J. Chem. Eng. Data **2006,** *51,* 2215−2221

Fluid-Phase Behavior of {1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) Imide, [C_6mim][NTf_2], + C_2-C_8 *n*-Alcohol} Mixtures: Liquid−Liquid Equilibrium and Excess Volumes[‡]

Joanna Łachwa,[†] Pedro Morgado,[§] José M. S. S. Esperança,[†] Henrique J. R. Guedes,[||] José N. Canongia Lopes,*[,†,§] and Luís Paulo N. Rebelo*[,†]

Instituto de Tecnologia Química e Biológica, ITQB2, Universidade Nova de Lisboa, Av. República, Apartado 127, 2780-901 Oeiras, Portugal, Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal, and REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

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In the frame of the IUPAC Project entitled *Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standarized systems*, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [C_6mim]-[NTf_2], was selected as the “model” ionic liquid to perform round-robin measurements on a series of ionic liquid properties. In this work, the temperature−composition liquid−liquid equilibria of this ionic liquid with linear alkan-1-ols, $C_nH_{(2n+1)}OH$, with $n = 4$, 5, 6, and 8, were determined at a nominal pressure of 0.1 MPa and up to 50 MPa for $n = 4$, 5, and 6. Excess molar volumes, V^E, of mixtures of this same ionic liquid with linear alkan-1-ols, $C_nH_{2n+1}OH$, with n ranging from 2 to 5, were measured at a nominal pressure of 0.1 MPa. The consistency between the two sets of experimental data (phase diagrams and V^E) was analyzed from a theoretical perspective; we noticed that as the alkyl chain length, n, of the linear alcohol varies both the pressure dependence of the phase diagrams and the critical excess molar volume change sign.

Introduction

Ionic liquids (ILs) are a class of salts with melting point (mp) temperatures below 100 °C. Apart from these unusually low mp temperatures, ILs are characterized by a negligible vapor pressure,[1,2] a broad liquid range,[3] and a very rich and complex behavior as solvents[4−7] that can be modified by changing the nature of the cation or anion. Their classification as “green” or “designer” solvents (based upon some of the above-mentioned characteristics) has triggered a wealth of attention from both the scientific community and industry. Studies as diverse as applications in synthesis and catalysis, separation methods, electrochemistry, or analytical methods are currently under way.[8−10] As well, several processes have already been implemented at a pilot or industrial scale.[11−13]

Ionic liquids usually consist of a large, asymmetric organic cation coupled with a generally smaller, weakly coordinating anion. The most commonly used cations are those of the 1-alkyl-3-methylimidazolium family, $[C_n\text{mim}]^+$. On the other hand, bis(trifluoromethylsulfonyl)imide, $[NTf_2]^-$, has gained in recent years some importance among the commonly used anions due to its stability to moisture, air, and high-temperature conditions. Therefore, this anion was recently selected[14] along with the 1-hexyl-3-methylimidazolium cation, $[C_6\text{mim}]^+$, as a standard IL reference against which the properties of other ILs can be compared.

In this context, a systematic investigation of the thermodynamic and thermophysical properties of [C_6mim][NTf_2] and its mixtures is an important issue. Particularly, studies involving the liquid−liquid equilibrium (LLE) and volumetric behavior of mixtures have a double objective: (i) they supply fundamental data which are paramount for, e.g., mass balance and mass transfer calculations in separation and extraction processes, and (ii) they provide insight about the nature of the interactions between the ionic liquid’s ions and solvent molecules.

In this work, we investigated mixtures of [C_6mim][NTf_2] with *n*-alkan-1-ols of different alkyl chain length (from C_2 to C_8): for the shorter alcohols (ethanol to pentan-1-ol), we measured the excess molar volume (V^E) of the (IL + alcohol) binary mixtures as a function of composition and temperature, whereas for alcohols with longer chains (butan-1-ol to octan-1-ol), we mapped the liquid−liquid phase diagram and its pressure dependence in analogous mixtures. The consistency between the two sets of experimental data was analyzed from a theoretical perspective because the sign of the molar excess volume results must reflect the pressure dependence of the liquid−liquid phase diagrams.

