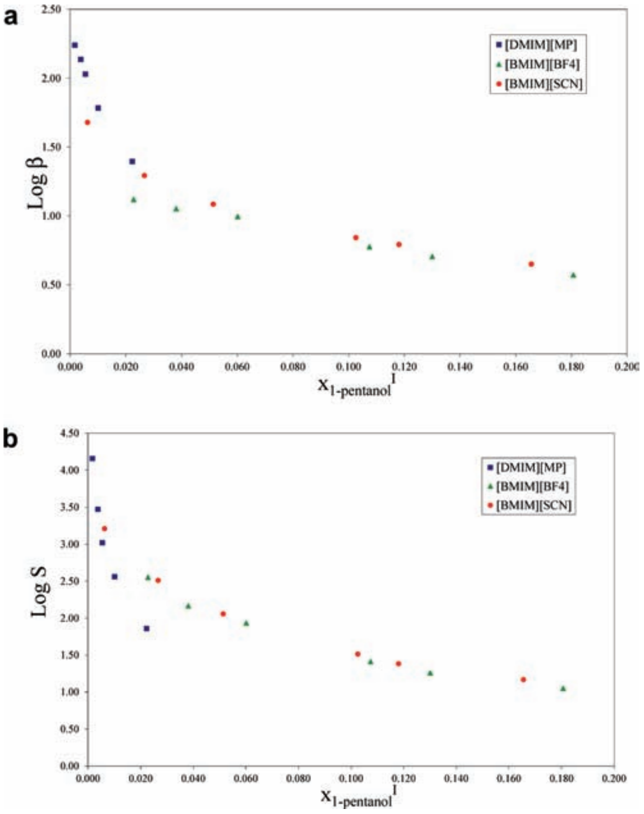

Figure 12. Evolution of 1-pentanol distribution ratio β (a) and selectivities (b) as function of mole fraction of 1-pentanol in the hydrocarbon-rich phase for the three ionic liquids.

Table 5. Molecular Structural Parameters of Pure Components Used in UNIQUAC Calculations

component	r	q
1-propanol	3.2499	3.128
1-butanol	3.9243	3.668
1-pentanol	4.5987	4.208
n-heptane	5.1742	4.396
[BMIM][BF$_4$]	9.4912	6.473
[BMIM][SCN]	9.5418	5.885
[DMIM][MP]	6.0170	4.756

This means that a total of two adjustable parameters per binary Δg_{ji} or Δu_{ji} have to be fitted for both models. For the binary parameters of {1-propanol + *n*-heptane}, {1-butanol + *n*-heptane}, or {1-pentanol + *n*-heptane}, published binary parameters fitted on vapor−liquid equilibria data at the system temperature were used.[20]

Binary interactions parameters for both NRTL and UNIQUAC correlations are those which minimize the difference between the experimental and calculated mol fractions

$$F_{\text{obj}} = \sum_{k=1}^{N}\sum_{i=1}^{3}\{(x_{i,k}^{I,\exp} - x_{i,k}^{I,calc})^2 + (x_{i,k}^{II,\exp} - x_{i,k}^{II,calc})^2\} \quad (5)$$

Table 6. Values of Binary Parameters for the NRTL Equation for the Ternary Mixtures

system	ij	Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})	α	rmsd
1-propanol (1) + *n*-heptane (2) + [BMIM][BF4] (3)	12	3329	4317	0.3	0.0138
	13	20293	1888		
	23	7277	13117		
1-propanol (1) + *n*-heptane (2) + [BMIM][SCN] (3)	12	3329	4317	0.3	0.0113
	13	−12225	1926		
	23	2737	11459		
1-propanol (1) + *n*-heptane (2) + [DMIM][MP] (3)	12	3329	4317	0.3	0.0163
	13	14612	−7674		
	23	6963	10601		
1-butanol (1) + *n*-heptane (2) + [BMIM][BF4] (3)	12	2186	5815	0.3	0.0062
	13	9123	188		
	23	12606	11129		
1-butanol (1) + *n*-heptane (2) + [BMIM][SCN] (3)	12	2186	5815	0.3	0.0064
	13	21122	−9010		
	23	9789	12870		
1-butanol (1) + *n*-heptane (2) + [DMIM][MP] (3)	12	2186	5815	0.3	0.0073
	13	9349	−184		
	23	11501	12188		
1-pentanol (1) + *n*-heptane (2) + [BMIM][BF4] (3)	12	2500	4120	0.3	0.0035
	13	1872	−2956		
	23	13008	12087		
1-pentanol (1) + *n*-heptane (2) + [BMIM][SCN] (3)	12	2500	4120	0.3	0.0090
	13	−59	−4610		
	23	9261	11677		
1-pentanol (1) + *n*-heptane (2) + [DMIM][MP] (3)	12	2500	4120	0.3	0.0031
	13	−23270	−2738		
	23	−2805	15307		

where N is the number of tie lines in the data set, $x_{i,k}^{\text{I,exp}}$ and $x_{i,k}^{\text{I,calc}}$ are the experimental and calculated mole fractions of phase I, and $x_{i,k}^{\text{II,exp}}$ and $x_{i,k}^{\text{II,calc}}$ are the experimental and calculated mole fractions of phase II.

