PHASE EQUILIBRIA FOR BINARY SYSTEMS CONTAINING IONIC LIQUID WITH WATER OR HYDROCARBONS

Dheiver Santos[1*], M. Góes[2], E. Franceschi[2], A. Santos[2], C. Dariva[2], M. Fortuny[2] and S. Mattedi[1]

[1]Programa de Pós-Graduação em Engenharia Química, Escola Politécnica, Universidade Federal da Bahia
(UFBA), R. Aristides Novis 2 Federação, 40210-630, Salvador - BA, Brazil.
[2]Núcleo de Estudos em Sistemas Coloidais–ITP/UNIT, Campus Farolândia, Av. Murilo Dantas 300,
49032-490, Aracaju - SE, Brazil.
Phone/Fax: + (55) (71) 3283-9809
E-mail: dheiver.santos@ufba.br

Abstract - In this work, the mutual solubilities of sets of ionic liquids ($[C_nMIM]$ $[TF_2N]$ (n = 4, 8, 12), $[C_4PY]$ $[TF_2N]$, $[C_8MIM]$ $[OTF]$) and organic compounds (heptane, o-xylene, toluene, or water) are investigated. The experimental data measured for these systems were used to adjust the binary interaction parameters between their components for the Non-Random Two Liquid (NRTL) model. The results showed that the solubility increased with temperature, with high hygroscopicity (10^{-1} in terms of mole fraction) of the ILs, low interactions with aliphatic hydrocarbons, high interactions with aromatic hydrocarbons and the presence of a lower critical solution temperature (LCST). In addition, this study is the first to show that $[C_{12}MIM]$ $[TF_2N]$ is completely soluble in toluene and ortho-xylene between 273.15 and 373.15 K at 1 bar. The average deviations related to the mole fraction between the experimental and calculated values by the NRTL were less than 2.4%.
Keywords: Phase equilibria; Ionic liquid; Hydrocarbon; Water; NRTL.

INTRODUCTION

Ionic liquids (ILs) are defined as ionic compounds with a melting point of less than 100 °C. Since the early 1990s, scientific research on ILs has grown, with the number of published papers increasing from 20 in 1995 to 300 in 2001 (Cravotto *et al*., 2008) and approximately 4000 in 2012. The particular physicochemical characteristics of ILs, such as their high solvation abilities and coordination properties, low flammability, wide liquid range, wide electrochemical window, high thermal stability, and negligible vapor pressures, make them suitable candidates for a large range of applications (Earle *et al*., 2006;

Plechkova *et al*., 2008). The possibility of controlling their properties by adequately manipulating the cations and/or anions allows for the design of these solvents to exhibit selective solubilities for particular components in the fluid mixtures. These characteristics allow ILs to serve as excellent alternative solvents for extraction purposes and as potential green solvents for industrial purposes (Bösmann *et al*., 2001).

In addition, the aqueous solubility of ionic liquids is relevant regarding their environmental impacts. Although it is well known that ILs reduce air pollution risks due to their negligible vapor pressures, their release into aquatic environments could result

---

*To whom correspondence should be addressed

in contamination because of their potential toxicity and limited biodegradability. Overall, ILs are mainly chosen as "green" solvents because they are non-volatile, which makes them ideal "green" substitutes for conventional organic solvents. Nevertheless, ecotoxicity is an important factor that defines the applicability of ILs and should be strictly assessed. The toxicities of ILs appear to be directly related and are mainly controlled by their lipophilicity. In addition, ILs are potentially toxic and can accumulate in organisms due to their lipophilicity (Ranke *et al*., 2007; Salminen *et al*., 2007; Torrecilla *et al*., 2010; Petkovic *et al*., 2011). Recent applications of ILs in the oil industry have demonstrated the performance of a set of ILs as demulsifiers during oil-water separation processes (Guzman-Lucero *et al*. 2010; Lemos *et al*. 2010). However, after the oil-water separation, it is unclear why some ionic liquids perform better as demulsifiers. Thus, this question should be addressed by investigating the phase equilibrium and interactions that involve ILs, water and oil compounds. This requirement for additional research is the main motivation for conducting this study.

In this study, the influences of IL structures on their solubility in water and hydrocarbons are presented. The liquid-liquid binary systems (LLE) containing $[C_nMIM][TF_2N]$ (n = 4, 8, 12), $[C_4PY][TF_2N]$, $[C_8MIM][OTF]$ with hydrocarbons (n-heptanes, toluene, o-xylene) or water were measured using vials and the cloud point methodology. The experimental data were correlated using the Non-Random Two Liquid (NRTL) model.