Experimental Section

Chemicals. The ionic liquid used in this project,[14] 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [C_6mim][NTf_2], came from a batch synthesized by Dr. Mark Muldoon in Professor Joan Brennecke’s laboratories at the University of Notre Dame, where it underwent several purification stages (see Supporting Information). This 50 cm^3 batch labeled as “Tube #8” came from the material being used for the entire IUPAC Project 2002-005-1-100 (http://www.iupac.org/projects/2002/2002-005-1-100.html) and is known to be of high purity. It is colorless to the eye, contains less than 10 ppm of halide, measured by an ion-selective electrode, and contains less than 20 ppm of water, analyzed by coulometric Karl Fischer titration. Additionally, ^1H and ^{19}F NMR spectra

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[‡] Work performed in the frame of the IUPAC Project 2002-005-1-100 entitled *Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems* (http://www.iupac.org/projects/2002/2002-005-1-100.html).

[*] Corresponding authors. E-mail: luis.rebelo@itqb.unl.pt; jnlopes@ist.utl.pt.

[†] Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa.

[§] Instituto Superior Técnico.

[||] Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa.

10.1021/je060307z CCC: $33.50

(see Supporting Information) show the ionic liquid purity to be greater than 99.5 % (excluding the water impurity and other peaks known to originate from the NMR solvent). During the manipulation of the sample, it is expected that the ionic liquid increases its water content. Karl Fischer analysis has never revealed levels of water after measurements greater than 240 ppm. After the initial set of experiments—volumetric and/or LLE determinations in (IL + alcohol) binary mixtures—the ionic liquid was recycled and reused in further experiments as it is very easy to fully separate the alcohol from the IL by moderate warming in a vacuum (0.1 Pa) line. During this process, the alcohol contained in the mixtures was distilled under reduced pressure at temperatures ranging from room temperature to 120 °C and the IL remaining in the residue was subjected to further degassing (in conditions similar to those stated above). The purity of the recovered IL was checked by further analyses (NMR, Karl Fischer), which showed purification levels similar to those for the original sample. Additionally, tests comparing the density of the recycled IL with that of the original sample revealed no difference within the experimental density uncertainty (±0.01 %).

All *n*-alcohols were dried with 3 Å molecular sieves. Their origin was the following: ethanol, 99.8 % (Panreac); 1-propanol, 99.7 % (Sigma-Aldrich); 1-butanol, 99.9 % (Merck); 1-pentanol, 99 % (Sigma-Aldrich); 1-hexanol, 99 % (Sigma-Aldrich); 1-octanol, 99 % (Sigma-Aldrich). Karl Fischer titrations performed on the dried alcohol samples revealed very low levels of water (less than 10 ppm).

Equipment and Procedure for the Density Measurements. Atmospheric pressure density measurements were performed in an Anton-Paar DMA 5000 vibrating-tube densimeter with temperature stability better than 0.005 K over periods of more than 10 min in the (293.15 to 303.15) K interval. The calibration of the apparatus was checked by the standard procedure, i.e., by measuring the densities of pure water and air at 298.15 K and at atmospheric pressure. The composition of the mixtures was determined by a standard gravimetric method; i.e., they were prepared by weighing the necessary amount of each component directly into a small (ca. 5 cm^3), sealed glass vial to an estimated mass fraction uncertainty of ±0.02 %. The density overall uncertainty is estimated to be about 0.01 %.

The thorough mixing of the two components was promoted by the movement of a small glass sphere (inserted in the vial prior to the addition of the ILs) as the flask was slowly and repeatedly inverted. After mixing, the homogeneous liquid (ca. 2 cm^3) was transferred to a syringe and injected into the densimeter. To check whether the mixture was well homogenized, the vibrating tube was first filled with some of the contents of the syringe (ca. 0.8 cm^3), and a first density measurement was taken (after the temperature set point was reached). Another measurement followed when the contents of the vibrating tube were replaced with the mixture that remained in the syringe. The agreement between both values is a measure of the effectiveness of the mixing process.

To guarantee the good internal consistency of the excess molar volume results, the densities of both pure components used to prepare a given binary mixture were also determined under experimental conditions similar to those employed during the density determination of the mixture (during the same series of density determinations, with all samples being prepared simultaneously from the same batch of pure components). This point is crucial in the determination of an accurate value for the excess volume of a binary mixture because it is impossible to guarantee that the amount of degassing—and the gas that is allowed to re-enter the samples during the mass measurements and the mixture and transfer processes—is exactly the same in samples obtained at different times. To check this point, different V^E determinations were performed using samples (pure IL and its mixtures) prepared from a batch that was thoroughly degassed, and other determinations were done with other samples obtained from a batch saturated in nitrogen. Although the density of the pure ILs and their mixtures was different in the two cases (obviously lower density for the gas-saturated samples), the V^E values were comparable within ±0.15 % as long as the excess property was calculated using exclusively data from one experiment (degassed) or the other (gas-saturated).

