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Phase Equilibria Study of the Binary Systems (*N*-Butyl-4-methylpyridinium Tosylate Ionic Liquid + Organic Solvent, or Water)^{†,‡}

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(Solid + liquid) equilibria (SLE) and (liquid + liquid) equilibria (LLE) for the binary systems ionic liquid (IL) *N*-butyl-4-methylpyridinium tosylate (*p*-toluenesulfonate) [BMPy][TOS] + an alcohol (1-butanol, or 1-hexanol, or 1-octanol, or 1-decanol), or water, or an alkane (hexane, heptane, octane), or benzene, or an alkylbenzene (toluene, ethylbenzene, propylbenzene), or tetrahydrofuran (THF) have been determined at ambient pressure. A dynamic method was used over a broad range of mole fractions and temperatures from (320 to 390) K. In the case of systems (IL + alkane, or alkylbenzene), the mutual immiscibility with an upper critical solution temperature (UCST) was detected. UV spectroscopy was used to determine the very small compositions of the IL in the alkanes, benzene, and alkylbenzenes (about $1 \cdot 10^{-5}$ IL mole fraction). For the binary systems containing alcohol and water, simple eutectic diagrams were observed with complete miscibility in the liquid phase. As usual, with increasing chain length of the alcohol, the solubility decreases. The basic thermal properties of the pure IL, i.e., melting and glass-transition temperatures as well as the enthalpy of fusion, have been measured using a differential scanning microcalorimetry technique (DSC). Well-known UNIQUAC, Wilson, and NRTL equations have been used to correlate experimental SLE data sets for alcohols and water. For the systems containing immiscibility gaps (IL + alkane, or benzene, or alkylbenzene, or tetrahydrofuran), parameters of the LLE correlation equations have been derived using only the NRTL equation.

Introduction

Ionic liquids (ILs) are a novel class of chemical compounds with interesting properties that are driving new research in many fields. In general, ILs are organic salts that are essentially liquids at ambient temperatures, in comparison with “traditional” inorganic molten salts, e.g., sodium chloride. Their specific properties, i.e., broad temperature range of liquid phase existence, extremely low vapor pressure, air and moisture stability, wide electrochemical window, and relatively easy and safe handling, make ILs interesting from the point of view of potential applications in many disciplines of pure and applied chemistry, catalysis, electrochemistry, separation methods, and organic synthesis.^{1–5} Knowledge of the phase equilibria (solid–liquid equilibria, SLE, and liquid–liquid equilibria, LLE) is fundamental for the ILs to be effectively used as solvents in liquid–liquid extraction.^{6–9}

Until recently, the most important and popular ILs considered as extractive solvents, imidazolium, tetraalkylammonium and phosphonium based ionic liquids with cation structures by alkyl, or hydroxyl, or alkoxyalkyl, or aromatic substituents and bis-((trifluoromethyl)sulfonyl)imide [NTf₂][–], alkylsulfate [RSO₄][–], trifluoroacetate [CF₃COO][–], and thiocyanate [SCN][–] anions, have attracted attention. Usually, SLE and LLE of binary or ternary systems containing the IL and an alcohol, or water, or ether, or ketone, or hydrocarbon have been measured.^{9–14} This

paper is a continuation of our wide ranging investigation into ILs containing the tosylate anion. Some tosylate based ILs were investigated by us as a separation media for aromatic and aliphatic hydrocarbons with very low selectivities and capacities.^{9,15,16} Determination of activity coefficients at infinite dilution of organic solutes in the ionic liquid, *N*-butyl-4-methylpyridinium tosylate ([BMPy][TOS]) by gas–liquid Chromatography (GLC) has been reported.¹⁶ The moderate selectivity values indicated that this ionic liquid is not the best for solvent extraction processes in separating aromatic compounds from aliphatic compounds. However, *N*-butyl-4-methylpyridinium tetrafluoroborate ([BMPy][BF₄]) was found as a suitable solvent for an industrial extraction process for the separation of aromatic and aliphatic hydrocarbons.¹⁷ Furthermore, 1-ethyl-3-methylimidazolium tosylate ([EMIM][TOS]) was reported earlier as a suitable solvent for separating aromatic compounds from aliphatic compounds.¹⁸ An interesting, theoretical analysis was presented by Freire et al.¹⁹ for the pyridinium-based ILs by COSMO calculations.

The purpose of this work is to present solubilities of *N*-butyl-4-methylpyridinium tosylate ionic liquid in alcohols, water, benzene, and alkylbenzenes and compare the existing data for the same cation with different anions: [PF₆][–] and [NTf₂][–]. We believe that this important information allows us to make predictions of phase behavior of unmeasured systems, at least in a semiquantitative way.

Experimental procedures and phase equilibria measurements for the binary systems of the IL with alcohols (1-butanol, 1-hexanol, 1-octanol, 1-decanol), water, aliphatic hydrocarbons (hexane, heptane, and octane), and aromatic hydrocarbons (benzene, toluene, ethylbenzene, and propylbenzene) and tet-

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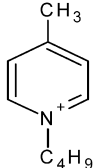
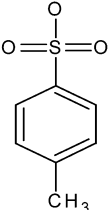
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Table 1. Investigated Ionic Liquid: Chemical Structure, Names, Abbreviation, and Measured Thermophysical Properties^b

structure	name				
		<i>N</i> -butyl-4-methylpyridinium tosylate			
		abbreviation	M	$V_{m,1}^a$	
		[BMPy][TOS]	$\text{g}\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	
			321.43	288.8	
		$T_{\text{fus},1}$	$\Delta_{\text{fus}}H_1$	$T_{l(g)}$	$\Delta C_{p(g),1}$
		K	$\text{kJ}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{mol}^{-1}$
		324.86 ± 0.05	14.33 ± 0.08	215.8 ± 0.1	153 ± 3

^a Calculated according to the group contribution method from ref 20. ^b Molar volume ($V_{m,1}$) at $T = 298.15$ K; temperature and enthalpy of fusion ($T_{\text{fus},1}$ and $\Delta_{\text{fus}}H_1$, respectively), glass transition temperature ($T_{g,1}$), and heat capacity change at $T_{g,1}$ ($\Delta C_{p(g),1}$).