EXPERIMENTAL PROCEDURE

Materials

The following ILs were used: 1-butyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide $[C_4MIM][TF_2N]$ (CAS 174899-83-3), 1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide $[C_8MIM][TF_2N]$ (CAS 862731-66-6), 1-dodecyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide $[C_{12}MIM][TF_2N]$ (CAS 433337-23-6), 1-octyl-3-methylimidazolium trifluoromethanesulfonate $[C_8MIM]$ $[OTF]$ (CAS 403842-84-2), and 1-butylpyridinium bis[(trifluoromethyl)sulfonyl]imide $[C_4PY][TF_2N]$ (CAS 187863-42-9). All ILs were purchased from IoLiTec and had purities greater than 98%. In addition, n-heptane (>99% purity, CAS 8031-33-2; Sigma-Aldrich), absolute ethyl alcohol (99.8% pa acs, CAS 9003-99-0; Vetec), and ultrapure Milli-Q Water were

used. The water levels present in the ionic liquids were determined by Karl Fischer and were 459.6 ppm for $[C_4MIM][TF_2N]$, 267.2 ppm for $[C_8MIM][TF_2N]$, 298.7 ppm for $[C_{12}MIM][TF_2N]$, 1788.9 ppm for $[C_8MIM][OTF]$ and 522.6 ppm for $[C_4PY][TF_2N]$.

LLE Experiments

For binary systems containing water and ionic liquids, the mutual interactions between water solubility and the ionic liquid were determined at temperatures of 293.15 to 313.15 K at atmospheric pressure. For these systems, 2-mL covered glass vials were used. Specific amounts of water and ionic liquid were weighed on a precision balance (Shimadzu, model: AX 200) and added to jars, which were then sealed. Next, the vials were mixed using a vortex for approximately 1 hour. After mixing, the samples were allowed to rest for at least 48 h to achieve phase separation. In these experiments, 48 hours was the minimum time that was required to ensure complete separation of the two phases because measurements made after 48 hours showed no significant variations. During the phase separation period, the bottles were placed in an air bath (recipient's jacketed glass) and the temperature was maintained using a thermostatic bath with a precision of ± 0.1 K.

Systems involving aliphatic hydrocarbon were held at temperatures of 293.15 to 313.15 K at atmospheric pressure. For these systems, 7-mL glass bottles were used. The glass bottles containing the aliphatic hydrocarbons were agitated vigorously and allowed to settle for 24 hours to observe the phase separation. The temperature was maintained in the glass bottles that contained the different phases by placing them within a block of aluminum Quimis that was capable of maintaining the temperature within ± 0.1 K.

All experiments for determining the phase equilibrium between the ionic liquids and the aromatics were held at constant temperatures using the cloud point method (at temperatures of 293.15, 303.15, 283.15, 313.15, or 323.15 K). A cell with a volume of approximately 50 mL was used and was maintained at a constant temperature in a thermostatic bath with a precision of 0.1 K. In addition, an analytical balance with an uncertainty of 0.1 mg and a magnetic stirrer were used. The cell was sealed using a polymeric septum to minimize solvent evaporation during the experiments. Thus, solvent evaporation was not significant when considering the forces acting in the binary numeral system. The masses of the aromatic compounds were known (approximately 8

to 10 g). At a constant temperature, the IL was removed slowly using a 1 mL syringe until the solution became slightly cloudy. Following careful observation, the temperature was recorded, together with the mass of the IL, which decreased during the turbidity process. The temperature was increased and decreased, and the different mass fractions were used based on the results of relevant scientific articles. Overall, six temperature runs were performed to increase the level of confidence because it was difficult to observe the cloud point. An uncertainty of 0.01% was obtained according to the standard deviation of the experimental results.

Analytical Methodology

After a rest period, the solubility of water in the ionic liquid-rich phase was determined using titration with Karl-Fischer reagent, and the solubility of the ionic liquid in water was determined using UV spectroscopy at wavelengths of 211 and 258 nm using previously constructed calibration curves. These wavelengths correspond to the maximum UV absorption wavelengths for the imidazolium and pyridine cations, respectively. Both phases were sampled using syringes. For the phases that were rich in ionic liquids, samples of approximately 0.1 to 0.2 g were directly injected into the KF titration solution. For the water-rich phase, samples of approximately 0.1 to 0.15 mL were taken and diluted using a factor ranging from (1:10:50) (v:v) with ultrapure water depending upon the solubility of the IL. The high precision and accuracy of this method is not only connected to the gravimetric procedure but also to the sample dilutions of the water-rich phase to avoid phase separation when working at non-ambient temperatures.