Finally, it was checked whether viscosity corrections[15,16] to the direct, raw density determinations needed to be considered. It is known that the bistriflamide anion combined with dialkylimidazolium cations yields low-viscosity ionic liquids, as compared with analogous ionic liquids based on other anions such as chloride or hexafluorophosphate.[17] In the case of $[C_6mim][NTf_2]$, the viscosity correction between (293 and 303) K corresponds to a decrease in density of less than 0.01 % and was not considered in the calculations.

Equipment and Procedure for the Liquid−Liquid Equilibrium Measurements. Part of the liquid−liquid equilibrium temperature data at 0.1 MPa nominal pressure was determined using a dynamic method with visual detection of the phase transitions (naked-eye determination of turbidity).

The appropriate mixtures of the ionic liquid and solvent were placed in Pyrex glass capillaries and heated, for two-phase to one-phase transitions (or cooled off, for one-phase to two-phase transitions), very slowly (less than $2\ K\cdot h^{-1}$ near the equilibrium temperature) with continuous stirring. For measurements between (283 and 343) K, a glass thermostatic bath filled with water was used, whereas for lower temperatures, ethanol/water mixtures were used. The capillaries were sealed at both ends, and the mixture occupied almost the entire internal volume (±0.5 cm^3), leaving a small dead volume of gas phase. The mixtures were gravimetrically prepared, and the error in the mass fraction composition was estimated to be within $\pm 2\cdot 10^{-5}$. The temperature at which the last/first signs of turbidity disappeared/appeared was taken as the temperature of the liquid−liquid transition. Because of the slow rate of heating/cooling, no significant hysteresis in the determination of the phase-transition temperatures was observed, at least within the uncertainty of the measurements (cf. below). The temperature was measured using a platinum resistance thermometer coupled to a Keithley 199 System DMM/Scanner. The thermometer was calibrated against high-accuracy mercury thermometers (±0.01 K). The overall temperature of the transition uncertainty in these visual determinations is obviously higher (estimated to be ±0.2 K).

As for the pressure effects on the liquid−liquid equilibrium temperature, two apparatuses (with pressure ranges below and above 5 MPa, respectively, and both working with a He−Ne laser light scattering technique) were used.

For pressures below 5 MPa, the apparatus and the methodology used for the determination of phase transitions have already been described in detail.[18] Here, only a brief description is provided: the cell (with an internal volume of ca. 1.0 cm^3 and an optical length of ca. 2.6 mm) is a thick-walled Pyrex glass tube that is connected to a pressurization line and separated from it by a mercury plug. The intensity of the scattered light is captured at a very low angle ($2° < 2\theta < 4°$) in the outer portion of a bifurcated optical cable, whereas transmitted light is captured in the inner portion of this cable. The intensities of scattered light (I_{sc}) and transmitted light (I_{tr}) are corrected for

Table 1. Excess Molar Volume of ([C$_6$mim][NTf$_2$] + *n*-Alcohol) Mixtures[a]