Table 2. Physicochemical Characteristics of Solvents (Literature Data) Utilized in Correlation of the Experimental (Solid + Liquid) Phase Equilibrium Data: Temperatures and Enthalpies of Fusion ($T_{\text{fus},2}$ and $\Delta_{\text{fus}}H_2$, Respectively) and Molar Volumes ($V_{m,2}$) at 298.15 K

	$T_{\text{fus},2}^a$	$\Delta_{\text{fus}}H_2$	$V_{m,2}$
	K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$
1-butanol			91.98 ^c
1-hexanol			125.26 ^d
1-octanol	258.54	23.70 ^b	158.34 ^d
1-decanol	280.09	28.79 ^b	191.57 ^d
water	273.15	6.01	18.06 ^e

^a This work. ^b Ref 21. ^c Ref 22. ^d Ref 23. ^e Calculated from density from ref 24.

rahydrofuran (THF) have been tabulated in detail and discussed and interpreted below. The characteristic investigation here includes the effect of the alkyl chain length of the alcohol and the effect of the alkyl chain length on the benzene ring, type of anion with the same cation, and type of cation with tosylate anion.

Experimental Section

Materials. The studied ionic liquid, i.e., *N*-butyl-4-methylpyridinium tosylate, [BMPy][TOS], was synthesized for us by request by IoLiTec Ionic Liquids technology GmbH, Germany, and was reported to have a mass fraction purity of $> 98\%$. Unfortunately, this IL is solid at $T = 315.52$ K. The ionic liquid was purified by subjecting the subcooled liquid to a very low pressure of about $5\cdot 10^{-3}$ Pa at a temperature of about 300 K for approximately 5 h. All utilized solvents, i.e., 1-butanol, 1-hexanol, 1-octanol, 1-decanol, hexane, heptane, octane, benzene, toluene, ethylbenzene, propylbenzene, and tetrahydrofuran were obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Before use, they were fractionally distilled over different drying reagents to the mass fraction purity $\geq 99.8\%$. They were each stored over freshly activated molecular sieves of type 4 Å (Union Carbide) and checked by gas–liquid chromatography (GLC). Basic volumetric and thermophysical properties of an alcohol and water are tabulated in Table 2. Data for benzene and alkylbenzenes were presented in our previous work.¹⁷

Water Content. Water content was analyzed by Karl Fischer titration (method TitroLine KF). Samples of [BMPy][TOS] and the solvents were dissolved in dry methanol and titrated with steps of $2.5\ \mu\text{L}$. The analysis showed that the water mass fraction in the solvents and in the mixtures with the ionic liquid was $< 230\cdot 10^{-6}$.

Differential Scanning Microcalorimetry. Basic thermal characteristics of the ionic liquid, i.e., temperature of fusion

($T_{\text{fus},1}$), enthalpy of fusion ($\Delta_{\text{fus}}H_1$), glass transition temperature ($T_{g,1}$), and change of heat capacity at the glass transition temperature, $T_{g,1}$ ($\Delta C_{p(g),1}$), have been measured using a differential scanning microcalorimetry technique (DSC). No one (solid–solid) phase transition was observed. The applied scan rate was $5\ \text{K}\cdot\text{min}^{-1}$, with power and recorder sensitivities of $16\ \text{mJ}\cdot\text{s}^{-1}$ and $5\ \text{mV}$, respectively. The apparatus (Perkin-Elmer Pyris 1) was calibrated with a 0.999999 mol fraction purity indium sample. The average value of the melting temperature was (324.86 ± 0.05) K (average over four scans). The repeatability of that value was ± 0.05 K and was comparable to the visual measurement. The enthalpy of fusion was $(14.33 \pm 0.08)\ \text{kJ}\cdot\text{mol}^{-1}$, and the $T_{g,1}$ was (215.8 ± 0.1) K with $\Delta C_{p(g),1}$ of $(153 \pm 3)\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The thermophysical properties are shown in Table 1 and GRS 1 of the Supporting Information.

Phase Equilibria Apparatus and Measurements. A dynamic (synthetic) method for the solubility measurements was used in the present work. Details of the procedures have been described previously.²⁵ The ionic liquid was kept under nitrogen in a drybox during the short time of adding the solvent to the vessel. Mixtures ([BMPy][TOS] + solvent) were prepared by weighing the pure components with an uncertainty of $1\cdot 10^{-4}$ g. Mixtures were prepared by mass, and errors did not exceed $5\cdot 10^{-4}$ in mole fraction. The sample was heated very slowly ($< 2\ \text{K}\cdot\text{h}^{-1}$) with continuous stirring inside a Pyrex glass cell placed in a thermostat. The crystal disappearance temperatures, detected visually, were measured with an electronic thermometer P 550 (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostating liquid. The uncertainties of the temperature measurements was judged to be 0.05 K. The repeatability of the SLE/LLE experimental points was ± 0.05 K. The results of the solubility measurements are presented in Tables 1S to 4S of the Supporting Information. Tables 1S, 2S, 3S, and 4S include direct experimental results of the SLE equilibrium temperatures, T^{SLE} , and of the LLE equilibrium temperatures, T^{LLE} , versus ionic liquid mole fraction, x_1 , for the system ([BMPy][TOS] + an alcohol and water, or aliphatic hydrocarbon, or aromatic hydrocarbon, or THF). The visual method was not applicable at very low mole fraction of the IL ($x_1 = 1\cdot 10^{-5}$) mainly because of uncertainties and verticality of the saturated equilibrium curve.