The solubilities of the heptane-rich phase ionic liquids were determined using UV spectroscopy at wavelengths of 212 and 211 nm with previously established calibration curves. For example, 1 mL of fluid in the upper phase (Hydrocarbon) was weighed (m) and placed in a jar. After evaporation in a furnace overnight to remove the volatile compounds, the amount of ionic liquid residue was too small. Thus, approximately 10 mL of ethyl alcohol was placed inside the jar to dilute the ionic liquid (dilution factor 1:10). Generally, the levels of absorbance were between 0.1 and 1.0 abs. Thus, it was possible to quantify the ionic liquid.

The solubilities of heptane in the rich phase ILs were determined using the gravimetric method, which was also used to quantify the levels of hep-

tane. In this method, the heavy and supposedly homogenized heptanes were placed in a furnace until a constant mass was achieved. The same method must be used due to the peculiar characteristics of the ionic liquid surfactants, including their low vapor pressure and lack of volatility at ambient pressure. Through mass balance, it was possible to quantify how much of the heptane was soluble in the ionic liquid-rich phase.

NRTL

The experimental data measured for the systems were used to adjust the binary interaction parameters for the NRTL (Renon and Prausnitz, 1968). All binary interaction parameters were adjusted to the experimental data. In this way, the iso-activity criterion of the LLE developed on a molar fraction basis can be expressed on a mass fraction basis as follows:

$$(\gamma_i x_i)^{GP} = (\gamma_i x_i)^{EP} \tag{1}$$

Here, x_i is the mole fraction of component i; y_i is the activity coefficient of component i. An algorithm developed in the FORTRAN programming language was used to estimate the NRTL parameters. This algorithm applies the modified simplex method to the objective function of composition (Equation (2)) to estimate thermodynamic parameters (shown in Table 1) that are considered as a generic number of implicit constraints, which is similar to the approach developed by Ferrari *et al.* (2009).

$$\text{OF} = \sum_m^D \sum_n^N \sum_i^{K-1} \left[\begin{array}{c} \left(x_{i,n,m}^{I,exp} - x_{i,n,m}^{I,calc} \right)^2 + \\ \left(x_{i,n,m}^{II,exp} - x_{i,n,m}^{II,calc} \right)^2 \end{array} \right] \tag{2}$$

where D is the total number of data groups; N is the total number of tie lines; K is the total number of components in the data group; x is the mole fraction; the subscripts i, n and m are the component, tie line and group numbers, respectively; exp and calc represent the experimental and calculated compositions, respectively. The procedure for calculating these parameters involves flash calculations.

The average deviations between the experimental and calculated compositions in both phases were calculated according to Equation (3). Stragevitch and d'Ávila (1997) applied a similar approach that used the mole fraction.

Table 1: Parameters (NRTL).

i	j	g_{ij} (K)	g_{ji} (K)	Δx Rmsd %
heptanes	[C$_4$MIM][TF$_2$N]	2499.99	821.84	1.0
heptanes	[C$_8$MIM][TF$_2$N]	1360.24	287.22	1.0
heptanes	[C$_{12}$MIM][TF$_2$N]	1453.68	-62.35	1.3
heptanes	[C$_4$PY][TF$_2$N]	2499.98	918.96	0.4
heptanes	[C$_8$MIM][OTF]	1236.30	301.825	2.4
Water	[C$_4$MIM][TF$_2$N]	1305.09	211.19	1.5
Water	[C$_8$MIM][TF$_2$N]	1275.97	303.32	1.7
Water	[C$_{12}$MIM][TF$_2$N]	1255.51	258.91	2.0
Water	[C$_4$PY][TF$_2$N]	1255.95	208.07	2.0
Water	[C$_8$MIM][OTF]	1335.12	87.85	1.5

*alpha 0.31

$$\Delta x = 100 \left[\frac{\sum_n^N \sum_i^K \left(x_{i,n}^{GP,exp} - w_{i,n}^{GP,calc} \right)^2 + \left(x_{i,n}^{EP,exp} - x_{i,n}^{EP,calc} \right)^2}{2NK} \right]^{1/2} \quad (3)$$