system	run	d_{293} pure kg·m^{-3}	d_{298} pure kg·m^{-3}	d_{303} pure kg·m^{-3}	x_{IL} –	$10^6 \cdot V^E_{293}$ m^3·mol^{-1}	$10^6 \cdot V^E_{298}$ m^3·mol^{-1}	$10^6 \cdot V^E_{303}$ m^3·mol^{-1}
[C$_6$mim][NTf$_2$] +	5	1372.6	1368.0	1363.4	0.0354	−0.23	−0.24	−0.24
ethanol		789.4	785.1	780.8	0.1970	−0.34	−0.35	−0.35
					0.3950	−0.24	−0.24	−0.24
					0.4977	−0.18	−0.17	−0.17
					0.5942	−0.12	−0.11	−0.11
					0.7946	−0.04	−0.04	−0.04
[C$_6$mim][NTf$_2$] +	6	1375.0	1370.4	1365.8	0.0998	−0.33	−0.34	−0.35
ethanol		789.4	785.1	780.8	0.1480	−0.34	−0.34	−0.35
					0.2232	−0.31	−0.32	−0.32
					0.3009	−0.28	−0.28	−0.28
					0.6939	−0.06	−0.05	−0.05
					0.4330	−0.22	−0.22	−0.22
[C$_6$mim][NTf$_2$] +	1	1376.4	1371.8	1367.2	0.1769	−0.14	−0.135	−0.135
1-propanol		803.5	799.5	795.5	0.3724	−0.08	−0.068	−0.064
					0.4923	−0.00	0.003	0.005
					0.5971	0.04	0.053	0.056
					0.7899	0.05	0.052	0.053
[C$_6$mim][NTf$_2$] +	2	1375.8	1371.2	1366.6	0.2008	−0.14	−0.134	−0.134
1-propanol		803.5	799.5	795.5	0.6764	0.04	0.046	0.050
[C$_6$mim][NTf$_2$] +	3	1374.7	1370.1	1365.5	0.2003	−0.01	−0.01	−0.01
1-butanol		809.6	805.7	801.9	0.3968	0.06	0.07	0.08
					0.5031	0.10	0.11	0.11
					0.5963	0.11	0.12	0.12
					0.7693	0.11	0.11	0.12
[C$_6$mim][NTf$_2$] +	4	1374.9	1370.3	1365.7	0.0511	−0.06	−0.06	−0.06
1-butanol		809.6	805.7	801.9	0.1023	−0.05	−0.05	−0.05
					0.1523	−0.03	−0.03	−0.03
					0.3013	0.03	0.04	0.05
					0.6851	0.11	0.12	0.12
[C$_6$mim][NTf$_2$] +	7	1375.4	1370.8	1.366.2	0.1011	0.03	0.03	0.03
1-pentanol		814.6	810.9	807.3	0.2010	0.08	0.09	0.09
					0.4967	0.20	0.21	0.21
					0.3987	0.18	0.19	0.20
					0.5988	0.20	0.21	0.21
					0.7995	0.16	0.16	0.16

[a] The number of significant digits shown reflects the uncertainty of each of the molar fraction, *x*, and density, *d*, measurements (see text).

density fluctuations, reflections, and multiple scattering effects. The cloud point is the point on the least-squares fits of $(I_{sc,corr})^{-1}$ against pressure (p) or temperature (T) where the slope changes abruptly. Temperature uncertainty is typically ±0.01 K in the range $240 < T/\mathrm{K} < 380$. As for pressure, uncertainty in the manometer readings is ±0.01 MPa in the range $0.1 < p/\mathrm{MPa} < 5$. The cell can be operated in the isobaric or isothermal mode. The overall uncertainties in the determination of the transition temperature and pressure are ±0.02 K and ±0.1 MPa, respectively.

The second apparatus uses the methodology mentioned above. The cell body is a stainless steel cylindrical cell[19] closed on both sides with thick sapphire windows. It was used for experiments in which the pressure was raised to 60 MPa. In this case, the hydraulic fluid is the pure alcohol under study that is in contact with a sufficiently long (1/16 in.) stainless-steel tube filled with the solution (buffer volume), to avoid contamination during compression/expansion cycles. The total volume (buffer + optical) of injected solution is typically 1.6 cm^3, although the optical volume roughly corresponds to a mere 0.5 cm^3. In the case of isothermal runs, temperature uncertainty is maintained (±0.01 K), but it worsens a bit for isobaric runs. As for pressure, the uncertainty is ±0.1 MPa in this higher-pressure range. Both cells can be operated in the isobaric or isothermal mode.

In this work, this apparatus was mainly used for the determination of phase transitions at pressures different from atmospheric. Whenever possible, isothermal runs are preferred over isobaric ones because pressure transmission (isothermal mode) is many orders of magnitude faster than thermal equilibration (isobaric mode). Also, the rate at which one is able to change pressure is much greater than that for temperature. Nonetheless, all runs had to be performed in the isobaric mode due to the very low $T-p$ slope presented by the binary mixtures being studied here.