UV Spectroscopy. UV spectroscopy was only applied to determine the mole fraction of [BMPy][TOS] in the alkane, or benzene, or alkylbenzene-rich liquid mixture that coexists with an ionic liquid-rich phase. For such an analysis, about 20 mL of a biphasic mixture (containing the mole fraction of about 0.01 % of the IL) was thermostatted in the temperature-controlled (thermostat: Lauda A 3, Germany) through the jacket of the vessel with stirring for about 8 h. After equilibration (18

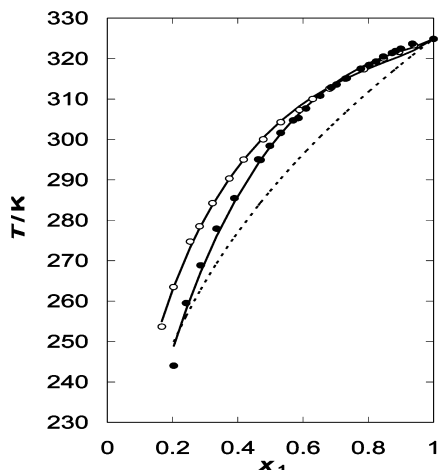


Figure 1. Experimental and calculated (solid + liquid) phase equilibria of ([BMPy][TOS] (1) + 1-alcohol (2)) binary systems: ●, 1-butanol; ○, 1-hexanol. Solid lines (—) have been calculated using the Wilson equation, and the dotted line (---) refers to ideal solubility.

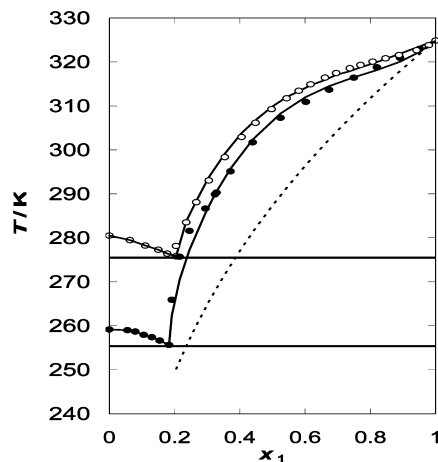


Figure 2. Experimental and calculated (solid + liquid) phase equilibria of ([BMPy][TOS] (1) + 1-alcohol (2)) binary systems: ●, 1-octanol; ○, 1-decanol. Solid lines (—) have been calculated using the NRTL equation, and the dotted line (---) refer to ideal solubility.

h) and phase separation, a sample was taken out with a syringe from the solvent-rich phase (i.e., hexane) and was mixed with a known amount of 2-propanol (complete miscibility). The masses of both the sample and the diluent were determined by a balance (Mettler Toledo AE 240). A quartz cuvette (path length 10 mm) was filled with the diluted 2-propanol solution of the IL, and the UV spectrum was recorded between (180 and 350) nm with a UV/vis spectrophotometer (PerkinElmer Life and Analytical Sciences, Shelton, USA). The reference cuvette was filled with the 2-propanol. The overall experimental uncertainty for the temperature was estimated to be 0.1 K. Photometric accuracy (NIST 930D Filter 1A) obtainable with a UV-vis spectrophotometer is ± 0.001 A and repeatability is ≤ 0.001 A. The uncertainty in composition (mole fraction) was $1 \cdot 10^{-6}$.

For the calibration process, several stock solutions including small quantities of ionic liquid dissolved in a large amount of solvent were prepared. Many series of UV spectra were recorded at $T = 273.15$ K, and for each sample, the obtained peaks were analyzed. For the pure IL and 2-propanol (background), the region of interesting spectrum $A = f(\lambda)$ (minimum after the maximum) was (200 to 300) nm. For the solutions of the IL in solvent, i.e., benzene, the region of interesting spectrum was narrow, (220 to 244) nm. In this sensitive region, the absorbance (A) was a linear function of mole fraction of the IL. The wavelength with the lowest correlation coefficient R^2 of a straight line was chosen. A more careful examination reveals that the interesting region of the spectrum measured here decreases with an increasing temperature. An analysis of the diagrams $T = f(x_1)$ indicates a subtle but clear wavelength, chosen for the binary system (IL + solvent).

The UV-vis spectra for three binary systems are shown in GRS 2-4 of the Supporting Information for hexane, benzene, and ethylbenzene, respectively.

Results

The data (temperature versus mole fraction of the IL) for the binary systems with alcohols, water, aliphatic hydrocarbons, aromatic hydrocarbons, and THF are presented in Figures 1 to 7. The experimental (solid, or/and liquid + liquid) phase equilibrium data for the systems ([BMPy][TOS] + an alcohol and water) are given in Table 1S of the Supporting Information and in Figures 1 to 4; for the systems ([BMPy][TOS] + aliphatic

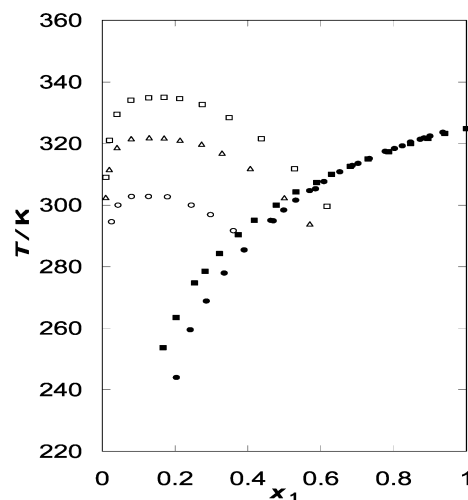


Figure 3. Experimental (solid + liquid) and (liquid + liquid) phase equilibria of ([BMPy][TOS] (1) + 1-alcohol (2)) binary systems: Δ , ([BMPy][BF₄] (1) + 1-butanol (2)) LLE;²⁶ ○, ([BMPy][NTf₂] (1) + 1-butanol (2)) LLE;²⁶ □, ([BMPy][NTf₂] (1) + 1-hexanol (2)) LLE;²⁶ ●, ([BMPy][TOS] (1) + 1-butanol (2)) SLE; ■, ([BMPy][TOS] (1) + 1-hexanol (2)) SLE.

hydrocarbon, or aromatic hydrocarbons) are given in Tables 2S and 3S of the Supporting Information, respectively, and in Figures 5 and 6; for the systems ([BMPy][TOS] + THF) are given in Table 4S of the Supporting Information and in Figure 7.