RESULTS AND DISCUSSION

Generally, for all of the studied ILs, the miscibility of both phases increased with temperature (Figures 1 and 2). All of the studied ILs are known as "hydrophobic", but the water solubility results indicate that they are substantially "hygroscopic". The mole fraction solubilities of the ILs in water varied from 10^{-4} to 10^{-5}, and the solubilities of water in the ILs were on the order of 10^{-1}. Thus, while the water-rich phase is considered nearly pure when the dissolved IL is infinitely diluted, the IL-rich phase cannot be considered as pure. The results obtained for all of the studied ILs indicate large differences in the mole fraction solubilities of water in ILs (ranging from 0.18 for [C$_8$MIM][TF$_2$N] to 0.42 for [C$_8$MIM][OTF]). When comparing the anions, it was established that their hydrophobicity increased from [OTF]$^-$ to [TF$_2$N]$^-$.
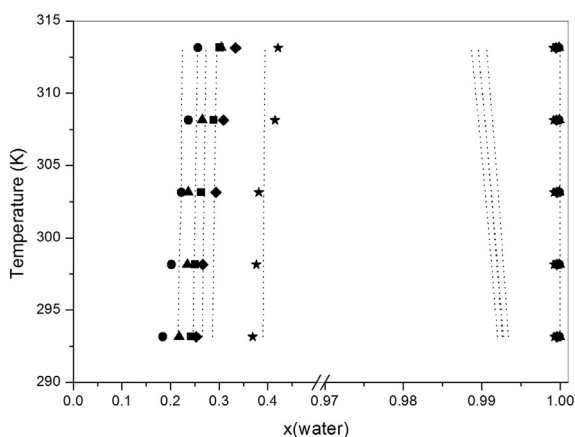

Figure 1: Liquid-Liquid phase diagram for water and ILs: ■ [C$_4$MIM][TF$_2$N], ▲ [C$_{12}$MIM][TF$_2$]; ★ [C$_8$MIM][OTF], ● [C$_8$MIM][TF$_2$N]; ♦ [C$_4$PY][TF$_2$N]. The symbols and solid lines represent the experimental data and NRTL predictions, respectively. The prediction results follow the same trend as the experimental data.

Figure 2: Liquid-Liquid phase diagram for heptane and ILs, ■ [C$_4$MIM][TF$_2$N], ▲ [C$_{12}$MIM][TF$_2$N], ★ [C$_8$MIM][OTF], ● [C$_8$MIM][TF$_2$N]; ♦ [C$_4$PY][TF$_2$N]. The symbols and solid lines represent the experimental data and the NRTL predictions, respectively. The prediction results follow the same trend as the experimental data.
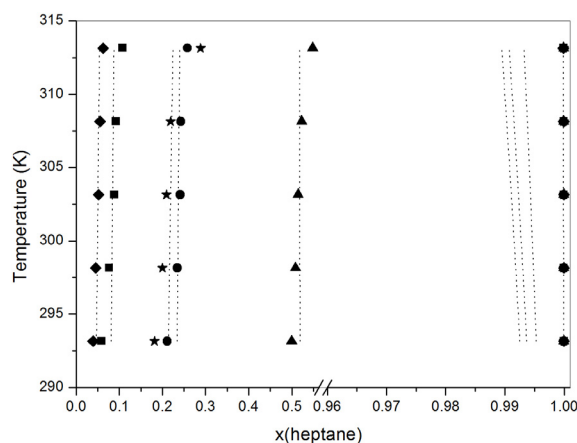
The solubility of water in the ILs (shown in Table 2) increased from the pyridinium to the imidazolium-based ILs. Because the imidazolium and pyridinium cations have an aromatic character, their solubilities in water are higher than when compared with pyrrolidinium and piperidinium-based ILs because they potentially interact with water (OH···π or O···π) (Freire et al., 2007a; Freire et al., 2007b; Maia et al., 2010). In some cases, the IL solubility significantly decreased as the length or number of the alkyl chain increased. However, according to Maia et al. (2012), a deviation from linearity occurred ((hygroscopicity) [C_{10}MIM][BF_4] > [C_6MIM][BF_4] > [C_8MIM][BF_4]) that followed the same trend as the upper critical solution temperature (UCST). In this study regarding the aqueous phase, the hydrophobicity of the ionic liquid decreased as follows: [C_{12}MIM] [TF_2N] > [C_8MIM] [TF_2N] > [C_4MIM] [TF_2N] (shown in Table 3). In addition, the hygroscopicity decreased as follows: [C_4MIM] [TF_2N] > [C_{12}MIM] [TF_2N] > [C_8MIM] [TF_2N]. The ILs with a larger molecular size had lower charge densities and polarities, which contributed to a lower IL solubility. As indicated, the mutual solubilities between the water and ILs are mainly controlled by anions. Therefore, the mixing behaviors of ILs and water can be manipulated by simply changing the anion. However, the cation structure, such as the alkyl chain length, side chain number, and substituent groups have a non-negligible influence on the thermodynamic properties of the ILs. In fact, these cationic factors can be used for fine-tuning the solubility properties (Freire et al., 2008).

