New Insight into Phase Equilibria Involving Imidazolium Bistriflamide Ionic Liquids and Their Mixtures with Alcohols and Water

7 AUTHORS, INCLUDING:

Ana Rodriguez
University of Vigo
97 PUBLICATIONS **2,239** CITATIONS

SEE PROFILE

Diana Ruivo
New University of Lisbon
7 PUBLICATIONS **24** CITATIONS

SEE PROFILE

Jose Nuno A Canongia Lopes
Technical University of Lisbon
179 PUBLICATIONS **8,341** CITATIONS

SEE PROFILE

José Esperança
New University of Lisbon
110 PUBLICATIONS **4,490** CITATIONS

SEE PROFILE

New Insight into Phase Equilibria Involving Imidazolium Bistriflamide Ionic Liquids and Their Mixtures with Alcohols and Water

Ana B. Pereiro,[†,‡] Francisco J. Deive,[†,‡] Ana Rodríguez,[‡] Diana Ruivo,[†] José N. Canongia Lopes,*[,†,§] José M. S. S. Esperança,*[,†] and Luís P. N. Rebelo[†]

Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa (UNL), Avenida República 127, 2780-901 Oeiras, Portugal, Chemical Engineering Department, Vigo University, P.O. Box 36310, Vigo, Spain, and Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa (IST/UTL), 1049-001 Lisboa, Portugal

Received: May 10, 2010

The fluid phase equilibria (liquid−liquid demixing behavior (LLE)) of mixtures of ionic liquids of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide family, [$C_n$mim][NTf$_2$], with 2-methylpropanol or *n*-octanol were investigated. Binary mixtures of [C_4mim][NTf$_2$] + alcohol and [C_6mim][NTf$_2$] + alcohol were compared to pseudobinary mixtures of (0.5[C_2mim] + 0.5[C_6mim])[NTf$_2$] + alcohol and (0.5[C_2mim] + 0.5[C_{10}mim])[NTf$_2$] + alcohol, respectively. Additionally, the presence of water in the studied alcohols or as a third component in the system was analyzed in order to check any possible deviation from the LLE observed for the anhydrous systems. Systems containing small fractions of ionic liquid show similar LLE between the corresponding binary and pseudobinary systems; however, large differences are observed in the presence of water when the IL mass fraction is increased.

Introduction

Ionic Liquids (ILs) are novel alternatives to conventional organic solvents that have allowed for the development of new extraction methods at an industrial scale.[1,2] Properties such as their low volatility,[3] nonflammability,[4] and recyclability[5] have granted them our perception of their potential to contribute to cleaner processes.

The main purpose of this work is to provide information concerning the fluid phase behavior of mixtures of ILs with linear and branched alcohols. The identification and quantification of liquid−liquid demixing phenomena (LLE) can supply the mass-balance and mass-transfer data needed for the design and optimization of useful extraction units.[6−8]

In the present study we will investigate IL + alcohol (strictly) binary mixtures to be compared with pseudobinary mixtures where the "IL" is an equimolar mixture of two homologous ILs (with different cations but the same anion). The rationale behind this approach is as follows: since most of the structure and energetics of ILs are dominated by electrostatic interactions between ions, this means that cations will tend to be surrounded by anions and vice versa. When two different (but homologous) cations are incorporated in the same IL mixture, they will not tend to interact directly with each other, which means that any deviations from ideality caused by weaker- or stronger-than-average cross-interactions will be minimized. In other words, mixtures of analogous ILs must have quasi-ideal behavior.[9,10] One of the objectives of the present work is to check whether such an idea can be generalized to pseudobinary mixtures of two ILs plus a molecular solvent.

Other goals of the present investigation include the discussion of the influence of water in the LLE behavior of the IL + alcohols mixtures (either present in the alcohols or added as a third component), and the effect of the length of the cation alkyl side-chain on the LLE of such systems.

The systems under discussion will comprise binary mixtures of ILs of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide family, [$C_n$mim][NTf$_2$], with 2-methylpropanol or *n*-octanol. Binary mixtures of [C_4mim][NTf$_2$] + alcohol and [C_6mim][NTf$_2$] + alcohol will also be compared with pseudobinary mixtures of (0.5 [C_2mim][NTf$_2$] + 0.5 [C_6mim][NTf$_2$]) + alcohol and (0.5 [C_2mim][NTf$_2$] + 0.5 [C_{10}mim][NTf$_2$]) + alcohol, respectively. 1-Alkyl-3-methylimidazolium-based compounds constitute one of the most studied homologous families of ILs, including studies that suggest the quasi-ideal behavior of the corresponding IL−IL mixtures.[9,10] Bis(trifluoromethylsulfonyl) imide-based ILs belong to one of the most widely used family of ILs due to their relatively low viscosity and melting point temperatures and their relatively high chemical and thermal stability. Mixtures of alcohols with [$C_n$mim][NTf$_2$] ILs exhibit interesting LLE behavior,[11−15] including immiscibility envelopes with upper critical solution temperature loci and complex response to the addition of water.[12,16]

Experimental Section

Materials. 2-Methylpropanol (≥0.99 mass fraction purity) and *n*-octanol (≥0.99 mass fraction purity) were supplied by Riedel-de Haën and Sigma-Aldrich, respectively. Both solvents were dried over freshly activated molecular sieves (type 3 × 10^{-10} m, supplied by Aldrich) for several weeks.

The ILs [C_2mim][NTf$_2$], [C_4mim][NTf$_2$], [C_6mim][NTf$_2$], and [C_{10}mim] [NTf$_2$] were prepared and purified according to synthetic routes found elsewhere.[17] The purity of the final products was checked by ^{1}H NMR, yielding spectra in accordance with literature values (cf. Supporting Information). To keep the IL water content at acceptable values (below 200 ppm), all samples were kept under vacuum (∼0.1 Pa) at moderate temperature (60 °C) during several hours and used immediately

* Corresponding author. E-mail: jnlopes@ist.utl.pt (J.N.C.L.); jmesp@itqb.unl.pt (J.M.S.S.E.).
† Universidade Nova de Lisboa (www.itqb.unl.pt).
‡ Vigo University.
§ Universidade Técnica de Lisboa (cqe.ist.utl.pt).