On the basis of the investigated phase diagrams for the systems ([BMPy][TOS] + an alcohol, or water), the following trends can be noticed: simple eutectic systems were observed with complete miscibility in the liquid phase and solubility of the IL in alcohols (Figures 1 and 2) decreases as the length of the carbon chain of the alcohol increases. In the case of each alcohol, solubilities of the IL are higher in comparison to those determined for tetra-*n*-butylphosphonium tosylate ([B₄P][TOS]) in the same systems.⁹ This is unquestionably the influence of the cation of the IL on its phase behavior with the same solvent and the melting temperature of the compound: 324.8 K for [BMPy][TOS] in comparison with 335.3 K for [B₄P][TOS]. The phase diagrams of the binary systems of the IL with 1-octanol, 1-decanol, and water have been completed (see Figures 2 and 4); i.e., solubilities of appropriate alcohol and water in the IL were measured, and the eutectic points for those mixtures were

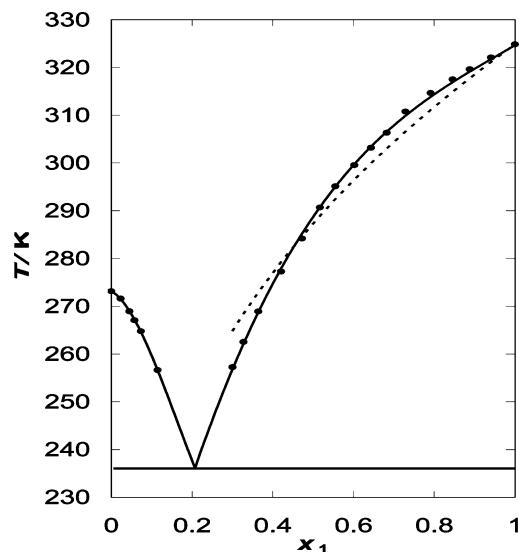


Figure 4. Experimental and calculated (solid + liquid) phase equilibria of the ([BMPy][TOS] (1) + water (2)) binary system. Solid lines (—) have been calculated using the NRTL equation, and the dotted line (---) refers to ideal solubility.

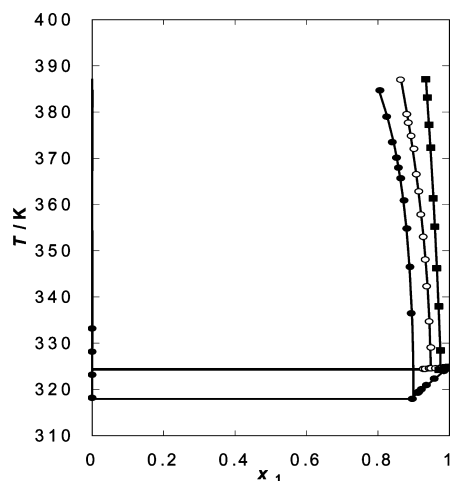


Figure 5. Experimental and calculated (solid + liquid) and (liquid + liquid) phase equilibria of ([BMPy][TOS] (1) + aliphatic hydrocarbons (2)) binary systems: ●, hexane; ○, heptane; ■, octane. Solid lines (—) have been calculated using the NRTL equation.

detected graphically. The eutectic compositions and temperatures are given in Table 3. The eutectic point shifts to the lower mole fraction of the IL ($x_{1,e}$), and the eutectic temperature (T_e) increases as the length of the carbon chain of an alcohol increases. For water, the mole fraction of the IL ($x_{1,e}$) is similar to the values for the two alcohols, but the eutectic temperature (T_e) is lower. It was observed that the solubilities of [BMPy][TOS] IL in alcohols and water were lower than the ideal solubility (see activity coefficients in Table 1S of the Supporting Information). These experimental results were compared to the previously measured binary systems with 1-butyl-4-methylpyridinium tetrafluoroborate ([BMPy][BF₄]) and 1-butyl-4-methylpyridinium bis((trifluoromethyl)sulfonyl)imide ([BMPy][N-Tf₂]). The comparison of the solubility in alcohols²⁶ of ILs with the same cation is presented in Figure 3. The LLE results for *N*-butyl-4-methylpyridinium tetrafluoroborate ([BMPy][BF₄]) in 1-butanol show an UCST of about 324 K. It means that both these ILs are miscible with 1-butanol at temperatures higher than 324 K. Replacing the anion [TOS][−] with [NTf₂][−] decreases the UCST to 304 K. New data reveal complete miscibility in

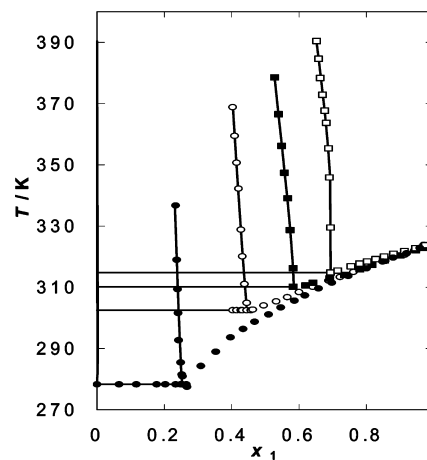


Figure 6. Experimental and calculated (solid + liquid) and (liquid + liquid) phase equilibria of ([BMPy][TOS] (1) + *n*-alkylbenzene (2)) binary systems: ●, benzene; ○, toluene; ■, ethylbenzene; □, *n*-propylbenzene. Solid lines (—) have been calculated using the NRTL equation.

