

Phase Equilibria Study in Binary Systems (Tetra-*n*-butylphosphonium Tosylate Ionic Liquid + 1-Alcohol, or Benzene, or *n*-Alkylbenzene)[‡]

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Ambient pressure (solid + liquid) equilibria (SLE) and (liquid + liquid) equilibria (LLE) of binary systems—ionic liquid (IL) tetra-*n*-butylphosphonium *p*-toluenesulfonate + 1-alcohol (1-butanol, 1-hexanol, 1-octanol, 1-decanol, or 1-dodecanol), benzene, or *n*-alkylbenzene (toluene, ethylbenzene, *n*-propylbenzene)—have been determined by using dynamic method in a broad range of mole fractions and temperatures from 250 to 335 K. For binaries containing alcohol, simple eutectic diagrams were observed with complete miscibility in the liquid phase. Only in the case of system {IL + *n*-propylbenzene} was mutual immiscibility with an upper critical solution temperature (UCST) with low solubility of the IL in the alcohol and high solubility of the alcohol in the IL detected. The basic thermal properties of pure IL, i.e., melting and glass-transition temperatures as well as enthalpy of melting, have been measured with differential scanning microcalorimetry technique (DSC). Well-known UNIQUAC, Wilson, NRTL, NRTL1, and NRTL2 equations have been fitted to obtain experimental data sets. For the system containing immiscibility gap {IL + *n*-propylbenzene}, parameters of the equations have been derived only from SLE data. As a measure of goodness of correlations, root-mean square deviations of temperature have been used. These experimental results were compared to the previously measured binary systems with tetra-*n*-butylphosphonium methanesulfonate. Changing anion from methanesulfonate to *p*-toluenesulfonate decreases solubilities in systems with alcohols and increases the solubilities in binary systems with benzene and alkylbenzenes.

Introduction

Since the beginning of 1990s, a new class of chemicals, called ionic liquids (ILs) or, in particular, room temperature ionic liquids (RTILs), has turned the attention of many scientific institutes all over the world. In general, ILs are organic salts consisting essentially only of ions in the liquid phase, which are formed at relatively low temperature in comparison with “traditional” inorganic molten salts, e.g., sodium chloride. Otherwise, their specific properties, i.e., broad temperature range of liquid phase existence, extremely low vapor pressure, air and moisture, stability, wide electrochemical window, and easy and safe handling, make ILs interesting from the point of view of potential applications in many disciplines of pure and applied chemistry: catalysis,^{1–4} electrochemistry,^{5–7} thermal and diffusional separation methods,^{8–10} organic synthesis,^{11–13} and recently even in tribology as lubricants^{14,15} and toxicology as chemicals able to capture highly toxic pollutants, e.g., sulfur dioxide and dioxins, in absorption processes.¹⁶ To design and lead in those applications in an efficient and profitable way, reliable physicochemical data are required. Thus, there is a big requisition for the physicochemical properties of the pure ILs and their mixtures (i.e., densities, viscosities, surface tensions, contact angles, diffusivities, thermal and electrochemical conductivities, etc.) and phase equilibria data of multicomponent systems containing IL as well.^{17–20}

Our team has focused on experimentally determining and investigating phase equilibria of systems of ILs with popular

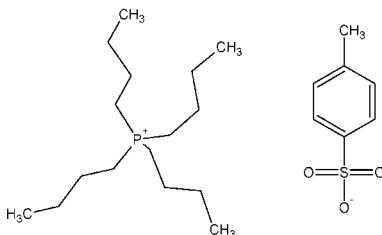
organic solvents, especially those that are highly polar and capable of most types of intermolecular interactions: dispersive, π – π , n – π , hydrogen bonding, dipolar, ionic/charge–charge, and van der Waals forces. The impact of the chemical structure of both solute and solvent and other factors having remarkable influence on the IL's phase behavior are also taken into our considerations. In that sense, ILs are interesting for us, as they can be easily functionalized giving an enormous number of possible combinations of structure.