Liquid-Liquid equilibrium was acquired for systems with heptanes at various temperatures using an analytical method. For all systems, solubility increased as the temperature increased. Therefore, the LLE diagrams have shapes that are typical for diagrams with upper critical solution temperatures. The results obtained are summarized in Tables 4, 5, 6. The solubility of the ionic liquid in all three compounds (heptane, toluene, o-xylene) is very low (excluding 1-dodecyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, which is completely soluble in toluene and ortho-xylene between 273.15 and 373.15 K at 1 bar and resulted in a very significant emulsion break) and the solubilities of the n-heptanes in the ionic liquids did not increase. These values corresponded (in order of magnitude) to the experimental uncertainty values. Experimental measurements of the solubilities of the ionic liquids in alkane are difficult to obtain because the equilibrium saturation values of ILs in heptane are very small for the mole fraction of the reported systems (between 1×10^{-5} to 10×10^{-5}). The cation alkyl chain length affected the mutual solubilities between the ionic liquids and heptanes. Indeed, the chain length had a significant impact on the phase diagrams, as shown in Figure 2. Figure 2 presents the linearity indexes for the solubility of heptane in an ionic liquid. The interactions and solubilities decreased as follows: [C_{12}MIM][TF_2N] > [C_8MIM][NTF_2] > [C_4MIM][TF_2N]. The effective hydrogen network present in the ionic liquids facilitated solvation in the same order, with indexes that were approximately 50% of the mole fraction. These results were useful regarding the study of oil-water separation by ionic liquids. In these systems, the chain is aliphatic and involves Van der Waals interactions. In addition, the effects of packaging govern the levels of solubility.

Table 2: Experimental Mole Fraction Solubility of Water in ILs as a Function of Temperature.

T/K	[C_4MIM][TF_2N]		[C_8MIM][TF_2N]		[C_{12}MIM][TF_2N]		[C_4PY][TF_2N]		[C_8MIM][OTF]	
	$(x_w \pm \sigma)$		$(x_w \pm \sigma)$		$(x_w \pm \sigma)$		$(x_w \pm \sigma)$		$(x_w \pm \sigma)$	
293.2	0.243	0.004	0.184	0.010	0.218	0.063	0.253	0.010	0.369	0.082
298.2	0.251	0.007	0.202	0.002	0.235	0.029	0.266	0.018	0.377	0.077
303.2	0.264	0.038	0.223	0.029	0.236	0.030	0.294	0.015	0.382	0.070
308.2	0.289	0.002	0.237	0.010	0.265	0.060	0.309	0.075	0.399	0.010
313.2	0.302	0.039	0.256	0.008	0.304	0.079	0.334	0.091	0.405	0.010

σ , Standard deviation.

Table 3: Experimental Mole Fraction Solubility of IL in water as a Function of Temperature.

T/K	[C_4MIM][TF_2N]		[C_8MIM][TF_2N]		[C_{12}MIM][TF_2N]		[C_4PY][TF_2N]		[C_8MIM][OTF]	
	$10^4(x_{IL} \pm \sigma)$		$10^4(x_{IL} \pm \sigma)$		$10^5(x_{IL} \pm \sigma)$		$10^4(x_{IL} \pm \sigma)$		$10^4(x_{IL} \pm \sigma)$	
293.2	4.030	2.080	0.927	0.5810	6.790	0.967	3.980	0.382	7.260	1.120
298.2	4.320	1.320	1.080	0.8270	8.430	1.870	3.990	0.324	7.600	0.525
303.2	4.430	0.723	1.100	0.6860	10.300	0.611	4.090	0.169	7.740	1.670
308.2	4.690	0.587	1.220	0.2030	11.300	0.330	4.400	0.928	8.150	0.552
313.2	4.800	0.670	1.420	0.4320	15.800	0.478	5.080	0.663	8.420	0.862

σ , Standard deviation.

Table 4: Experimental Mole Fraction Solubility of Heptane in IL as a Function of Temperature.

T/K	[C$_4$MIM][TF$_2$N]		[C$_8$MIM][TF$_2$N]		[C$_{12}$MIM][TF$_2$N]		[C$_4$PY][TF$_2$N]		[C$_8$MIM][OTF]	
	$(x_{c_7} \pm \sigma)$		$(x_{c_7} \pm \sigma)$		$(x_{c_7} \pm \sigma)$		$(x_{c_7} \pm \sigma)$		$(x_{c_7} \pm \sigma)$	
293.2	0.059	0.006	0.211	0.014	0.500	0.049	0.039	0.016	0.182	0.053
298.2	0.077	0.024	0.235	0.042	0.509	0.014	0.045	0.008	0.200	0.080
303.2	0.089	0.017	0.241	0.089	0.515	0.041	0.051	0.001	0.209	0.041
308.2	0.093	0.014	0.243	0.027	0.523	0.058	0.055	0.002	0.219	0.048
313.2	0.108	0.018	0.258	0.064	0.548	0.135	0.063	0.008	0.288	0.134

σ, Standard deviation.