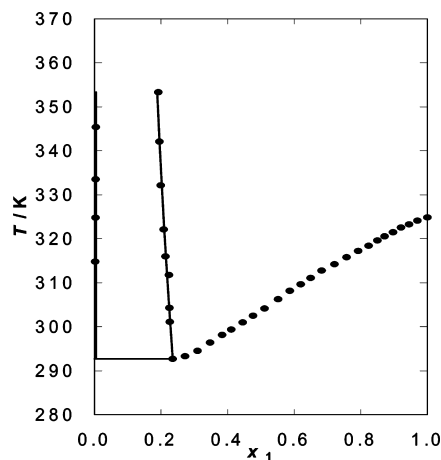


Figure 7. Experimental and calculated (solid + liquid) and (liquid + liquid) phase equilibria of ([BMPy][TOS] (1) + tetrahydrofuran (2)) binary system. Solid lines (—) have been calculated using the NRTL equation.

Table 3. Eutectic Temperatures (T_e) and Compositions ($x_{1,e}$) for ([BMPy][TOS] (1) + 1-Alcohol, or Water (2)) Binary Systems

mixture	$x_{1,e}$	T_e
[BMPy][TOS]		K
+ 1-octanol	0.184 ± 0.002	255.5 ± 0.5
+ 1-decanol	0.209 ± 0.002	275.6 ± 0.5
+ water	0.205 ± 0.002	236.1 ± 0.5

the liquid phase at temperatures higher than liquidus curves. Replacing the [BF₄][−] anion or [NTf₂][−] anion with the tosylate anion increases the solubilities in the systems involving alcohols.

Figures 5 and 6 show the LLE diagram for mixtures of [BMPy][TOS] in aliphatic and aromatic compounds with the UCST. The maximums of the binodal curves were at very high temperatures, and it was impossible to measure them in water or in an oil bath using the static method. Generally, the trend observed in the solubility of [BMPy][TOS] in solvents with respect to the alkyl chain length and benzene substitution is the same as was observed previously for ammonium and phosphonium salts. An increase in the alkyl chain of the substituent decreases the solubility of the IL. In the systems of ([BMPy][TOS] + aliphatic hydrocarbon, or aromatic hydrocarbon), the consolute temperatures are at very low mole fraction of the IL and were undetectable with the visual method. UV spectroscopy was applied in the present work to determine the

Table 4. Results of Correlation of the Experimental (Solid + Liquid) Equilibrium Data of ([BMPy][TOS] (1) + Solvent (2)) Binary Systems by Means of the UNIQUAC, Wilson, NRTL Equations: Obtained Values of Parameters and Root-Mean-Square Deviations (rmsd) of Temperature (σ_T) as a Measure of Goodness of the Correlation*

solvent	Parameters			rmsd		
	UNIQUAC	Wilson	NRTL	UNIQUAC	Wilson	NRTL
	$\Delta u_{12}, \Delta u_{21}$ J·mol ⁻¹	$\Delta \lambda_{12}, \Delta \lambda_{21}$ J·mol ⁻¹	$\Delta g_{12}, \Delta g_{21}$ J·mol ⁻¹		σ_T K	
1-butanol	4321.51 -1907.71	-4595.90 11087.06	9021.15 -3637.25	2.34	1.30	1.41 ^a
1-hexanol	3253.12 -1537.83	-2993.79 7660.25	5528.87 -1303.17	1.70	0.78	0.95 ^b
1-octanol	3249.21 -1540.88	-2164.98 8139.88	12316.20 -6171.72	2.46	2.96	2.64 ^c
1-decanol	3061.72 -1445.78	-1139.18 7977.91	6747.75 -1100.78	0.94	0.74	0.69 ^d
water	7838.63 -2141.99	-8518.85 10234.18	7853.04 -4303.63	1.66	1.12	0.54 ^e

* Calculated with nonrandomness parameter: ^a $\alpha = 0.25$. ^b $\alpha = 0.4$. ^c $\alpha = 0.1$. ^d $\alpha = 0.3$. ^e $\alpha = 0.25$.

mole fraction of the IL in the solvent-rich phase, particularly only in the systems with hexane, benzene, and ethylbenzene.

Comparing two ionic liquids with different anions such as [BMPy][TOS] and tetra-*n*-butylphosphonium tosylate, [B₄P][TOS], we can state that the IL used in this work has much lower solubility in benzene than that measured previously. The LLE for mixtures of [BMPy][TOS] in the aromatic compounds are very different from that of [B₄P][TOS] in the same aromatic hydrocarbons.⁹ For [BMPy][TOS], the immiscibility gap in the liquid phase was (as for many ILs) from a low IL mole fraction ($1 \cdot 10^{-4}$) to 0.26 (benzene) or 0.7 (propylbenzene). For the phosphonium-based IL, the immiscibility in the liquid phase was observed only for the binary system ([B₄P][TOS] + propylbenzene).⁹ This is most likely due to the influence of the cation of the IL. The interaction between the IL and the solvent is not significant for [BMPy][TOS]. Aromatic hydrocarbons demonstrate that the interaction is most likely due to π - π interactions between the benzene ring of the tosylate anion of the IL (for both ILs) and of the solvent. The phosphonium-based salt has probably better interstitial accommodation with the solvent.

The solubility of [BMPy][TOS] in the THF also exhibits immiscibility in the liquid phase and also exhibits an UCST.