Until recently, the most popular imidazolium and tetraalkylammonium ILs with cation structures by alkyl, hydroxyl, alkoxyalkyl, or aromatic substituents, and bromide [Br][–], nitrate [NO₃][–], tetrafluoroborate [BF₄][–], hexafluorophosphate [PF₆][–], bis(trifluoromethylsulfonyl)imide [NTf₂][–], dicyanoimide [N(CN)₂][–], alkylsulfate [RSO₄][–], and trifluoroacetate [CF₃COO][–] anions have attracted our attention. In the past months we have measured (solid + liquid) phase equilibria (SLE) and (liquid + liquid) phase equilibria (LLE) of binary or ternary systems containing IL and alcohol, ether, ketone, hydrocarbon, or water.^{21–26} This paper is a continuation of our wide ranging investigation into the ILs containing quaternary phosphonium cations, since, to our best knowledge, the data of phase equilibria of systems with those ILs are few and obscure. Moreover, phosphonium molten salts can be also considered a potential equivalent for ammonium ILs, since some of the properties of these salts are similar to each other. A brief study of synthesis and physical properties was performed by del Sesto et al.²⁷ On the other hand, Tsunashima and Sugiyama have recently reported that some of the phosphonium ILs show lower viscosities and higher conductivities, which makes them more attractive for electrochemical applications.⁷ Furthermore, other investigations

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TABLE 1: Investigated IL: Chemical Structure, Names, Abbreviation, CAS Number, and Measured Thermophysical Properties [Molar Volume ($V_{m,1}$) at 298.15 K, Temperature and Enthalpy of Fusion ($T_{fus,1}$ and $\Delta_{fus}H_1$, respectively), Glass Transition Temperature ($T_{g,1}$), and Heat Capacity Change at $T_{g,1}$ ($\Delta C_{p(g),1}$)]

structure	name			
	tetra- <i>n</i> -butylphosphonium <i>p</i> -toluenesulfonate			
	tetra- <i>n</i> -butylphosphonium tosylate			
	abbreviation	CAS Number	$V_{m,1}/\text{cm}^3 \cdot \text{mol}^{-1}$	
	B ₄ PTOS	116237-97-9	458.7 ^a	
<hr/>				
$T_{\text{fus},1}/\text{K}$	$\Delta_{\text{fus}}H_1/\text{kJ} \cdot \text{mol}^{-1}$	$T_{\text{g},1}/\text{K}$	$\Delta C_{\text{p(g),1}}/\text{J} \cdot \text{mol}^{-1}$	
335.25	17.98	223.3	109.8	

^a Calculated according to the group contribution method from ref 39.

involving those salts have been and still are carried out: they have been used as chemical reaction solvents,^{2,11–13} or even as a plasticizers in ion-selective electrodes.²⁸ New investigations were performed to use phosphonium ILs as media in chromatography as gas–liquid chromatography (GLC) stationary phases.^{29,30} Densities, surface tension, and temperature relationships were tested for many synthesized quaternary phosphonium, ammonium, and imidazolium ILs.³¹

Some phosphonium ILs were tested by us as separation media for aromatic and aliphatic hydrocarbons with negative results.^{32–34} Determination of activity coefficients at infinite dilution of organic solutes in the ILs trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl)-trifluorophosphate, trihexyltetradecylphosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate, or trihexyl-(tetradecyl)-phosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate by GLC has been performed. The small selectivity values indicated that these ILs are probably of little use in solvent extraction processes for separating aromatic compounds from aliphatic compounds.^{32–34} These results again show the influence of the cation's alkyl chain length. On the other side, the trihexyl(tetradecyl)-phosphonium-bis-(2,4,4-trimethylpentyl)-phosphinate was used previously as a reactive extractant of lactic acid or butyric acid.^{35–37}