Phase Equilibria of [Cnmim][NTf2] ILs

J. Phys. Chem. B, Vol. 114, No. 27, 2010 **8979**

TABLE 1: Experimental LLE Cloud-Point Temperatures for [C4mim][NTf2] + Alcohol Binary Systems and (0.5[C2mim][NTf2] + 0.5[C6mim][NTf2]) + Alcohol Pseudobinary Systems

w_1	T/K	w_1	T/K	w_1	T/K	w_1	T/K	w_1	T/K	w_1	T/K
[C4mim] [NTf2] (1) +											
Commercial 2-Methyl Propanol (2)				Dried 2-Methyl Propanol (2)				Dried n-Octanol (2)			
0.8111	285.6	0.3172	300.6	0.8132	285.3	0.3795	303.7	0.0734	307.6	0.4723	360.3
0.7635	291.4	0.2753	300.0	0.7651	291.6	0.3015	303.5	0.0945	319.9	0.5220	360.3
0.7073	296.1	0.2344	298.7	0.7155	296.4	0.2387	302.8	0.1384	350.3	0.5721	360.6
0.6612	298.8	0.2046	297.5	0.6533	299.9	0.1928	301.6	0.1797	357.0	0.6449	360.5
0.6129	300.6	0.1682	296.3	0.6094	301.7	0.1561	299.4	0.2224	358.4	0.7186	360.6
0.5659	301.5	0.1377	293.7	0.5676	302.8	0.1279	298.0	0.2642	360.1	0.8070	357.4
0.5141	302.1	0.1119	291.2	0.5204	303. 5	0.1050	296.4	0.3108	360.2	0.8570	353.1
0.4564	301.9	0.0868	288.2	0.4750	303.8	0.0794	293.1	0.3572	360.2	0.8987	342.2
0.4062	301.7	0.0696	284.8	0.4320	303.7	0.0596	288.1	0.3980	360.4	0.9308	331.3
0.3598	301.3							0.4396	359.9	0.9637	318.1
(0.5 [C2mim] + 0.5 [C6mim] [NTf2]) (1) +											
Commercial 2-Methyl Propanol (2)				Dried 2-Methyl Propanol (2)				Dried n-Octanol (2)			
0.8158	280.2	0.3744	300.0	0.7812	287.0	0.3697	303.0	0.0878	301.4	0.5267	357.3
0.7986	282.6	0.3330	299.9	0.7509	291.6	0.2989	303.2	0.1163	314.0	0.5646	357.1
0.7755	286.1	0.2946	299.8	0.6865	296.9	0.2299	302.3	0.1433	336.6	0.6648	353.5
0.7288	291.7	0.2333	299.3	0.6388	299.5	0.1795	301.4	0.1900	354.0	0.7379	348.2
0.6747	295.6	0.1990	298.3	0.5996	300.6	0.1381	299.9	0.2455	357.1	0.8054	338.1
0.6140	297.9	0.1702	297.5	0.5828	301.2	0.1086	298.5	0.3076	358.4	0.8461	319.2
0.5680	298.9	0.1414	296.0	0.5179	302.1	0.0871	296.2	0.3842	357.8	0.8847	309.6
0.5284	299.2	0.1267	294.4	0.4376	302.8	0.0676	293.6	0.4431	357.9	0.9216	298.3
0.4947	299.4	0.0984	291.8	0.3728	302.8	0.0548	290.6	0.4859	357.6		
0.4553	299.7	0.0672	286.7								
0.4151	299.7	0.0481	281.5								

after this procedure. The final water mass fraction of the dried ILs, measured by Karl Fisher coulometric titration (Metrohm 831 KF Coulometer), was always less than 150 ppm.

LLE Determination. Visual detection of the solution turbidity was employed to determine solubility data on the temperature−composition phase diagrams corresponding to LLE at atmospheric pressure. For this purpose, Pyrex glass cells incorporating magnetic stirrers were used. Samples were gravimetrically prepared directly inside the cells using an analytical high-precision balance with an uncertainty of 0.00002 g. The cells were then immersed in one of two thermostatic baths, depending on the temperature range, and were continuously stirred. An ethanol-filled bath, cooled off by adding liquid nitrogen, was used for measurements from $T = 240-300$ K. Measurements at higher temperatures, in the range of 300 K < T < 430 K, were performed using a silicone-oil-filled bath. Starting from the heterogeneous region, the temperature at which the last sign of turbidity disappeared was taken as the temperature of the liquid−liquid phase transition. 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 ±0.5 K), and the estimated uncertainty of the mixtures composition was of 0.0001 in mass fraction.

Results and Discussion

LLE data (composition of the homogeneous phase, cloud-point temperatures) of binary mixtures containing [C4mim][NTf2] + 2-methylpropanol or n-octanol are contrasted with similar results for pseudobinary mixtures of (0.5[C2mim][NTf2] + 0.5[C6mim]-[NTf2]) + 2-methylpropanol or n-octanol in Table 1. The table also reports the effect of using commercial versus dried alcohols. Table 2 shows the effect of adding controlled quantities of water to the previous systems (those that contained dried alcohol),

effectively transforming the binary mixtures into ternary ones. Table 3 shows data for the binary mixtures containing [C6mim][NTf2] + 2-methylpropanol or n-octanol and the pseudobinary mixtures of (0.5[C2mim][NTf2] + 0.5[C10mim][NTf2]) + 2-methylpropanol or n-octanol. In this case, all alcohol samples were previously dried.

Effects of Alcohol Size and Cation Alkyl Side-Chain Length on LLE. Figures 1 and 2 show the LLE behavior of binary (or pseudobinary) mixtures of an IL (or an equimolar mixture of two ILs) with either 2-methylpropanol or n-octanol. In Figure 1a, only small differences are observed between the miscibility curves describing the LLE for the binary mixture [C4mim][NTf2] + 2-methylpropanol and the corresponding pseudobinary mixture (0.5[C2mim][NTf2] + 0.5[C6mim][NTf2]) + 2-methylpropanol. Slightly larger differences can be detected, specially in the ionic-liquid-rich side of the phase diagram (Figure 1b), when the alcohol present in the two previous systems is replaced by n-octanol. On the other hand, distinct trends are noticeable (Figure 2a,b) for the binary mixtures of [C6mim][NTf2] + alcohol and (0.5[C2mim][NTf2] + 0.5[C10mim][NTf2]) + alcohol.

In order to rationalize these trends, one must consider in the first place the notion that ILs are nanostructured liquids composed of a polar network (formed by the high-density charged parts of the cations and anions) permeated by nonpolar domains (formed by the alkyl side-chains present in the ions).[18,19] The solubility of a given molecular solute in a given IL depends on its ability to interact and accommodate itself inside these regions.[20] For instance, alkanes are solvated inside the nonpolar regions, dipolar aprotic molecules such as acetone or acetonitrile occupy positions in the vicinity of the polar network, and dipolar protic molecules such as water usually exhibit strong localized interactions with the anions.[21,22] Alkanols tend to orient the hydroxy group toward the polar network and their alkyl chain toward the nonpolar domains. Within this context, is not hard to explain the experimental solubilities of alcohols