Table 5: Experimental Mole Fraction Solubility of IL in Heptane as a Function of Temperature.

T/K	[C$_4$MIM][TF$_2$N]		[C$_8$MIM][TF$_2$N]		[C$_{12}$MIM][TF$_2$N]		[C$_4$PY][TF$_2$N]		[C$_8$MIM][OTF]	
	$10^5(x_{IL} \pm \sigma)$		$10^5(x_{IL} \pm \sigma)$		$10^5(x_{IL} \pm \sigma)$		$10^5(x_{IL} \pm \sigma)$		$10^5(x_{IL} \pm \sigma)$	
293.2	1.910	0.547	1.990	0.552	6.320	0.495	3.120	0.226	3.170	0.995
298.2	2.380	1.490	3.040	0.426	6.330	0.995	4.820	1.000	7.150	0.675
303.2	2.540	0.056	4.140	0.716	6.610	0.103	5.540	2.270	7.330	0.596
308.2	5.420	1.690	4.700	3.690	7.490	0.223	7.220	1.620	8.250	4.090
313.2	9.050	2.670	5.300	1.670	8.850	0.873	14.40	4.110	8.950	0.643

σ, Standard deviation.

Table 6: Cloud point measurements for toluene and o-xylene.

T/K	[C$_4$MIM][TF$_2$N]		T/K	[C$_8$MIM][TF$_2$N]		T/K	[C$_8$MIM][TFO]	
				Toluene				
	$10^4(x_{IL})$	$\pm \sigma$		$10^3(x_{IL})$	$\pm \sigma$		$10^3(x_{IL})$	$\pm \sigma$
293.2	5.550	1.220	293.2	5.560	0.129	283.2	0.850	0.164
303.2	4.470	0.127	298.2	4.610	0.315	293.2	1.190	0.095
313.2	3.830	0.349	308.2	3.560	0.242	303.2	1.540	0.093
323.2	6.840	1.090	318.2	2.700	0.208	313.2	1.740	0.129
			323.2	2.620	0.142			
T/K			T/K	O-Xylene		T/K		
	$10^4(x_{IL})$	$\pm \sigma$		$10^3(x_{IL})$	$\pm \sigma$		$10^3(x_{IL})$	$\pm \sigma$
283.2	4.700	0.359	283.2	1.570	0.101	283.2	0.451	0.046
293.2	5.210	0.780	293.2	1.820	0.049	293.2	0.749	0.053
303.2	5.610	0.598	303.2	2.190	0.089	303.2	1.010	0.060
323.2	6.020	0.441	313.2	2.370	0.055	313.2	1.130	0.466
			323.2	2.700	0.088	323.2	1.600	0.194

Obs: This group also showed that [C$_{12}$MIM][TF$_2$N] is completely soluble in toluene and o-xylene between 273.15 and 373.15 K at 1 bar.

The experimental miscibility observed for the aromatic hydrocarbons in the IL was larger than that in the n-alkanes. Thus, the aromatics were more soluble in the ionic liquids. However, the solubilities of the aromatic ILs in this study were very low (approximately 10^{-4} and 10^{-3}), as shown in Table 6. Strong interactions occurred between the π-electrons delocalized in the aromatic structure with the polar ionic liquids, especially with the pyridinium cation, which resulted in better solubility. Consequently, in this case, the main role of solubility, apart from van der Waals interactions and packing effects, was to induce dipole interactions (Marciniak *et al*., 2010; Marciniak *et al*., 2011; Ferreira *et al*., 2011; Domanska *et al*.,

2012). The systems ([C$_4$MIM] [TF$_2$N] +, [C$_4$MIM] [TF$_2$N] + o-xylene, [C$_8$MIM] [TF$_2$N] + toluene) used in this study provided evidence that suggested the emergence of the lower critical solution temperature (LCST) phenomenon, where the phase separation of the solution occurs at high temperatures. Moreover, the experimental data (Lachwa *et al*., 2006); Domańska *et al*., 2009; Domanska *et al*., 2010; Marciniak *et al*., 2010) suggested that a number of IL + aromatic systems may have a phase diagram that corresponds to a LCST type ([C$_4$MIM] [CF$_3$SO$_3$], [1,3C$_4$MPY] [CF$_3$SO$_3$], [C$_4$MPYR] [CF$_3$SO$_3$], [C$_4$MIM] [SCN], [C$_6$MIM] [SCN], or [C$_2$MIM][TF$_2$N]). Furthermore, the authors show that this phenomenon results from

the π electrons of polar ionic liquids due to the different attractive interactions and the effects of free volume that result in negative enthalpies of mixing, hydrogen bonds, and dipole moments. Furthermore, other interactions occurred, such as between the quadrupole moment of the aromatic ring and the ionic liquid.