Recently, the solubilities of tetra-*n*-butylphosphonium methanesulfonate (B₄PCH₃SO₃) IL in alcohols, benzene, and *n*-alkylbenzenes have been presented.³⁸ The solubility of ILs in alcohols is typical for every kind of IL as imidazolium, phosphonium, or ammonium. The (IL + an alcohol) binary mixtures show LLE with upper critical solution temperature (UCST) shifted to the alcohol high mole fraction. An increase in the alkyl chain length of an alcohol resulted in an increase of the UCST. The solubility of the IL in alcohols increases as the length of the chain of an alcohol decreases, as was observed for all ILs measured.³⁸ In the case of (IL + benzene), a simple eutectic system was observed, whereas substitution of the benzene ring by an alkyl chain changes the phase behavior significantly—in the range of low IL, a mole fraction immiscibility gap with UCST appears. An increase in the alkyl chain length of the substituent at the benzene ring resulted in an increase in the UCST. To correlate the SLE data, the UNIQUAC Associated Solution Model (UNIQUAC ASM) equation was used together with the association parameters of alcohols available in the literature.³⁸

The purpose of this work is to compare the same set of data for tetra-*n*-butylphosphonium IL, with different anions, specifically, *p*-toluenesulfonate (tosylate) anion (B₄PTOS). The influence of the anion, corresponding to leading the aromatic ring to the system will be discussed. It seems to be important

information, allowing one to make predictions of phase behavior of unmeasured systems, at least in a semiquantitative way.

The full set of basic information concerning investigated IL, including determined physicochemical properties of its (melting temperature and enthalpy, glass transition temperature, and heat capacity at glass transition temperature) are presented in Table 1. Experimental procedures and phase equilibria measurement results for binary systems of IL with 1-butanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol and with benzene, toluene, ethylbenzene, and *n*-propylbenzene have been tabulated in detail and then briefly discussed and interpreted below. Thus, the characteristics investigated here include the effect of the alkyl chain length of the alcohol (solvent) and the effect of the alkyl chain length at the benzene ring (solvent).

Experimental Procedures and Results

Materials. The studied IL, i.e., tetra-*n*-butylphosphonium *p*-toluenesulfonate, was delivered by Fluka, BuchsGG, Switzerland. The purity of the sample was ≥ 0.98 mass fraction, and thus it was used in investigations without any purification procedures. Chemical structure of the IL is presented in Table 1. All utilized solvents, i.e., 1-butanol, 1-hexanol, 1-octanol, 1-dodecanol, benzene, toluene, ethylbenzene, and *n*-propylbenzene, were obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Before direct use, they were fractionally distilled over different drying reagents to a mass fraction purity of ≥ 0.998 mass fraction. They were also stored over freshly activated molecular sieves of type 4 Å (Union Carbide) and checked by GLC. Basic volumetric and thermophysical properties of both the IL and solvents are tabulated in Table 2.

Water Content. Water content was analyzed by using the Karl Fischer titration technique (method TitroLine KF). Samples of B₄PTOS and the solvents were dissolved in methanol and titrated with 2.5 μL steps. The analysis showed that the water contents in the solvents and the mixtures with the IL were < 180 ppm, respectively.

Differential Scanning Microcalorimetry. Basic thermal characteristics of the IL, i.e., temperature of fusion ($T_{fus,1}$), enthalpy of fusion ($\Delta_{fus}H_1$), 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 with differential scanning microcalorimetry technique (DSC). No one (solid–solid) phase transitions was observed. The applied scan rate was 5 K \cdot min^{−1}, with power and recorder sensitivities of 16 mJ \cdot s^{−1} and 5 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 (335.25 \pm 0.05) K (four scans). The repeatability of that value was \pm 0.05 K,