Modeling

Correlation of (Solid + Liquid) Equilibrium. Since no solid–solid phase transitions were observed in this work and the change of heat capacity at the melting temperature was not measured, a simplified general thermodynamic equation relating temperature, T^{SLE} , and the mole fraction of the IL, x_1 , in respective solvent (only an alcohol and water) has been fitted to all the sets of experimental SLE data²⁷

$$-\ln x_1 = \frac{\Delta_{\text{fus}}H_1}{R} \left(\frac{1}{T^{\text{SLE}}} - \frac{1}{T_{\text{fus},1}} \right) + \ln \gamma_1 \quad (1)$$

where $T_{\text{fus},1}$, $\Delta_{\text{fus}}H_1$, T^{SLE} , x_1 , and γ_1 stand for melting temperature for the pure IL, enthalpy of fusion for the pure IL, solid–liquid equilibrium temperature, equilibrium mole fraction, and the activity coefficient of the IL in the saturated solution, respectively. The first two values are given in Table 1, and the experimental data together with the calculated activity coefficients are listed in Table 1S of the Supporting Information. The enthalpy of melting is assumed to be temperature independent, whereas the activity coefficient is temperature as well as solubility dependent. It can be calculated from any equation

expressing excess Gibbs energy (G^E) by using the Gibbs–Duhem equation. In this work, three equations were used to describe the experimental data: UNIQUAC equation proposed by Abrams and Prausnitz,²⁸ Wilson equation,²⁹ and NRTL equation proposed by Renon.³⁰ Molar volumes of solvents utilized in the equations are presented in Table 2 (literature, experimental data). In the case of the IL used in this work, the molar volume $V_{m,1}$ (298.15 K) as for a hypothetical subcooled liquid was calculated by the group contribution method described by Barton.²⁰ The calculated value is $288.8 \text{ cm}^3 \cdot \text{mol}^{-1}$. Parameters r_i and q_i (number of segments and external contacts of the molecule of type i , respectively) occurring in the UNIQUAC equation, are related to the molar volumes by the following expressions

$$r_i = 0.029281 V_{m,i} \quad Zq_i = (Z - 2)r_i + 2 \quad (2)$$

where Z denotes the coordination number (it was assumed that $Z = 10$) and the bulk factor l_i was assumed to be equal to 1 for the globular molecule. All the applied equations have two adjustable parameters P_1 and P_2 (for the NRTL equation, the α parameter is fixed, additionally), which are determined by minimization of the objective function $F(P_1, P_2)$, defined as follows

$$F(P_1, P_2) = \sum_{i=1}^n [T_{\text{exp},i} - T_{\text{calc},i}(x_i, P_1, P_2)]^2 \quad (3)$$

where n denotes the number of experimental points. In this work, the parameter α_{12} , a constant of proportionality similar to the nonrandomness constant of the NRTL equation ($\alpha_{12} = \alpha_{21} = 0.10$, or 0.25 , or 0.30 , or 0.40), was taken into account in the calculations. The Marquardt algorithm for solving of the nonlinear least-squares problem was successfully used in this work. As a measure of the reliability of the correlations, the root-mean-square deviation of temperature, σ_T/K , has been calculated according to the following definition

$$\sigma_T = \left\{ \sum_{i=1}^n \frac{(T_{\text{exp},i} - T_{\text{calc},i})^2}{n - 2} \right\}^{1/2} \quad (4)$$

The values of the parameters and the corresponding root-mean-square deviations of temperature, σ_T/K , are shown in Table 4, and the resulting curves are presented together with the experimental points in Figures 1 to 4.

On the basis of obtained results, one can state that equations used are appropriate to provide a reliable description of SLE in the systems ([BMPy][TOS] (1) + alcohol, or water (2)). The

Table 5. Correlation of the Liquid–Liquid Equilibria Data by Means of the NRTL Equation: Parameters ($g_{12} - g_{22} = a_{12} + b_{12}T$), ($g_{21} - g_{11} = a_{21} + b_{21}T$) and Deviations σ_x

solvent	NRTL parameters ^a				σ_x
	$(g_{12} - g_{22})$		$(g_{21} - g_{11})$		
	$\text{J}\cdot\text{mol}^{-1}$		$\text{J}\cdot\text{mol}^{-1}$		
	a_{12}	b_{12}	a_{21}	b_{21}	
hexane	16267	-58.54	123185	-249.59	0.0011
heptane	21967	-70.29	-104545	376.84	0.0009
octane	17048	-51.30	7568	62.79	0.0003
benzene	1883	-57.61	333.6	119.67	0.009
toluene	2958	-47.51	6769	90.52	0.0005
ethylbenzene	3366	-40.77	27761	24.32	0.0006
propylbenzene	7996	-46.80	-75350	309.32	0.0006
THF	8699	-78.83	-12608	153.81	0.0016

^a $\alpha = 0.1$.

average value of the root-mean-square deviations of temperature, σ_T/K , is 1.57 K. In particular, the Wilson equation yields the same fitting as NRTL in systems containing alcohols and water (average σ_T is 1.4 K). The worst correlation with all three equations was observed for 1-octanol (the lower solubility).

The mixtures investigated in this work show positive deviations from ideality in all the different solvents. For each mixture, the experimental activity coefficients are listed in Table 1S of the Supporting Information. The differences from ideality were not significant in most of the systems. The values of activity coefficients in the saturated solutions ranged from 1 to about 1.6. The highest values of activity coefficients were calculated for the solvent-rich phase in water.