Results and Discussion

Table 1 contains volumetric data (excess molar volume, V^E) for seven runs corresponding to four (IL + *n*-alcohol) binary mixtures at three temperatures (293.15, 298.15, and 303.15 K) and at a nominal atmospheric pressure of 0.1 MPa. The excess volume data were calculated taking into account the definition of an excess property: $V^E = V_{mix} - V_{ideal} = V_{mix} - x_1V_1 - x_2V_2$, where V_{mix}, V_{ideal}, V_1, and V_2 are the molar volumes of the mixture, of the hypothetical ideal mixture, and of the two pure components, respectively, and x_i (i = 1 or 2) are the corresponding mole fractions. The density of each mixture can be calculated from the data presented in the table and is not presented.

Table 1 also reports the densities of the ionic liquid used to prepare each set of mixtures. Small run-to-run fluctuations (of ±0.15 %) in these latter values reflect the fact that, as discussed in the previous section, the ionic liquid used in different sets of mixtures underwent different degrees of degassing and drying. However, such scattering in the data does not affect the V^E results owing to the cancellation effect implicit in the definition

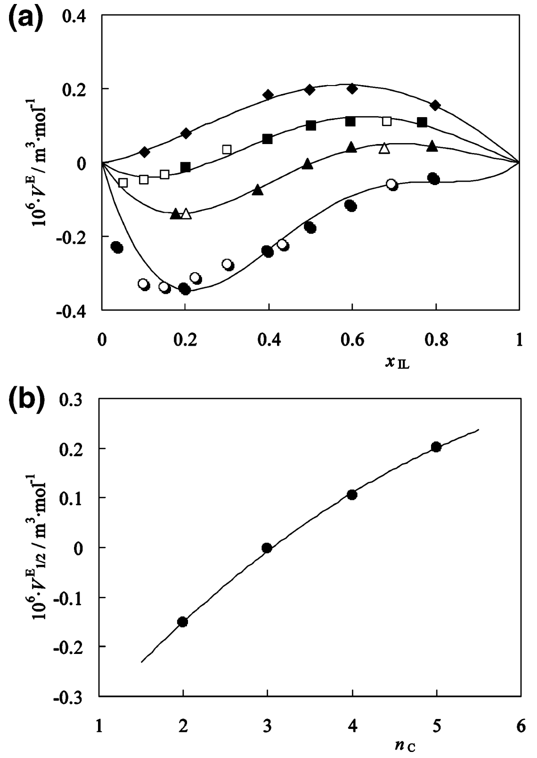

Figure 1. (a) Excess molar volume of binary mixtures of ([C$_6$mim][NTf$_2$] + *n*-alcohol) at 298.15 K: circles, ethanol; triangles, 1-propanol; squares, 1-butanol; and rhombs, 1-pentanol. The shaded and nonshaded markers correspond to two independent runs. The lines represent three-parameter Redlich−Kister fits and are merely used as guides to the eye. (b) Regular trend and change of sign of the excess volume, illustrated here for the equimolar mixtures, $V^E_{1/2}$, vs the number of carbon atoms in the alcohol.

of an excess property, provided an internally consistent procedure is followed (see above, Experimental Section). Judging from the repeatability of the results within each binary mixture, including those presenting slightly different density values for a given pure IL component, the estimated uncertainty of the V^E results is typically ±0.03 cm^3·mol^{-1}.

Irrespective of the nature of the mixture (the size of the alcohol alkyl chain), all excess molar volumes are small (of the order of tenths of cm^3·mol^{-1}—less than 0.1 % of the mixture's molar volume). Therefore, for practical estimates of the mixture's molar volume, and to good approximation, the ideal mixture model can be used. It was also found that the V^E values for these liquid mixtures are basically insensitive to temperature. Figure 1 depicts the behavior of the excess volumes vs composition for these systems at 298.15 K (if the data obtained at other temperatures were also presented in Figure 1, the resulting curves would be superimposed).