CONCLUSIONS

New data have been acquired for the mutual solubility of water, heptane, toluene, o-xylene and a series of ionic liquids at atmospheric pressure. The surfactant ionic liquids became hydrophobic when the cationic alkyl chain became longer. Knowledge regarding the impacts on the liquid phase structure of the salt with the model oil is useful for the formation of new "designer solvents" that are less aggressive to the environment and useful for extracting aromatic hydrocarbons and aromatic/aliphatic mixtures. In addition, these designer solvents are potential demulsifiers. The solubilities of the heptanes in the ionic liquids studied were very low. However, these solubilities were significant, and the different solubilities of the IL-rich phases in heptane were large for the longer IL cationic chains. The dilution of the IL in water was qualitatively similar to that observed for n-alkanes (heptanes) and other organic compounds that are insoluble in water. The aromatic hydrocarbons studied were completely soluble in the ionic liquids. The solubilities of the ionic liquids in the aromatic solutions were on the order of 10^{-3} to 10^{-5} (excluding 1-dodecyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, which presented full miscibility ranging from 273.15 to 373.15 K and resulted in a very significant emulsion break). Some binary systems presented evidence of a LCST ([C$_4$MIM] [TF$_2$N] + toluene, [C$_4$MIM] [TF$_2$N] + o-xylene, [C$_8$MIM] [TF$_2$N] + toluene), which excludes the use of these ILs as demulsifiers because the water-oil separation process occurred at high temperatures. The models applied in this work yielded satisfactory results.

LIST OF SYMBOLS

T	Absolute temperature
ij	Component
x_i	Mole fraction of component i
γ	Activity coefficient of component i
g_{ij}, g_{ij}	NRTL binary molecular energy interaction parameters

REFERENCES

Bösmann, A., Datsevich, L., Jess, A., Lauter, A., Schmitz, C., Wasserscheid, P., Deep desulfurization of diesel fuel by extraction with ionic liquids. Chemical Communications, 23, 2494-2495 (2001).

Cravotto, G. E. C., Gaudino, L., Boffa, J. M., Lévêque, J., Estager, Bonrat, W., Preparation of second generation ionic liquids by efficient solvent-free alkylation of N-heterocycles with chloroalkanes. Molecules, 13, 149-156 (2008).

Domanska, U., Krlikowska, M., Arasimowicz, M., Phase equilibria of (1-hexyl-3-methylimidazolium thiocyanate + water, alcohol, or hydrocarbon) binary systems. J. Chem. Eng. Data., 55, 773-777 (2010).

Domanska, U., Zawadzki, M., Krolikowski, M., Lewandrowska, A., Phase equilibria study of binary and ternary mixtures of {N-octylisoquinolinium bis {(trifluoromethyl) sulfonyl} imide + hydrocarbon, or an alcohol, or water}. Chemical Engineering Journal, 181-182, 63-71 (2012).

Domańska, U., Laskowska, M., Pobudkowska, A., Phase equilibria study of the binary sytems (1-butyl-3-methylimidazolium thiocyanate ionic liquid + organic solvent, or water). J. Phys. Chem., B, 113, 6397-6404 (2009).

Earle, J. M., Esperança, J. M. S. S., Gilea, M. A., Canongia Lopes, J. N., Rebelo, L. P. N., Magee, J. W., Seddon, K. R., Widegren, J. A., The distillation and volatility of ionic liquids. Nature, 439, 831-834 (2006).

Ferrari, J. C., Nagatani, G., Corazza, F. C., Oliveira, J. V., Corazza, M. L., Application of stochastic algorithms for parameter estimation in the liquid–liquid phase equilibrium modeling. Fluid Phase Equilibria, 280, 110-119 (2009).

Ferreira, A. R. Freire, M. G., Ribeiro, J. C., Lopes, F. M., Crespo, J. G. and Coutinho, J. A. P., An overview of the liquid−liquid equilibria of (ionic liquid + hydrocarbon) binary systems and their modeling by the conductor-like screening model for real solvents. Ind. Eng. Chem. Res., 50, 5279-5294 (2011).