Liquid–Liquid Equilibrium Correlation. In this study, one method was used to correlate the solute activity coefficients, γ_1 , based on the NRTL model describing the excess Gibbs energy³⁰

$$\frac{G^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{G_{12} x_1 + x_2} \right] \quad (5)$$

The description of this equation and the activity coefficient formula were presented by us earlier.²³

The model adjustable parameters ($g_{12} - g_{22}$) and ($g_{21} - g_{11}$) were found by minimization of the objective function OF

$$OF = \sum_{i=1}^n [(\Delta x_i)^2 + (\Delta x_i^*)^2] \quad (6)$$

where n is the number of experimental points and Δx is defined as

$$\Delta x = x_{\text{calc}} - x_{\text{exp}} \quad (7)$$

The root-mean-square deviation of mole fraction was defined as follows

$$\sigma_x = \left(\sum_{i=1}^n \frac{(\Delta x_i)^2}{n-2} + \sum_{i=1}^n \frac{(\Delta x_i^*)^2}{n-2} \right)^{1/2} \quad (8)$$

In this work, the parameter α_{12} , a constant of proportionality similar to the nonrandomness constant of the NRTL equation ($\alpha_{12} = \alpha_{21} = 0.1$), was taken into account in the calculations. The calculated values of the equation parameters and corresponding root-mean-square deviations are presented in Table 5. In binary systems, all deviations are in the range σ_x from 0.0003 to 0.0011, being especially large for the ([BMPy][TOS] + THF) system.

For some mixtures under study, the liquid–liquid equilibrium data in the solvent-rich phase did not allow one to do calculations of the above type in the area of LLE because in many mixtures it was impossible to detect phase changes by the visual method or by UV spectra. These data were calculated previously for some ILs by COSMO-RS to within $x_1 \approx 1 \cdot 10^{-4}$.¹¹ It was assumed that the solubility in the dilute IL region was in range of few experimental points measured in our experimental work with UV spectra: for hexane, $x_1 \approx 1 \cdot 10^{-5}$ (see Table 2S); for benzene, $x_1 \approx 7 \cdot 10^{-5}$ (see Table 3S); for ethylbenzene, $x_1 \approx 1 \cdot 10^{-5}$ (see Table 3S, Supporting Information). The results of the correlations are plotted in Figures 5, 6, and 7. Positive deviations from ideality were found. The values of activity coefficients of the IL in the saturated solution, calculated from the NRTL correlation, were higher than one. For the aliphatic hydrocarbons, the parameters taken from the LLE correlation have described also SLE data (see Figure 5).

Conclusions

Phase equilibrium data, including SLE and LLE, for mixtures of *N*-butyl-4-methylpyridinium tosylate (*p*-toluenesulfonate) [BMPy][TOS] ionic liquid and 1-alcohol, or water, or benzene, or alkylbenzene, or THF have been measured. The results were compared to an analogous study of [BMPy][BF₄] and [BMPy][NTf₂] in alcohols and also to [B₄P][TOS] in solvents similar to those used in this work. A comparison of phase diagrams indicate that an exchange of the anion, from tetrafluoroborate or bis((trifluoromethyl)sulfonyl)imide to tosylate, changes the solubility of the IL in alcohols. This is largely due to the melting point of the [BMPy][TOS]; the SLE diagrams were observed vs LLE diagrams for [BMPy][BF₄] and [BMPy][NTf₂] ILs. A very important point is that for the tosylate anion complete solubility was observed in the liquid phase for mixtures with alcohols. Moreover, the solubility of the IL decreases as the length of the carbon chain of an alcohol or substituent on benzene increases.

The solid–liquid phase diagrams for the systems studied here have shown simple eutectic mixtures. The correlation of the SLE data was carried out by means of three commonly known G^E equations for the alcohols and water and with the NRTL for the hydrocarbons and THF. The results of the correlation of SLE and LLE were acceptable for all equations with an average rmsd of temperature $\sigma_T < 1.48$ K and $\sigma_x < 0.0018$.

Supporting Information Available:

Table 1S, experimental SLE data and the activity coefficients in the saturated solutions (alcohols, water); Tables 2S and 3S, experimental SLE/LLE data (aliphatic and aromatic hydrocarbons); Table 4S, experimental SLE/LLE data for THF; GRS 1: DSC diagram; GRS 2 UV–vis Spectra for ([BMPy][TOS] + hexane); GRS 3 UV–vis Spectra for ([BMPy][TOS] + benzene); GRS 4 UV–vis Spectra for ([BMPy][TOS] + ethylbenzene). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Crosthwaite, J. M.; Farmer, V. A.; Hallett, J. P.; Welton, T. Epoxidation of Alkenes by Oxone Using 2-Alkyl-3,4-dihydroisoquinolinium Salts as Catalysts in Ionic Liquids. *J. Mol. Catal. A: Chem.* **2008**, 279, 148–152.
- (2) Yang, W.; Cang, H.; Tang, Y.; Wang, J.; Shi, Y. Electrodeposition of Tin and Antimony in 1-Ethyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid. *J. Appl. Electrochem.* **2008**, 38, 537–542.
- (3) Domańska, U.; Pobudkowska, A.; Królikowski, M. Separation of Aromatic Hydrocarbons from Alkanes Using Ammonium Ionic Liquid C₂NTf₂ at $T = 298.15$ K. *Fluid Phase Equilib.* **2007**, 259, 173–179.