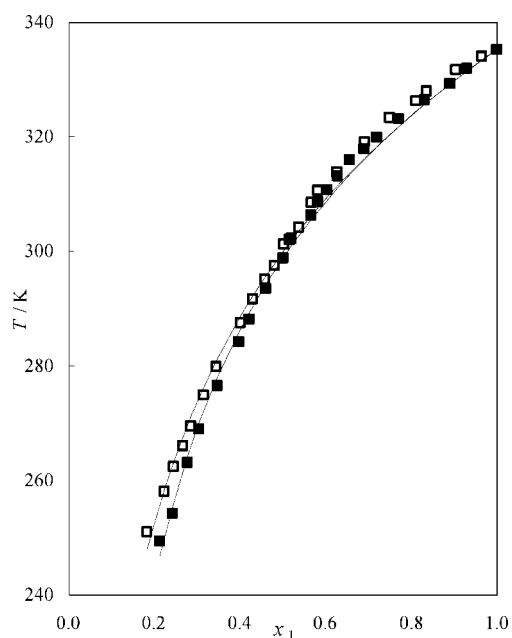
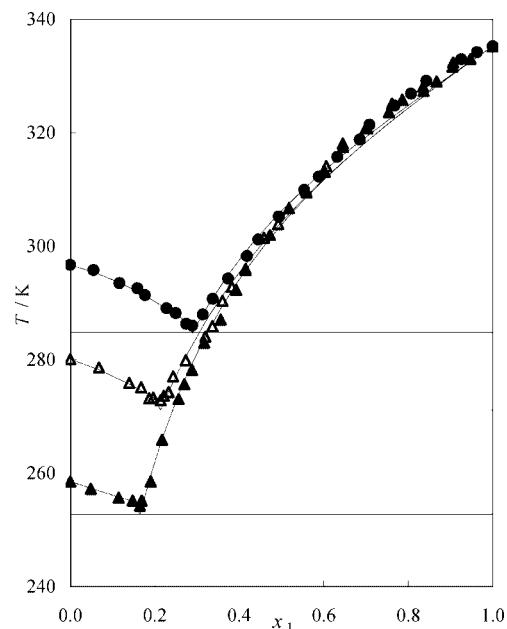
TABLE 2: Physicochemical Characteristics of Solvents (Literature Data) Utilized in Correlation of the Experimental SLE Data [Temperatures and Enthalpies of Fusion ($T_{\text{fus},2}$ and $\Delta_{\text{fus}}H_2$, respectively) and Molar Volumes ($V_{\text{m},2}$) at 298.15 K]

	$T_{\text{fus},2}/\text{K}$ ^a	$\Delta_{\text{fus}}H_2/\text{kJ}\cdot\text{mol}^{-1}$	$V_{\text{m},2}/\text{cm}^3\cdot\text{mol}^{-1}$
1-butanol			91.98 ^b
1-hexanol			125.26 ^c
1-octanol	258.54	23.70 ^d	158.34 ^c
1-decanol	280.09	28.79 ^d	191.57 ^c
1-dodecanol	296.71	38.42 ^d	224.57 ^c
benzene	278.61	9.834 ^e	89.4 ^f
toluene			106.9 ^f
ethylbenzene			123.1 ^f
<i>n</i> -propylbenzene			123.1 ^f

^a This work. ^b Reference 42. ^c Reference 43. ^d Reference 40. ^e Reference 41. ^f Reference 44.

in comparison with the visual measurement. The enthalpy of melting was $(17.98 \pm 0.01) \text{ kJ}\cdot\text{mol}^{-1}$, and the $T_{\text{g},1}$ was 223.5 K with a $\Delta C_{\text{p(g)},1}$ of $109.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The thermophysical properties are shown in Table 1 and GRS 1 of the Supporting Information.

Phase Equilibria Apparatus and Measurements. A dynamic (synthetic) method of the solubility measurements was used in the present work, according to all the procedures described in detail previously.⁴⁴ The IL was provided under nitrogen in the drybox. Mixtures {B₄PTOS + solvent} were prepared by weighing the pure components within an accuracy of $1 \times 10^{-4} \text{ g}$. The sample was heated very slowly (at less than $2 \text{ K}\cdot\text{h}^{-1}$) 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 thermometer was calibrated on the basis of ITS-90. The accuracy of the temperature measurements was judged to be $\pm 0.05 \text{ K}$. Mixtures were prepared by mass, and errors did not exceed 5×10^{-4} in mole fraction. The reproducibility of the SLE/LLE experimental