A more peculiar feature of the curves is their asymmetry and, in some cases, their change of sign. In fact, the small magnitude of the V^E values could lead one to think that the precision of the results was simply not enough to conclude anything about the shape (and sign) of the curves of V^E vs composition. However, such a notion was dismissed because the analysis of different independent runs for the same mixture (obtained with samples prepared from different IL batches) produced consistent results (runs 1 and 2; 3 and 4; 5 and 6, cf. Table 1), and the trend along the series with increasingly longer *n*-alcohols also exhibited a regular behavior (cf. Figure 1b, in which the trend is plotted for the equimolar condition, $V^E_{1/2}$). In fact, V^E asymmetrical curves are more likely to occur when the two components of the mixture have a large molar volume difference, as is indeed the case. Furthermore, it is known that in

Table 2. Liquid−Liquid Phase Equilibria of [C$_6$mim][NTf$_2$] + C$_n$H$_{(2n+1)}$OH, in which *n* is the Number of Carbon Atoms in the Alcohol, at a Nominal Atmospheric Pressure of 0.1 MPa, w_{IL} and x_{IL} are the Mass and Mole Fraction of the Ionic Liquid in the Mixture, Respectively, and *T* is the Temperature of Transition

x_{IL}	w_{IL}	T/K	x_{IL}	w_{IL}	T/K	x_{IL}	w_{IL}	T/K
				$n = 4$				
0.01829	0.10107	260.11	0.08011	0.34453	269.20	0.16393	0.54202	269.01
0.02813	0.14872	264.52	0.09883	0.39830	269.44	0.19937	0.60048	268.17
0.03987	0.20039	266.93	0.10685	0.41931	269.45[a]	0.23802	0.65343	266.90
0.05236	0.25011	267.97	0.11947	0.45024	269.46	0.27730	0.69843	265.04
0.06599	0.29898	268.69	0.14224	0.50024	269.30	0.32046	0.74002	262.00
				$n = 5$				
0.01142	0.05536	272.94	0.09594	0.35006	289.44	0.22635	0.59758	288.46
0.02147	0.10018	281.13	0.11610	0.40000	289.62	0.26737	0.64940	287.04
0.02724	0.12444	283.31	0.11622	0.40028	289.62[a]	0.31615	0.70117	284.50
0.03372	0.15047	285.08	0.13966	0.45172	289.64	0.34027	0.72359	282.94
0.04706	0.20040	287.30	0.16444	0.49972	289.52	0.37491	0.75273	280.58
0.06095	0.24781	288.49	0.19134	0.54564	289.20	0.44041	0.79978	275.02
0.07807	0.30061	289.10	0.19400	0.54989	288.94[a]			
				$n = 6$				
0.01188	0.05001	288.41	0.10888	0.34853	306.21	0.29698	0.64909	303.35
0.02489	0.10054	297.40	0.12973	0.39494	306.30	0.34941	0.70164	300.33
0.03031	0.12040	299.50	0.15293	0.44150	306.32[a]	0.37049	0.72044	299.17
0.03868	0.14980	301.76	0.15745	0.45003	306.33	0.40548	0.74915	295.76
0.05384	0.19947	303.79	0.18893	0.50495	306.15	0.47827	0.80056	290.24
0.07020	0.24844	304.99	0.21692	0.54811	305.84	0.55978	0.84774	281.78
0.08838	0.29801	305.75	0.25160	0.59548	305.11			
				$n = 8$				
0.01488	0.04933	316.25	0.13627	0.35149	333.50	0.34523	0.64431	329.32
0.03134	0.10003	325.97	0.16148	0.39816	333.62	0.40333	0.69900	325.95
0.04779	0.14707	329.66	0.19309	0.45118	333.46	0.47166	0.75411	321.33
0.06762	0.19945	331.91	0.22455	0.49871	333.14	0.62114	0.84923	305.79
0.08787	0.24865	332.86	0.26092	0.54809	332.48	0.71942	0.89805	287.75
0.10969	0.29739	333.32	0.30860	0.60528	331.23			

[a] Values obtained from extrapolation of $T = f(p)$ to $p = 0.1$ MPa.

Table 3. Liquid−Liquid Phase Equilibria of [C_6mim][NTf_2] + $C_nH_{(2n+1)}OH$, in which *n* is the Number of Carbon Atoms in the Alcohol, as a Function of Pressure, w_{IL} and x_{IL} are the Mass and Mole Fraction of the Ionic Liquid in the Mixture, Respectively, and *T* and *p* are the Temperature and Pressure, Respectively, of Transition