TABLE 2: Experimental LLE Cloud-Point Temperatures for [C₄mim][NTf₂] + 2-Methylpropanol + Water or (0.5 [C₂mim][NTf₂]+ 0.5[C₆mim][NTf₂]) + 2-Methyl Propanol + Water Systems

w_1:$w_2 \approx$ 1:3 (d in Figure 5)				w_1:$w_2 \approx$ 1:1 (c in Figure 5)				w_1:$w_2 \approx$ 2:1 (b in Figure 5)				w_1:$w_2 \approx$ 3:1 (a in Figure 5)			
w_1	w_2	w_3	T/K	w_1	w_2	w_3	T/K	w_1	w_2	w_3	T/K	w_1	w_2	w_3	T/K
[C₄mim] [NTf₂] (1) + 2-Methyl Propanol (2) + Water (3)															
0.2499	0.7501	0.0000	302.8	0.5042	0.4958	0.0000	303.6	0.6445	0.3555	0.0000	300.0	0.7479	0.2521	0.0000	294.1
0.2470	0.7413	0.0117	291.9	0.4982	0.4899	0.0120	291.6	0.6336	0.3494	0.0170	278.5	0.7463	0.2516	0.0021	286.3
0.2455	0.7368	0.0178	286.8	0.4950	0.4868	0.0182	281.9	0.6274	0.3460	0.0266	263.3	0.7452	0.2512	0.0036	278.1
0.2429	0.7292	0.0279	278.7	0.4884	0.4802	0.0314	272.2	0.6143	0.3388	0.0469	277.8	0.7398	0.2494	0.0108	267.2
0.2407	0.7224	0.0370	271.7	0.4821	0.4741	0.0439	266.5	0.6093	0.3360	0.0547	295.6	0.7294	0.2459	0.0247	282.1
0.2377	0.7136	0.0487	265.6	0.4753	0.4673	0.0574	261.7	0.6019	0.3319	0.0662	308.9	0.7259	0.2447	0.0294	291.2
0.2350	0.7053	0.0598	261.5	0.4486	0.4411	0.1103	289.3	0.5972	0.3293	0.0735	319.6	0.7186	0.2422	0.0392	308.9
0.2326	0.6980	0.0694	258.8	0.4418	0.4344	0.1238	302.9	0.5914	0.3262	0.0824	330.3	0.7134	0.2405	0.0461	320.2
0.2302	0.6910	0.0788	257.4	0.4359	0.4287	0.1354	314.6					0.7096	0.2392	0.0512	330.2
0.2136	0.6411	0.1453	288.7												
0.2101	0.6307	0.1592	301.4												
0.2075	0.6229	0.1696	314.1												
0.2061	0.6186	0.1753	320.9												
(0.5 [C₂mim] + 0.5 [C₆mim] [NTf₂]) (1) + 2-Methyl Propanol (2) + Water (3)															
0.2497	0.7503	0.0000	303.3	0.5029	0.4971	0.0000	302.8	0.6474	0.3526	0.0000	299.8	0.7440	0.2560	0.0000	292.6
0.2455	0.7378	0.0167	287.5	0.4981	0.4923	0.0096	292.9	0.6413	0.3493	0.0094	287.7	0.7418	0.2552	0.0030	283.5
0.2409	0.7239	0.0352	271.8	0.4952	0.4895	0.0153	282.8	0.6364	0.3466	0.0170	277.6	0.7371	0.2536	0.0094	267.7
0.2387	0.7173	0.0440	265.5	0.4901	0.4844	0.0255	272.1	0.6339	0.3452	0.0209	270.5	0.7324	0.2519	0.0157	260.8
0.2366	0.7110	0.0524	261.9	0.4785	0.4730	0.0484	259.3	0.6307	0.3435	0.0258	265.2	0.7283	0.2505	0.0212	259.5
0.2146	0.6448	0.1406	276.5	0.4473	0.4422	0.1105	287.2	0.6077	0.3309	0.0614	276.2	0.7176	0.2468	0.0356	280.1
0.2128	0.6395	0.1477	287.1	0.4428	0.4377	0.1194	299.3	0.6041	0.3290	0.0669	285.7	0.7139	0.2456	0.0405	292.1
0.2107	0.6331	0.1563	300.3	0.4371	0.4320	0.1309	317.0	0.6025	0.3281	0.0693	293.2	0.7117	0.2448	0.0434	301.5
0.2089	0.6278	0.1633	309.2					0.5982	0.3258	0.0760	308.9	0.7096	0.2441	0.0463	308.5
0.2062	0.6196	0.1742	318.0					0.5959	0.3246	0.0795	315.0	0.7063	0.2430	0.0507	317.4
								0.5919	0.3224	0.0858	324.0	0.7029	0.2418	0.0553	322.6

TABLE 3: Experimental LLE Cloud-Point Temperatures for [C₆mim][NTf₂] + Alcohol Binary Systems and (0.5[C₂mim][NTf₂] + 0.5[C₁₀mim] [NTf₂]) + Alcohol Pseudobinary Systems

| w_1	T/K	w_1	T/K	w_1	T/K	w_1	T/K	w_1	T/K	w_1	T/K
[C₆mim] [NTf₂] (1) +											
2-Methylpropanol (2)						*n*-Octanol (2)					
0.7103	274.0	0.4072	282.9	0.1824	281.6	0.7035	322.4	0.4739	331.8	0.2497	330.6
0.6516	278.7	0.3553	283.0	0.1482	280.8	0.6656	326.1	0.4159	332.5	0.1997	329.4
0.5940	281.5	0.3053	283.0	0.1156	278.2	0.6379	327.6	0.3584	332.2	0.1522	327.0
0.5199	282.3	0.2615	282.7	0.0834	275.4	0.5932	329.2	0.3142	331.6	0.1275	322.9
0.4635	282.8	0.2188	282.2			0.5177	330.8	0.2751	331.0		
(0.5 [C₂mim] + 0.5 [C₁₀mim] [NTf₂]) (1) +											
2-Methylpropanol (2)						*n*-Octanol (2)					
0.7406	268.2	0.4679	280.7	0.1731	285.0	0.6255	320.6	0.4445	328.2	0.1483	331.4
0.7270	269.2	0.4162	281.7	0.1433	284.5	0.5895	322.7	0.4065	329.1	0.1198	329.9
0.7073	270.8	0.3744	282.6	0.1196	283.7	0.5523	324.4	0.3512	330.1	0.1030	328.6
0.6787	273.1	0.3345	283.3	0.0920	281.8	0.5245	325.6	0.3056	330.8	0.0876	323.2
0.6572	274.6	0.3005	284.1	0.0675	277.9	0.4905	326.4	0.2550	331.4		
0.6135	277.1	0.2709	284.6	0.0522	275.5	0.4722	326.9	0.2031	331.9		
0.5707	278.4	0.2390	284.8								
0.5033	280.0	0.2048	285.2								

of different sizes in different ILs:[11−16,23] the general rule is that the solubility of a given alcohol in an homologous series of ILs increases as the alkyl side-chains of the ILs increase (the nonpolar domains get larger and are able to accommodate more efficiently the alkyl chain of the alcohol); conversely the solubility of alkanols from an homologous series in a given IL increases when the alkyl chain of the alkanol decreases (for a given size of the nonpolar domains, it is easier to accommodate shorter than longer alkyl chains). In other words, the alkyl chains of alkanols are a part of the solute molecule that has to be "tolerated" or "disposed of" by the IL within its nanoseggregated structure. Such task is accomplished in a more straightforward manner if the alcohol chains are smaller or the nonpolar domains larger. This state of affairs can be easily appreciated in Figure 3a, where the

LLE envelopes for a series of different alkanols in [C₆mim][NTf₂] (including the two alcohols studied in this work) are compared with each other:[11] the upper critical solution temperatures increase (and solubilities at a given temperature decrease) as the alkyl chains of the alkanol increase in size.

The effect of the shape of the alkyl side chain can also be tested if the data for 2-methylpropanol is compared to that of its structural isomer *n*-butanol.[11] In this case, the bulkier and less flexible nature of the branched alcohol leads to a slightly higher upper critical solution temperature (lower solubilities at a given temperature), as shown in Figure 3a.