The binary parameters and root mean-square deviation (rmsd), calculated using the above procedure for the NRTL and UNIQUAC correlations are given in Tables 6 and 7, respectively. The rmsd values, which provide a measure of the accuracy of the correlations, were calculated according to the following equation:

$$\text{rmsd} = \left(\frac{\sum_{k=1}^{N}\sum_{i=1}^{3}\{(x_{i,k}^{\text{I,exp}} - x_{i,k}^{\text{I,calc}})^2 + (x_{i,k}^{\text{II,exp}} - x_{i,k}^{\text{II,calc}})^2\}}{6N}\right)^{1/2} \quad (6)$$

As can be inferred from the rmsd values, fairly good correlation of the experimental values with NTRL and UNIQUAC was obtained. The values of the binary parameters Δg_{ji} for the system 1−3 and 2−3 are relatively high and irregular. This fact is often observed when correlating liquid−liquid equilibria or vapor−liquid equilibria of systems including ionic liquids with activity coefficients models such as NRTL or UNIQUAC.[20,23,24] This indicates that

Table 7. Values of the Binary Parameters for the UNIQUAC Equation

system	ij	Δu_{ij} (J mol^{-1})	Δu_{ji} (J mol^{-1})	rmsd
1-propanol (1) + *n*-heptane (2) + [BMIM][BF4] (3)	12	−754	2798	0.0091
	13	755	−155	
	23	6284	262	
1-propanol (1) + *n*-heptane (2) + [BMIM][SCN] (3)	12	−754	2798	0.0059
	13	−2202	681	
	23	3004	76	
1-propanol (1) + *n*-heptane (2) + [DMIM][MP] (3)	12	−754	2798	0.0067
	13	3323	−2889	
	23	2366	2960	
1-butanol (1) + *n*-heptane (2) + [BMIM][BF4] (3)	12	−1201	3410	0.0054
	13	−1277	2119	
	23	5570	88	
1-butanol (1) + *n*-heptane (2) + [BMIM][SCN] (3)	12	−1201	3410	0.0116
	13	960	−1032	
	23	2715	661	
1-butanol (1) + *n*-heptane (2) + [DMIM][MP] (3)	12	−1201	3410	0.0108
	13	8301	−5718	
	23	21440	244	
1-pentanol (1) + *n*-heptane (2) + [BMIM][BF4] (3)	12	41	1323	0.0034
	13	3170	−2430	
	23	1236	1124	
1-pentanol (1) + *n*-heptane (2) + [BMIM][SCN] (3)	12	41	1323	0.0090
	13	5120	−3644	
	23	1706	902	
1-pentanol (1) + *n*-heptane (2) + [DMIM][MP] (3)	12	41	1323	0.0022
	13	26700	−4080	
	23	850	3809	

these models may be only used to interpolate data and not extrapolate.

CONCLUSIONS

In this work, phase equilibria of nine ternary systems involving [BMIM][BF$_4$], [BMIM][SCN], or [DMIM][MP] with 1-propanol, 1-butanol, or 1-pentanol and *n*-heptane were measured at 298.15 K. Selectivities and solute distribution ratio were calculated from experimental data. The experimental results have been successfully correlated using the NRTL and UNIQUAC models. According to the high values of selectivities and solute distribution ratio, [DMIM][MP] seems to be a good choice to act as solvent for n-alcohols extraction from aliphatic hydrocarbons.

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LIST OF SYMBOLS

A	surface area
F_{obj}	objective function
G	NRTL parameter
Δg	binary interaction parameter of NRTL model
l	bulk factor
N	number of tie lines
q	surface parameter in UNIQUAC model
Q	group area parameter
r	volume parameter in UNIQUAC model
R	group volume parameter
rmsd	root-mean-square deviation
S	selectivity
T	temperature
Δu	binary interaction parameter of UNIQUAC model
V	volume
x	molar fraction
z	coordination number

GREEK LETTERS

α	NRTL parameter
β	solute distribution ratio
δ	chemical shift
γ	activity coefficient
Φ	volume fraction
θ	area fraction
τ	energy parameter
υ	number of groups

SUPER/SUBSCRIPTS

calc	calculated
exp	experimental
HC	hydrocarbon rich phase
i,j	components
IL	ionic liquid rich phase

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