$C_nH_{(2n+1)}OH$	w_{IL}	x_{IL}	p/MPa	T/K	T/K (p = 0.1 MPa)	dT/dp (K/MPa)
$n = 4$	0.41931	0.10685	10.129	269.16	269.45	−0.027
			20.101	268.90		
			30.054	268.66		
			40.026	268.36		
			50.258	268.06		
$n = 5$	0.40028	0.11622	10.148	289.67	289.62	0.004
			20.089	289.70		
			24.965	289.72		
			30.055	289.74		
			39.508	289.76		
			49.981	289.83		
$n = 5$	0.54989	0.19400	10.240	288.96	288.94	0.007
			20.316	289.01		
			30.245	289.09		
			40.251	289.18		
			50.141	289.24		
$n = 6$	0.44150	0.15293	10.055	306.53	306.32	0.023
			14.881	306.65		
			20.176	306.84		
			24.967	306.85		
			30.110	307.01		
			35.077	307.18		
			40.046	307.25		
			45.079	307.36		
			49.926	307.46		
			55.067	307.56		

several binary mixtures containing ionic liquids the locus of maxima/minima in depictions of volumetric- or LLE-related phenomena against composition is also away from the equimolar.[4,20−23] Domańska et al.[24] and Arce et al.[25] measured the excess molar volume of mixtures of (ionic liquid + alcohol) for alkylsulfate-based and tetrafluoroborate-based ionic liquids, respectively, and their results are consistent with ours, exhibiting asymmetric curves with negative-to-positive trends as the alcohol alkyl chain increases (see, for instance, Figure 3 of ref 24 or Figure 6 of ref 25).

Liquid−liquid equilibrium data of (IL + *n*-alcohol) binary mixtures are shown in Tables 2 and 3. All four mixtures (containing 1-butanol, 1-pentanol, 1-hexanol, and 1-octanol) exhibit upper critical solution temperature (UCST) behavior. The results are also illustrated in Figures 2 and 3 as atmospheric-pressure temperature−composition diagrams (Figure 2a) and temperature−pressure plots (Figure 3a) along with the corresponding trends along the *n*-alcohol family (Figures 2b and 3b). As previously observed for other cases involving alcohols and ionic liquids,[21,24,26−30] the UCSTs increase regularly as the alcohol alkyl chain length increases (Figure 2b). As can be judged by analyzing Figure 2a, the agreement between our results and those of ref 21 is excellent.

Finally, the consistency of the experimental data can be tested by correlating the dT/dp and V^E results. Pressure effects are extremely small (see dT/dp values in Table 3) but correlate very well with the trends observed for V^E: dT/dp changes from negative (−270 K·Pa^{-1}) to an almost null but positive value (+40 K·Pa^{-1}) to a positive value (+230 K·Pa^{-1}) as *n* varies from 4 to 6. On the other hand, V^E exhibits a similar trend (from negative to positive as the alkyl chain length increases) in the left side of Figure 1. By taking the maximum of each UCST envelope as the critical concentration and expressing it in molar fractions, we can conclude that the liquid−liquid critical concentrations are found at ca. 0.10, 0.11, 0.13, and 0.16, for n = 4, 5, 6, and 8, respectively. For these critical mole fractions, and likewise for the trend found for the L−L temperature−pressure slopes, the critical V^E values also change from negative to positive between n = 4 and 5.

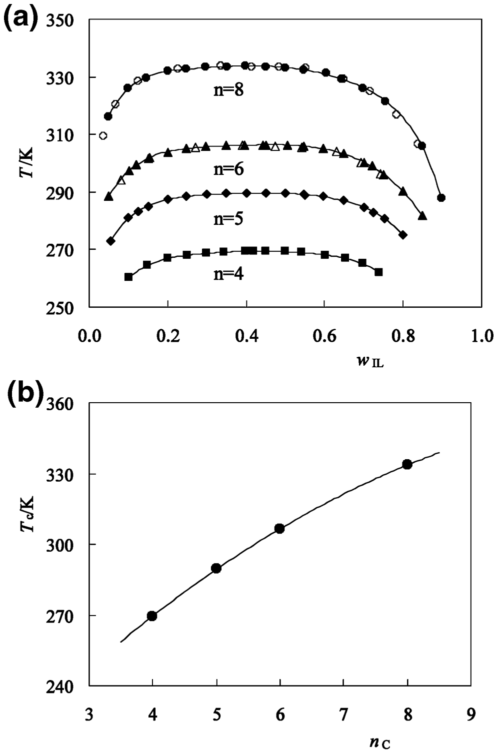

Figure 2. (a) Liquid−liquid phase equilibria of ([C_6mim][NTf_2] + $C_nH_{(2n+1)}OH$), in which *n* is the number of carbon atoms in the alkyl chain of the alcohol and w_{IL} is the weight fraction of the ionic liquid. Experimental data: solid symbols, this work ; empty symbols, ref 21. The two-phase regions are inside the envelopes defined by the data points−upper critical solution temperature (UCST). (b) Regular trend of L−L critical temperatures vs the number of carbon atoms in the alcohol.