The relations between the upper critical solution temperatures exhibited by the different binary mixtures studied in this work (schematized in the $T-x$ phase diagrams of Figures 1c and 2c)
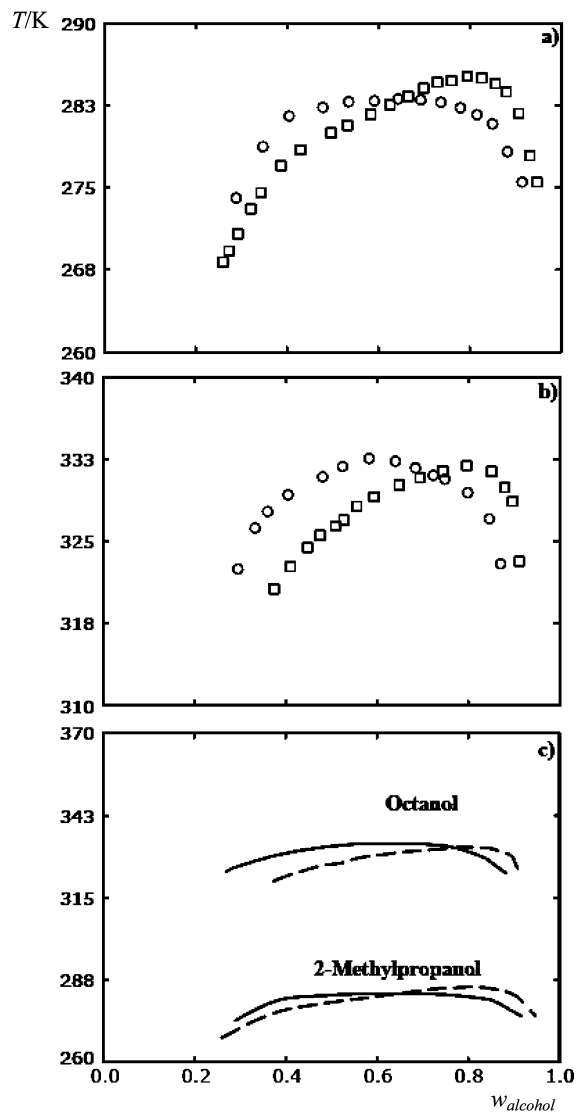
Phase Equilibria of [C$_n$mim][NTf$_2$] ILs

J. Phys. Chem. B, Vol. 114, No. 27, 2010 **8981**
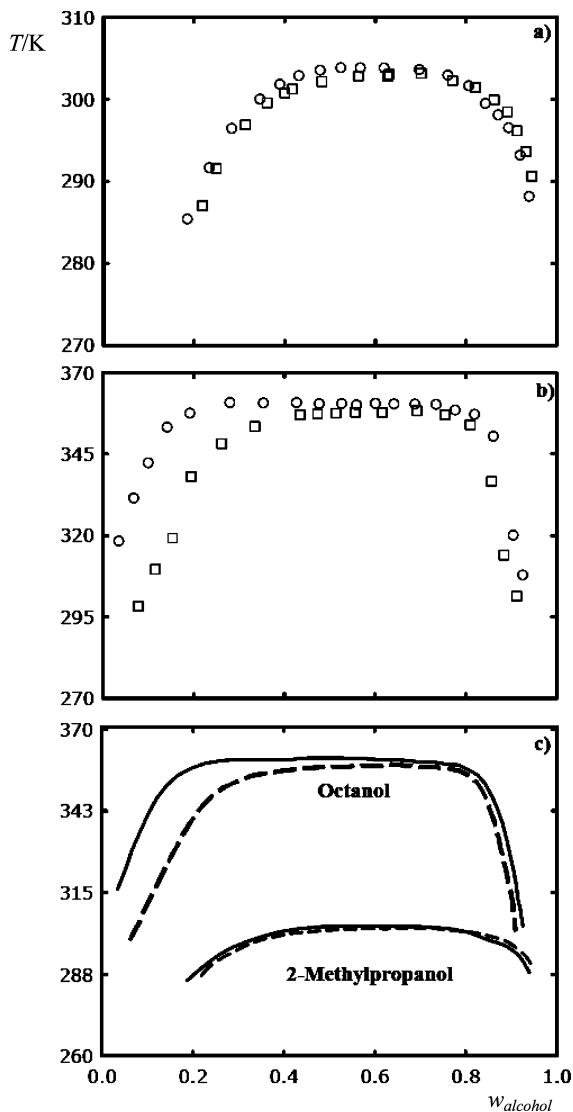
Figure 1. $T-x$ phase diagrams showing the LLE behavior of binary and pseudobinary IL + alcohol mixtures. (a) (○) [C$_4$mim][NTf$_2$] + 2-methylpropanol, (□) (0.5[C$_2$mim][NTf$_2$]+0.5[C$_6$mim][NTf$_2$]) + 2-methylpropanol. (b) (○) [C$_4$mim][NTf$_2$] + *n*-octanol, (□) (0.5[C$_2$mim][NTf$_2$]+0.5[C$_6$mim][NTf$_2$]) + *n*-octanol. (c) The two previous diagrams are compared in the same scale.

Figure 2. $T-x$ phase diagrams showing the LLE behavior of binary and pseudobinary IL + alcohol mixtures. (a) (○) [C$_6$mim][NTf$_2$] + 2-methylpropanol, (□) (0.5[C$_2$mim][NTf$_2$]+0.5[C$_{10}$mim][NTf$_2$]) + 2-methylpropanol. (b) (○) [C$_6$mim][NTf$_2$] + *n*-octanol, (□) (0.5[C$_2$mim][NTf$_2$]+0.5[C$_{10}$mim][NTf$_2$]) + *n*-octanol. (c) The two previous diagrams are compared in the same scale.

are also obvious: T_{UCST} ([C$_4$mim][NTf$_2$] + *n*-octanol) > T_{UCST} ([C$_6$mim][NTf$_2$] + *n*-octanol) > T_{UCST} ([C$_4$mim][NTf$_2$] + 2-methylpropanol) > T_{UCST} ([C$_6$mim][NTf$_2$] + 2-methylpropanol).

So far we have focused the discussion on the mutual solubility of ILs and alkanols on the IL-rich side of the diagram (where the IL is the solvent and the alkanol is the solute). In the following material, we analyze the solubility of the ILs in an alkanol-rich media.

It should be noted that all $T-x$ diagrams presented in this work are given as a function of weight fraction of one of the components (instead of the more traditional representation in terms of mole fractions). Both representations are possible and correct, but due to the large differences between the molar masses (and molar volumes) of the components of the mixtures it is preferable to make all representations in terms of weight or volume fractions in order to avoid phase diagrams overtly slanted toward the side of the lighter or smaller component (cf. Figure 3b). This is a situation typically found in polymer + small molecule solutions.[24,25] Note that similarities between

polymers, on one hand, and IL nanostructured networks, on the other, are obvious, including molecular weight dispersion effects, which for ILs can be induced, for instance, by mixing ad-hoc cations with different alkyl side chains.