- (4) Cao, H.; McNamee, L.; Appler, H. Palladium-Catalyzed Thiocarbonylation of Iodoarenes with Thiols in Phosphonium Salt Ionic Liquids. *J. Org. Chem.* **2008**, *73*, 3530–3534.
- (5) Kulkarni, P. S.; Branco, L. C.; Crespo, J. G.; Alfonso, C. A. M. Capture of Dioxins by Ionic Liquids. *Environ. Sci. Technol.* **2008**, *42*, 2570–2574.
- (6) Holbrey, J. D.; López-Martin, I.; Rothenberg, G.; Seddon, K. S.; Silvero, G.; Zheng, X. Desulfurisation of Oils Using Ionic Liquids: Selection of Cationic and Anionic Components to Enhance Extraction Efficiency. *Green Chem.* **2008**, *10*, 87–92.
- (7) Losada-Pérez, P.; Blesic, M.; Pérez-Sánchez, G.; Cerdereña, C. A.; Troncoso, J.; Romani, L.; Szydłowski, J.; Rebelo, L. P. N. Solution Thermodynamics Near the Liquid-Liquid Critical Point. I. First-order Excess Derivatives. *Fluid Phase Equilib.* **2007**, *258*, 7–15.
- (8) Crosthwaite, J. M.; Aki, S. N. V.; 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*–228, 303–309.
- (9) Domańska, U.; Padaszyński, K. Phase Equilibria Study in the Binary Systems (Tetra-*n*-butylphosphonium Tosylate Ionic Liquid + 1-Alcohol, or benzene, or *n*-Alkylbenzene). *J. Phys. Chem. B* **2008**, *112*, 11054–11059.
- (10) Domańska, U.; Marciniak, A. Phase Behaviour of 1-Hexyloxymethyl-3-methyl-imidazolium and 1,3-Dihexyloxymethyl-Imidazolium Based Ionic Liquids with Alcohols, Water, Ketones and Hydrocarbons: the Effect of Cation and Anion on Solubility. *Fluid Phase Equilib.* **2007**, *260*, 9–18.
- (11) Domańska, U.; Pobudkowska, A.; Eckert, F. (Liquid + Liquid) Phase Equilibria of 1-Alkyl-3-methylimidazolium Methylsulfate with Alcohols, or Ethers, or Ketones. *J. Chem. Thermodyn.* **2006**, *38*, 685–695.
- (12) Domańska, U.; Marciniak, M.; Królikowski, M. Phase Equilibria and Modeling of Ammonium Ionic Liquid, C₂N₂F₂, Solutions. *J. Phys. Chem. B* **2008**, *112*, 1218–1225.
- (13) Domańska, U.; Laskowska, M.; Marciniak, A. Phase Equilibria of (1-Ethyl-3-methylimidazolium Ethylsulfate + Hydrocarbon, + Ketone, and + Ether) Binary Systems. *J. Chem. Eng. Data* **2008**, *53*, 498–502.
- (14) Domańska, U.; Laskowska, M.; Pobudkowska, A. (Solid, or Liquid + Liquid) Phase Equilibria of 1-Butyl-3-methylimidazolium Thiocyanate with Alcohols, or Water, or Hydrocarbons. *J. Phys. Chem. B* **2009**, in preparation.
- (15) Domańska, U.; Zołek-Tryznowska, Z.; Królikowski, M. Thermodynamic Phase Behavior of Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 1872–1880.
- (16) Letcher, T. M.; Ramjugernath, D.; Królikowski, M.; Laskowska, M.; Naidoo, P. Domańska, U. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes in the Ionic Liquid *N*-Butyl-4-methylpyridinium Tosylate using GLC at *T* = (328.15, 333.15, 338.15, and 343.15) K. *Fluid Phase Equilib.* **2009**, *276*, 31–36.
- (17) Meindersma, G. W.; Podt, A.; de Hann, A. B. Ternary Liquid-Liquid Equilibria for Mixtures of an Aromatic + an Aliphatic Hydrocarbon + 4-Methyl-*N*-butylpyridinium Tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1814–1819.
- (18) Mutelet, F.; Jaubert, J.-N. Accurate Measurements of Thermodynamic Properties of Solutes in Ionic Liquids Using Gas Chromatography. *J. Chromatogr. A* **2006**, *1102*, 256–267.
- (19) Freire, M. G.; Santos, L. M. N. B. F.; Marrucho, I. M.; Coutinho, J. A. P. Evaluation of COSMO-RS for the Prediction of LLE and VLE of Alcohols + Ionic Liquids. *Fluid Phase Equilib.* **2007**, *255*, 167–178.
- (20) Barton, A. F. M. *CRC Handbook of Solubility Parameters*; CRC Press: Boca Raton, FL, 1985; p 64.
- (21) Domańska, U.; Łachwa, J. (Solid + Liquid) Phase Equilibria of Binary Mixtures Containing *N*-Methyl-2-pyrrolidinone and Long-chain *n*-Alkanols at Atmospheric Pressure. *Fluid Phase Equilib.* **2002**, *198*, 1–14.
- (22) Nagata, I. On the Thermodynamics of Alcohol Solutions. Phase Equilibria of Binary and Ternary Mixtures Containing any Number of Alcohols. *Fluid Phase Equilib.* **1985**, *19*, 153–174.
- (23) Domańska, U.; Marciniak, A. Liquid Phase Behaviour of 1-Butyl-3-methylimidazolium 2-(2-Methoxyethoxy)-ethylsulfate with Organic Solvents and Water. *Green Chem.* **2007**, *9*, 262–266.
- (24) Girard, G. *Recommended Reference Materials for the Realization of Physicochemical Properties*; Marsh, K. N., Ed.; Blackwell Scientific Publications: Oxford, 1987; p 27.
- (25) Domańska, U. Vapour-Liquid-Solid Equilibrium of Eicosanoic Acid in One- and Two-component Solvents. *Fluid Phase Equilib.* **1986**, *26*, 201–220.
- (26) Crosthwaite, M.; Muldoon, M. J.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Liquid Phase Behavior of Ionic Liquids with Alcohols: Experimental Studies and Modeling. *J. Phys. Chem. B* **2006**, *110*, 9354–9361.
- (27) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular thermodynamics of fluid-phase equilibria*, 2nd ed.; Prentice-Hall Inc.: Englewood Cliffs, NJ, 1986.
- (28) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116–128.
- (29) Wilson, G. M. Vapour-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.
- (30) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.

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