Freire, M. G., Santos, L. M. N. B. F., Fernandes, A. M., Coutinho, J. A. P., Marrucho, I. M., An overview of the mutual solubilities of water−imidazolium-

based ionic liquids systems. Fluid Phase Equilibria, 261, 449-454 (2007a).

Freire, M. G., Neves, C. M. S. S., Carvalho, P. J., Gardas, R. L., Fernandes, A. M., Marrucho, Santos, L. and Coutinho, J. A. P., Mutual solubilities of water and hydrophobic ionic liquids. J. Phys. Chem., B, 111, 13082-13089 (2007b).

Freire, M. G., Carvalho, P. J., Gardas, R. L., Marrucho, I. M., Santos, L. M. N. B. F., Coutinho, J. A. P., Mutual solubilities of water and the [Cnmim][Tf2N] hydrophobic ionic liquids. J. Phys. Chem. B 112, 1604-1610 (2008).

Guzman-Lucero, D., Flores, P., Rojo T. and Martinez-Palou, R., Ionic liquids as demulsifiers of water-in-crude oil emulsions: Study of the microwave effect. Energy Fuels, 24, 3610-3615 (2010).

Lachwa, J., Szydlowski, A., Makowska, K. R., Seddon, J. M. S. S., Esperança, H. J. R., Guedes, L. P. N., Rebelo, Changing from an unusual high-temperature demixing to a UCST-type in mixtures of 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl} amide and arenas. Green Chemistry, 8, 262-267 (2006).

Lemos, R. C. B., da Silva, E. B., dos Santos, A., Guimarães, R. C. L., Ferreira, B. M. S., Guarnieri, R. A., Dariva, C., Franceschi, E., Santos, A. F., Fortuny, M., Demulsification of water-in-crude oil emulsions using ionic liquids and microwave irradiation. Energy & Fuels, 24, 4439-4444 (2010).

Maia, F. M., Rodríguez, O., Macedo, E. A., LLE for (water + ionic liquid) binary systems using [Cxmim] [BF4] (x = 6, 8) ionic liquids. Fluid Phase Equilibria, 296, 184-191 (2010).

Maia, F. M., Rodríguez, O., Macedo, E. A., Relative hydrophobicity of equilibrium phases in biphasic systems (ionic liquid plus water). J. Chem. Thermodynamics, 48, 221-228 (2012).

Marciniak, A., Karczemna, E., Influence of cation structure on binary liquid-liquid equilibria for systems containing ionic liquids based on trifluoromethanesulfonate anion with hydrocarbons. J. Phys. Chem., B, 114, 5470-5474 (2010).

Marciniak, K., Influence of anion structure on the liquid-liquid equilibria of 1-(3-hydroxypropyl) pyridinium cation based ionic liquid-hydrocarbon binary systems. Fluid Phase Equilibria, 304, 121-124 (2011).

Petkovic, M., Seddon, K. R., Rebelo, L. P. N., Pereira, C. S., Ionic liquids: A pathway to environmental acceptability. Chem. Soc. Rev., 40, 1383-1403 (2011).

Plechkova, N. V., Seddon, K. R., Applications of ionic liquids in the chemical industry. Chem. Soc. Rev., 37, 123-150 (2008).

Ranke, J., Muller, A., Bottin-Weber, U., Stock, F., Stolte, S., Arning, J., Störmann, R., Jastorff, B., Ecotoxicol. Environ. Saf., 67, 430-438 (2007).

Renon, H. and Prausnitz, J. M., Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J., 14, 135-144 (1968).

Salminen, J., Papaiconomou, N., Kumar, R. A., Lee, J. M., Kerr, J., Newman physicochemical properties and toxicities of hydrophobic piperidinium and pyrrolidinium ionic liquids. J. Fluid Phase Equilibria, 261, 421-426 (2007).

Stragevitch, L. and d'Ávila, S. G., Application of a generalized maximum likelihood method in the reduction of multicomponent phase equilibrium data. Braz. J. Chem. Eng., 14, 41-52 (1997).

Torrecilla, J. S., Palomar, J., Lemus, J., Rodríguez, F., A quantum-chemical-based guide to analyze/ quantify the cytotoxicity of ionic liquids. Green Chem., 12, 123-134 (2010).

Zhou, T., Chen, L., Ye, Y., Chen, L., Qi, Z., Freund, H., Sundmacher, K., An overview of mutual solubility of ionic liquids and water predicted by COSMO-RS. Ind. Eng. Chem. Res., 51, 6256-6264 (2012).