In many cases when ILs are added to a molecular solvent, the solubility of the IL is almost null. This is the case of IL + hydrocarbon mixtures, where there is limited solubility of the hydrocarbon in the IL but almost null solubility of the IL in the hydrocarbon. The corresponding phase diagrams exhibit immiscibility envelopes extending to regions very close to the unit molar fraction of the molecular component and are therefore positioned in a quite asymmetrical way. These facts just show that, if the molecular solvent is incapable of interacting strongly with the isolated ions of the IL, effectively solvating them as isolated ions or small clusters, then any small amount of IL added to the molecular solvent will tend to phase-separate and form an IL-rich second phase where the polar network of the IL can remain unbroken. In the case of alkanols, the molecular solvent is capable of interacting (through the hydroxyl groups) with the ions that compose the IL, and we see finite solubilities
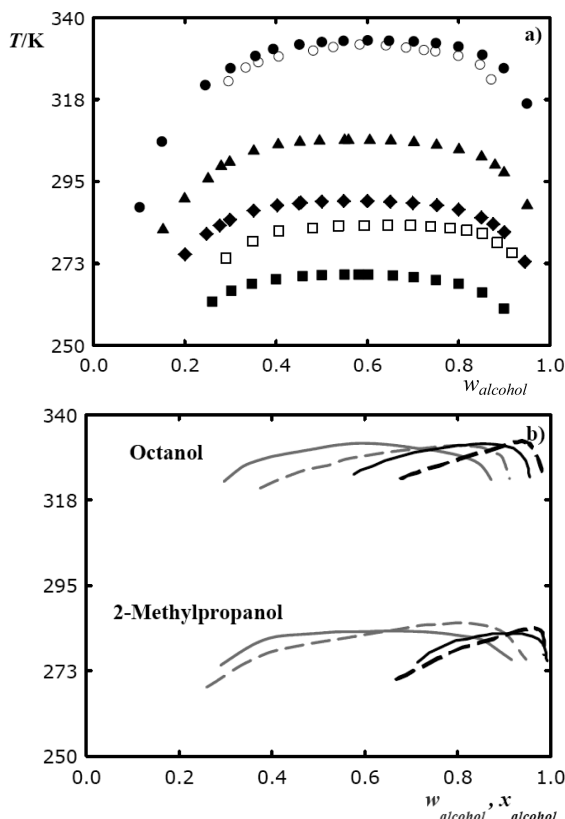
Figure 3. (a) Comparison between the LLE behavior of different [C$_6$mim][NTf$_2$] + alcohol binary mixtures: 1-butanol (■, ref 11); 2-methylpropanol (□, this work); 1-pentanol (◆, ref 11); 1-hexanol (▲, ref 11); 1-octanol (○,this work, and ●, ref 11). (b) Comparison between the $T-x$ phase diagrams from Figure 2c depicted in mole (black line) and weight fraction (gray line) of alcohol: binary IL + alcohol mixture (solid line); pseudobinary IL + alcohol mixture (dashed line).

of the ILs in the different alkanols. One important point to be stressed here is that the solubilities of the different ILs in the different alkanols do not show such a strong dependence on the size of the alkyl chains (either in the alkanol or in the imidazolium ring) as in the case of the solubilities of the alkanols in the ILs (compare the right sides of Figures 1c and 2c with the corresponding left sides). This can be easily explained by the fact that what decides the solubility of the IL in the alkanol are the hydroxyl–cation and hydroxyl–anion interactions (there is always one hydroxyl group per alcohol, independent of the size of its alkyl chain) and not, like in the case of the solubility of alkanols in the IL, the accommodation of the alkyl chains in the nonpolar regions of the IL. The fact that many (small) hydroxyl groups are needed to solvate the (bulkier) isolated ions or small cluster of the IL can also explain the asymmetry of the phase diagrams (that are even more asymmetric in per mole fraction representations, cf. Figure 3b): only with high concentrations of alkanol are there enough hydroxyl groups to effectively disrupt the polar network of the IL. At higher temperatures, such disruption is also facilitated by the enhanced thermal motion of the species present in the mixture and can help explain the appearance of the UCSTs in the immiscibility windows envelopes.

The next point to be discussed is the relation between the mutual solubilities in the binary and pseudobinary (IL + alcohol) systems.

The differences between pure [C$_4$mim][NTf$_2$] and an equimolar mixture of [C$_2$mim][NTf$_2$] + [C$_6$mim][NTf$_2$] or between [C$_6$mim]-

[NTf$_2$] and an equimolar mixture of [C$_2$mim][NTf$_2$] + [C$_{10}$mim]-[NTf$_2$] are very subtle, as can be attested both by experimental volumetric data[10,26] and by molecular dynamics (MD) studies.[9] The latter also probed the nanostructure morphology of those mixtures. The molar volumes of pure [C$_2$mim][NTf$_2$], [C$_4$mim][NTf$_2$], [C$_6$mim][NTf$_2$], and [C$_{10}$mim][NTf$_2$] are, respectively, 258.3, 292.0, 326.3, and 393.9 cm$^3 \cdot$mol^{-1}.[26] On the other hand, the molar volumes of the [C$_2$mim][NTf$_2$] + [C$_6$mim][NTf$_2$] and [C$_2$mim]-[NTf$_2$] + [C$_{10}$mim][NTf$_2$] mixtures were calculated either by MD simulation[9] or from experimental data,[16] respectively. The corresponding excess molar values at the equimolar composition ($V^E_{1/2}$ = V_m(mix) − 0.5 $\cdot$ V_m(component 1) − 0.5 $\cdot$ V_m(component 2)) are just −1.5 ± 2.3 and 0.24 ± 0.02 cm$^3 \cdot$mol^{-1}, respectively. This means that from a volumetric point of view, these mixtures can be considered quasi-ideal. The difference between the molar volumes of [C$_4$mim][NTf$_2$] and (0.5[C$_2$mim][NTf$_2$] + 0.5[C$_6$mim]-[NTf$_2$]) or between [C$_6$mim][NTf$_2$] and (0.5[C$_2$mim][NTf$_2$] + 0.5[C$_{10}$mim][NTf$_2$]) are virtually null taking into account the overall accuracy of the determinations (involving MD or experimental data, respectively): 1.2 ± 2.5 and 0.0 ± 0.1 cm$^3 \cdot$mol^{-1}. However, when alcohols are mixed either with the pure IL or with the corresponding equimolar mixture, the results show some deviations in the LLE behavior.

The above-mentioned MD studies[9] have shown that the size-distribution of the nonpolar domains (that, as we have seen, conditions the solubility of the alcohols in the ILs) is slightly different in the pure ILs or in the corresponding equimolar IL mixtures. This can be rationalized from a strictly statistical point of view. In pure [C$_4$mim][NTf$_2$], the average size of the nonpolar domains is determined by the segregation of several C4 alkyl chains into a common domain. Since all alkyl chains have the same length, the dispersion of nonpolar domain sizes is rather low and is basically determined by the average number of segments in each domain. In the equimolar mixture of [C$_2$mim][NTf$_2$] + [C$_6$mim][NTf$_2$], even if each domain continues to have the same number of alkyl chains, the dispersion of alkyl chain sizes increases simply because now there are two alkyl side chains of different size (2 C$_4$ chains are similar to a C$_2$ + C$_6$ pair of chains, but this would imply that the latter would always have to pair as such and never as C$_2$ + C$_2$ or C$_6$ + C$_6$). This means that the alcohols (specially the longer ones such as *n*-octanol) are able to find larger domains in the [C$_2$mim][NTf$_2$] + [C$_6$mim][NTf$_2$] IL than in the [C$_4$mim][NTf$_2$] IL. The solubility in the former should be slightly better. This is what was found experimentally (cf. Figure 1), specially for the case of *n*-octanol (Figure 1b).