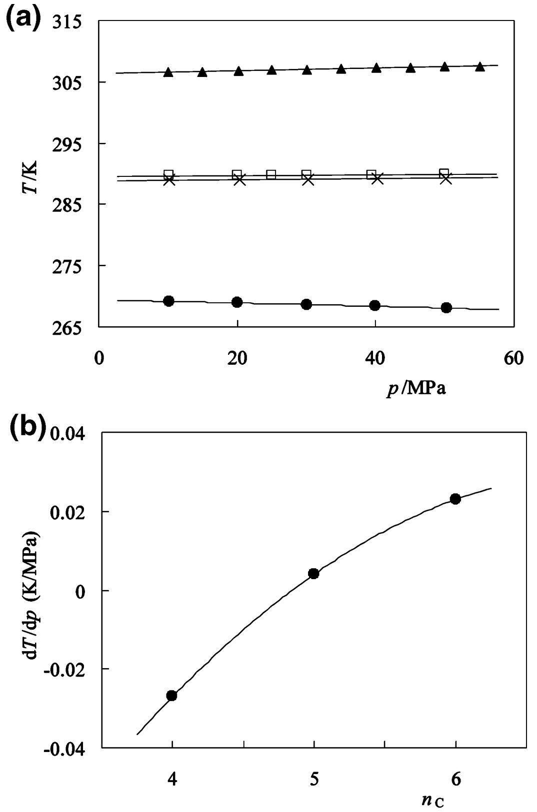

Figure 3. (a) Liquid−liquid equilibrium temperatures as a function of the pressure of [C_6mim][NTf_2] + $C_nH_{(2n+1)}OH$, where n is the number of carbon atoms in the alkyl chain of the alcohol and w_{IL} is the weight fraction of the ionic liquid. Experimental data: ●, $n = 4$ and $w_{IL} = 0.41931$; □, $n = 5$ and $w_{IL} = 0.40028$; ×, $n = 5$ and $w_{IL} = 0.54989$; ▲, $n = 6$ and $w_{IL} = 0.44150$. (b) Regular trend of critical dT/dp vs n.

This correlation can be understood in light of the so-called Prigogine and Defay equation, which reflects a Clapeyron-type of relation for binary liquid−liquid equilibria (see, for instance, refs 31 and 32 and references therein)

$$\left(\frac{\mathrm{d}T}{\mathrm{d}p}\right)_{\mathrm{c}} \cong T_{\mathrm{c}}(p)\frac{V^{\mathrm{E}}(T_{\mathrm{c}}(p)x)}{H^{\mathrm{E}}(T_{\mathrm{c}}(p)x)} \qquad (1)$$

where the subscript c stands for critical conditions and V^E and H^E are, respectively, the excess molar volume and the excess molar enthalpy. Equation 1 is an approximate, simplified version of the original equality and should only accurately hold under some restrictive assumptions.[31] A system that phase separates on cooling must present a positive excess enthalpy, $H^E > 0$ (endothermic process upon mixing). Therefore, for a positive or negative $T-p$ slope of a critical demixing line (see Figure 3), one can anticipate an excess volume with the same sign, $V^E > 0$ or $V^E < 0$, i.e., an expansion or contraction upon mixing. At L−L critical conditions, the current family of mixtures evolves from contraction to expansion upon mixing as the alcohol alkyl chain increases, and concomitantly, one observes a change from improved to worsened miscibility as pressure is applied.

Supporting Information Available:

Synthesis, purification, and ^{1}H NMR and ^{19}F NMR of [C_6mim]-[NTf_2]. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review July 6, 2006. Accepted August 30, 2006. This work was financially supported by FC&T, Portugal, under contract nos. POCI/QUI/57716/2004 and POCI/EQU/60963/2004. J.Ł. and J.M.S.S.E. are grateful to FC&T for postdoctoral grants.

JE060307Z