In the case of the [C$_6$mim][NTf$_2$] versus [C$_2$mim][NTf$_2$] + [C$_{10}$mim][NTf$_2$] systems, the differences are even more striking. Since the two ILs that compose the resulting IL are now further apart in the homologous series, it is expected that the size dispersion of the nonpolar domains is also larger. Moreover it is known, both from experimental[27] and theoretical studies,[19] that there is a topological change in the morphology of the nonpolar domains around [C$_6$mim][NTf$_2$]: for alkyl side chains smaller than that threshold value, the nonpolar domains are dispersed in a continuous polar network; above that value the nonpolar domains coalesce and form a second continuous nanophase (the whole IL structure becomes bicontinuous). This means that, albeit on average the volume occupied by the nonpolar domains is similar in the systems containing [C$_6$mim][NTf$_2$] or (0.5[C$_2$mim][NTf$_2$] + 0.5[C$_{10}$mim][NTf$_2$]), their size-distribution and morphologies are different, leading to enhanced solubilities of the alcohols in the pseudobinary system (cf. left side of Figure 2).
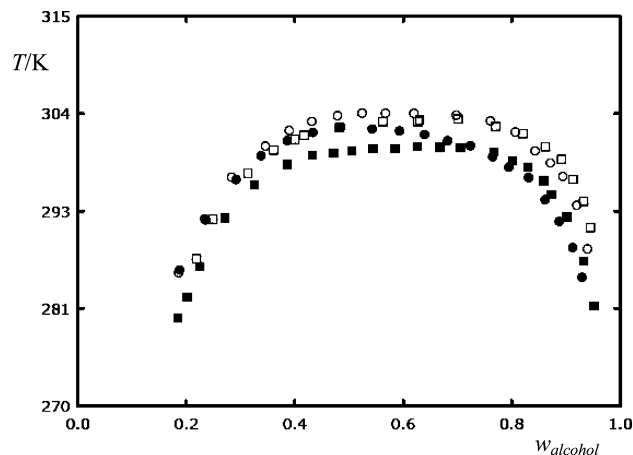
Figure 4. (a) Comparison between the $T-x$ phase diagrams of [C₄mim][NTf₂] + 2-methylpropanol binary systems (○) and (0.5[C₂mim] [NTf₂]+ 0.5[C₆mim][NTf₂]) + 2-methylpropanol pseudobinary systems (□). The filled and empty symbols represent commercial and dried 2-methylpropanol, respectively.

Figure 5. Effect of the addition of water to the binary system [C₄mim][NTf₂] + 2-methylpropanol (filled symbols) and pseudobinary system (0.5[C₂mim] [NTf₂]+ 0.5[C₆mim][NTf₂]) + 2-methylpropanol (empty symbols). The symbols used represent the mass fraction of IL in the binary/pseudobinary mixture: (□) 25%; (△) 50%; (◇) 64%; (○) 75%.

Interestingly, the presence of larger cations that enhanced the solubility of the alcohols in the IL-rich phase of the pseudobinary systems is detrimental to the solubility of the ILs in the alcohol-rich phases (there are now larger cations to solvate by the hydroxyl groups). This explains the solubility crossovers that show up in most of the immiscibility boundaries in Figures 1 and 2.

Influence of Water on LLE Data. The differences between the binary system [C₄mim][NTf₂] + 2-methylpropanol and the pseudobinary system (0.5[C₂mim][NTf₂] + 0.5[C₆mim][NTf₂]) + 2-methylpropanol were so subtle (Figure 1a) that we have decided to check whether any small deviations were not just an artifact caused by trace amounts of water in either component; after all, it is known that water can produce quite dramatic cosolvency effects in some IL + alcohol systems, including some that are similar to those studied in this work.[12,16]

The influence of water on the LLE of the two above-mentioned systems is shown in Figure 4. In light if the remarkable similarities between the LLE behavior of systems containing dried 2-methylpropanol (water content of 200 ppm mass fraction) and commercial one (water content of 6000 ppm mass fraction), one immediately observes that a small amount of water present in the system really increases the mutual solubility between the ILs and the alcohol. Moreover, the addition of water seems to unveil some solubility differences between the binary and pseudobinary systems, specially in the 0.2 to 0.7 alcohol-mass-fraction region. This means that if one includes the uncertainty caused by trace amounts of water in the overall experimental error associated with the solubility determinations, one can conclude that the solubility of 2-methylpropanol is the same in the binary and pseudobinary systems, at least when water content was controlled to levels around or below 200 ppm.

On the other hand, these results suggest the interest of pursuing an in-depth analysis of the role of water on the relative LLE behavior between binary and pseudobinary mixtures. For this purpose, four distinct pairs of binary and pseudobinary mixtures ([C₄mim][NTf₂] + 2-methylpropanol and (0.5[C₂mim][NTf₂] + 0.5[C₆mim][NTf₂]) + 2-methylpropanol) were prepared. Controlled amounts of water were added to those systems, and the corresponding cloud-points were determined. The results are presented in Figure 5, with the paths followed in the corresponding ternary diagram shown in the figure inset. The four pairs of curves show
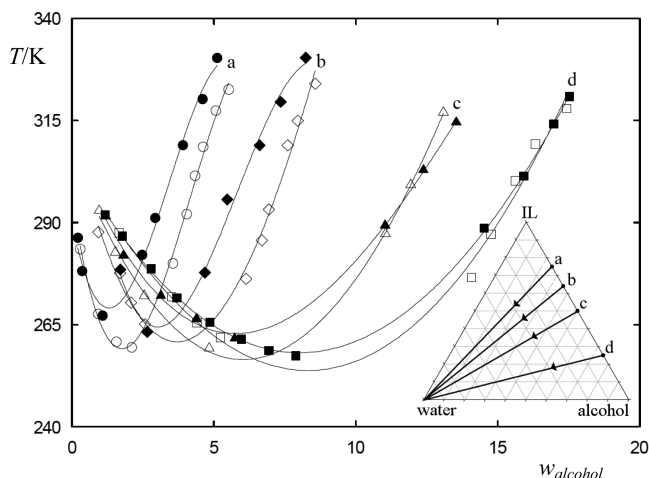
that the addition of water promotes at first the miscibility between the IL and alcohol (cosolvent effect), but as the amount of water is further increased, the trend reverses, and at high water concentrations there is an antisolvent effect.

The cosolvent effect is quite striking in terms of temperature, with drops of more than 30 K in some cases. This kind of behavior was discovered and reported by Rebelo and coworkers[12,16] more than 6 years ago. The nonmonotonous behavior of the curves shown in Figure 5 can be rationalized if one takes into account the corresponding ternary phase diagrams at a given temperature. These data are depicted in Figure 6a, along with a previously studied IL−alcohol−water mixture ([C₄mim][PF₆] + ethanol + water) taken from ref 12 (Figure 6b). In the case of the ([C₄mim][NTf₂] + 2-methylpropanol + water), the three binary mixtures at the edges of the ternary diagram correspond to situations where there is always limited miscibility. However, and in spite of the three immiscibility windows at the edges of the triangular diagram, there is a miscibility corridor uniting the IL + water system to the alcohol + water system. This explains the cosolvency effect promoted by the addition of small quantities of water to the IL + alcohol mixture. Such a corridor is easier to explain in the case of the ([C₄mim][PF₆] + ethanol + water) system since ethanol and water are miscible in all proportions; the corridor tends to "widen-up" as the ethanol + water edge of the diagram is approached, as seen at the bottom of Figure 6b.

From a molecular point of view, the existence of the corridor can be explained by the fact that water interacts strongly with the polar network (specially the anions) (cf. Figure 2d of ref 21). If the proportion of water and alcohol molecules as compared to those of IL is not too big (the corridor will be defined by that proportion), then a balance can be achieved where the water molecules will be able to mediate the interactions between the IL and the alcohol molecules: the water will position itself closer to the polar network and pushes the alcohol molecules further into the nonpolar domains. On the other hand, the alcohol molecules will be able to establish hydrogen bonds with the water molecules (instead of trying to reach further inside the polar network) while orienting their alkyl chains inside the nonpolar domains of the IL. This can be confirmed by analysis of the radial distribution functions (rdf's) of Figure 2c,d
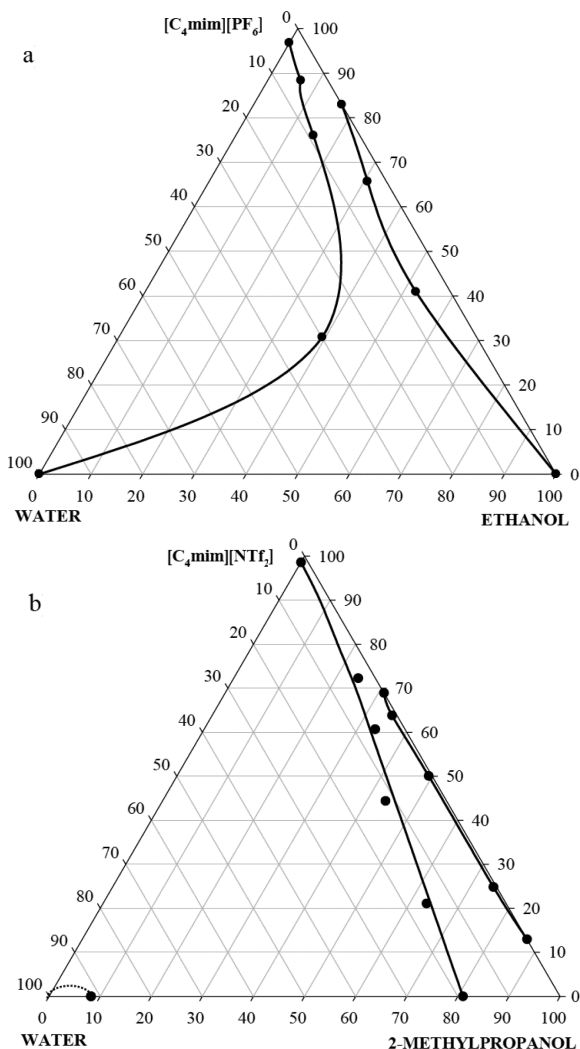
Figure 6. Ternary phase diagrams at 298.15 K (weight percentage) of the systems: (a) [C$_4$mim][PF$_6$] + ethanol + water (ref 12), (b) [C$_4$mim][NTf$_2$]+ 2-methylpropanol + water. The data for the water + 2-methylpropanol binary system was taken from ref 28.

of ref 21, where it can be seen that the water molecules are able to interact more strongly and at closer distances with the anions of the polar network. The bargain is good for both solute molecules: water is "shielded" from the nonpolar domains by the presence of the alcohol molecules, the alcohol, while still interacting via a hydrogen bond (with water instead of the polar network), is able to orient its alkyl side chain in a more flexible way inside the nonpolar domains.

The fine balance between the interactions of the IL with both water and alcohol (and the role that the nonpolar domains may have in such interplay), can help explain the differences between the LLE behavior in the ternary and pseudoternary (IL+ alcohol + water) systems. Figure 5 shows that such differences are much more pronounced in systems with a larger IL-to-alcohol proportion (the two left-most curves in Figure 5, where the solubility differences at a given ternary composition can be as high as 25 K). If water sends the alcohol solute more into the nonpolar domains, then more size-dispersed nonpolar domains are able to better accommodate the alcohol molecules, meaning enhanced solubility for the pseudoternary systems. When the IL-to-alcohol ratio is decreased, the size and dispersion of the nonpolar domains in the mixture is changed by the alkyl chains of the alcohol, which means that any differences between a pure

IL and the corresponding equimolar mixture become "diluted" as alcohol is added to the mixture.

Conclusions

From the point of view of density or other equilibrium properties that represent molecular-level overall averages, the excess properties of mixtures of ILs can be considered quasi-ideal. This almost ideal behavior can also be observed when one compares a pure IL with a pseudospecies formed by the mixture of two ILs in the correct proportion: V_m([C$_6$mim][NTf$_2$]) $\approx V_m$ (0.5[C$_2$mim][NTf$_2$] + 0.5[C$_{10}$mim][NTf$_2$]).

However, when a property (such as the solubility of a molecular solute in the IL) depends not only on the average value of a given molecular feature of the IL (such as the relative size and morphology of their polar and nonpolar domains), but also on the distribution of those values, then, the quasi-ideal behavior is no longer observed, and differences between the behavior of true and pseudobinary mixtures of an IL with different molecular species is revealed.

In this work, a large molecular solute such as *n*-octanol was able to immediately expose those differences. On the other hand, systems containing a smaller solute such as 2-methylpropanol exhibited more subdued effects. However, the addition of a third component (water) to those systems was able to reveal again the differences between binary and pseudobinary mixtures. The strong cosolvency effects exhibited by these IL + water + alcohol mixtures are in the origin of those differences.

One of the most important conclusions of the present work is that the complex nature of ILs at a molecular level (their nanosegregated structure) not only has a very important role in the determination of the unique properties of the IL as a solvent toward different classes of molecular solutes, but that subtle changes in the underlying morphology of the IL can also have important effects. Those subtle changes can be accomplished using pseudocomponents formed by the mixture of two ILs.

IILs have been commonly dubbed as designer or tailored solvents. This work shows that they are even more stylish than that.

Supporting Information Available: ^{1}H NMR of the pure ILs used in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bösmann, A.; Datsevich, L.; Jess, A.; Lauter, A.; Schmitz, C.; Wasserscheid, P. Deep Desulfurization of Diesel Fuel by Extraction with Ionic Liquids. *Chem. Commun.* **2001**, *23*, 2494–2495.

(2) Plechkova, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2007**, *36*, 1–29.

(3) Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The Distillation and Volatility of Ionic Liquids. *Nature* **2006**, *439*, 831–834.

(4) Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L. Y.; Thrasher, J. S.; Kirichenko, K.; Singh, S.; Katritzky, A. R.; Rogers, R. D. Combustible Ionic Liquids by Design: Is Laboratory Safety Another Ionic Liquid Myth? *Chem. Commun.* **2006**, *24*, 2554−2556.

(5) Wu, B.; Liu, W.; Zhang, Y.; Wang, H. Do We Understand the Recyclability of Ionic Liquids? *Chem.−Eur. J.* **2009**, *15*, 1804−1810.

Phase Equilibria of [C$_n$mim][NTf$_2$] ILs

J. Phys. Chem. B, Vol. 114, No. 27, 2010 **8985**

(6) Pereiro, A. B.; Rodriguez, A. Azeotrope-Breaking Using [BMIM] [MeSO$_4$] Ionic Liquid in an Extraction Column. *Sep. Purif. Technol.* **2008**, *62*, 733–738.

(7) Pereiro, A. B.; Rodriguez, A. Separation of Ethanol−Heptane Azeotropic Mixtures by Solvent Extraction with an Ionic Liquid. *Ind. Eng. Chem. Res.* **2009**, *48*, 1579–1585.

(8) Pereiro, A. B.; Rodriguez, A. Purification of Hexane with Effective Extraction using Ionic Liquid as Solvent. *Green Chem.* **2009**, *11*, 346–350.

(9) Shimizu, K.; Tariq, M.; Rebelo, L. P. N.; Lopes, J. N. C. Binary Mixtures of Ionic Liquids with a Common Ion Revisited: A Molecular Dynamics Simulation Study. *J. Mol. Liq.* **2010**, *153*, 52–56.

(10) Lopes, J. N. C.; Cordeiro, T. C.; Esperanca, J. M. S. S.; Guedes, H. J. R.; Huq, S.; Rebelo, L. P. N.; Seddon, K. R. Deviations from Ideality in Mixtures of Two Ionic Liquids Containing a Common Ion. *J. Phys. Chem. B* **2005**, *109*, 3519–3525.

(11) Lachwa, J.; Morgado, P.; Esperança, J. M. S. S.; Guedes, H. J. R.; Lopes, J. N. C.; Rebelo, L. P. N. Fluid-Phase Behavior of {1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) Imide, [C$_6$mim][NTf$_2$], + C-2-C-8 *n*-Alcohol} Mixtures: Liquid−Liquid Equilibrium and Excess Volumes. *J. Chem. Eng. Data* **2006**, *51*, 2215–2221.

(12) Najdanovic-Visak, V.; Esperanca, J. M. S. S.; Rebelo, L. P. N.; da Ponte, M. N.; Guedes, H. J. R.; Seddon, K. R.; de Sousa, H. C.; Szydlowski, J. Pressure, Isotope, and Water Co-solvent Effects in Liquid−Liquid Equilibria of (Ionic Liquid + Alcohol) Systems. *J. Phys. Chem. B* **2003**, *107*, 12797–12807.

(13) Heintz, A.; Lehmann, J. K.; Wertz, C.; Jacquemin, J. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 4. LLE of Binary Mixtures of [C$_2$MIM][NTf$_2$] with Propan-1-ol, Butan-1-ol, and Pentan-1-ol and [C$_4$MIM][NTf$_2$] with Cyclohexanol and 1,2-Hexanediol Including Studies of the Influence of Small Amounts of Water. *J. Chem. Eng. Data* **2005**, *50*, 956–960.

(14) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Liquid Phase Behavior of Imidazolium-Based Ionic Liquids with Alcohols. *J. Phys. Chem. B* **2004**, *108*, 5113–5119.

(15) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Liquid Phase Behavior of Imidazolium-Based Ionic Liquids with Alcohols: Effect of Hydrogen Bonding and Non-Polar Interactions. *Fluid Phase Equilib.* **2005**, *228*, 303–309.

(16) Najdanovic-Visak, V.; Esperança, J. M. S. S.; Rebelo, L. P. N.; da Ponte, M. N.; Guedes, H. J. R.; Seddon, K. R.; Szydlowski, J. Phase Behaviour of Room Temperature Ionic Liquid Solutions: an Unusually Large Co-solvent Effect in (Water + Ethanol). *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701–1703.

(17) Bonhôte, P.; Armand, A.-P.; Dias, M.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.

(18) Wang, Y. T.; Voth, G. A. Unique Spatial Heterogeneity in Ionic Liquids. *J. Am. Chem. Soc.* **2005**, *127*, 12192–12193.

(19) Lopes, J. N. A. C.; Padua, A. A. H. Nanostructural Organization in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 3330–3335.

(20) Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Guedes, H. J. R.; Łachwa, J.; Najdanovic-Visak, V.; Visak, Z. P. Accounting for the Unique, Doubly Dual Nature of Ionic Liquids from a Molecular Thermodynamic, and Modeling Standpoint. *Acc. Chem. Res.* **2007**, *40*, 1114–1121.

(21) Lopes, J. N. A. C.; Gomes, M. F. C.; Padua, A. A. H. Nonpolar, Polar, and Associating Solutes in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 16816–16818.

(22) Shimizu, K.; Gomes, M. F. C.; Pádua, A. A. H.; Rebelo, L. P. N.; Lopes, J. N. C. Three Commentaries on the Nano-segregated Structure of Ionic Liquids. *J. Mol. Struct.: THEOCHEM* **2010**, *946*, 70–76.

(23) Wertz, C.; Tschersich, A.; Lehmann, J. K.; Heintz, A. Liquid−Liquid Equilibria and Liquid−Liquid Interfacial Tension Measurements of Mixtures Containing Ionic Liquids. *J. Mol. Liq.* **2007**, *131*, 2–6.

(24) Rebelo, L. P. N. A Simple *G(E)*-Model for Generating All Basic Ttypes of Binary Liquid−Liquid Equilibria and their Pressure Dependence. Thermodynamic Constraints at Critical Loci. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4277–4286.

(25) de Sousa, H. C.; Rebelo, L. P. N. A Continuous Polydisperse Thermodynamic Algorithm for a Modified Flory-Huggins Model: The (Polystyrene + Nitroethane) Example. *J. Polym. Sci. B: Polym. Phys.* **2000**, *38*, 632–651.

(26) Tariq, M.; Forte, P. A. S.; Costa Gomes, P. F.; Lopes, J. N. C.; Rebelo., L. P. N. Densities and Refractive Indices of Imidazolium- and Phosphonium-Based Ionic Liquids: Effect of Temperature, Alkyl Chain Length, and Anion. *J. Chem. Thermodyn.* **2009**, *41*, 790–798.

(27) Triolo, A.; Russina, O.; Bleif, H.-J.; Di Cola, E. Nanoscale Segregation in Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 4641–4644.

(28) Stephenson, R. M. Mutual Solubilities - Water Ketones, Water Ethers, and Water Gasoline Alcohols. *J. Chem. Eng. Data* **1992**, *37*, 80–95.