**Figure 1.** Experimental and calculated SLE of {B₄PTOS (1) + 1-alcohol (2)} binary systems: (■) 1-butanol, (□) 1-hexanol. Solid lines (—) have been designated by the UNIQUAC equation.**Figure 2.** Experimental and calculated SLE of {B₄PTOS (1) + 1-alcohol (2)} binary systems: (▲) 1-octanol, (Δ) 1-decanol, (●) 1-dodecanol. Solid lines (—) have been designated by the UNIQUAC equation.**TABLE 3: Eutectic Temperatures (T_e) and Compositions ($x_{1,e}$) for {B₄PTOS (1) + 1-Alcohol or Benzene (2)} Binary Systems**

mixture: B ₄ PTOS	$x_{1,e}$	T_e/K
+ 1-octanol	0.165	253.2
+ 1-decanol	0.212	272.8
+ 1-dodecanol	0.291	285.7
+ benzene	0.248	268.0

points was $\pm 0.1 \text{ K}$. The schematic diagram of the method was presented previously in Figure 1S of the Supporting Information of ref 26. The results of the solubility measurements are

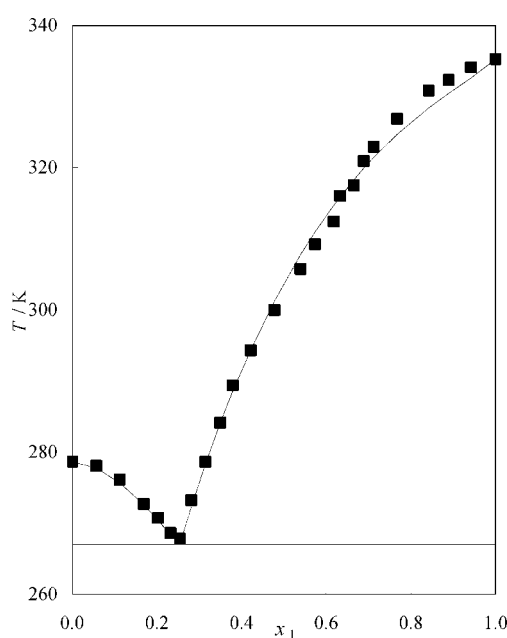
**Figure 3.** Experimental and calculated SLE of {B₄PTOS (1) + benzene (2)} binary system. Solid lines (—) have been designated by the Wilson equation.

TABLE 4: Results of Correlation of the Experimental SLE Data of {B₄PTOS (1) + Solvent (2)} Binary Systems by Means of the UNIQUAC, Wilson, NRTL, NRTL1 and NRTL2 ($\alpha = 0.6$) Equations^a

solvent	parameters					rmsd's				
	$\Delta u_{12}\Delta u_{21}/\text{J}\cdot\text{mol}^{-1}$	$\Delta\lambda_{12}\Delta\lambda_{21}/\text{J}\cdot\text{mol}^{-1}$	$\Delta g_{12}\Delta g_{21}/\text{J}\cdot\text{mol}^{-1}$			σ_T/K				
	UNIQUAC	Wilson	NRTL	NRTL1	NRTL2	UNIQUAC	Wilson	NRTL	NRTL1	NRTL2
1-butanol	2428.52 −1603.87	−374.61 243.31	−2741.83 2166.13	158.30 −252.16	2105.49 −1410.59	1.53	2.25	1.84	2.24	1.59
1-hexanol	1761.98 −1252.77	−471.90 351.61	−2169.32 1864.91	314.72 −444.82	1488.20 −1064.31	1.77	2.18	1.92	2.17	1.82
1-octanol	1996.15 −1313.03	−4897.92 7277.33	−1364.34 1390.22	4059.83 −3456.56	1667.01 −1094.71	1.41	0.56	1.40	1.17	1.49
1-decanol	1418.33 −983.09	−3663.98 4923.04	2977.41 −1481.80	2841.85 −2352.12	1183.85 −807.01	1.82	1.59	1.47	1.76	1.84
1-dodecanol	1689.33 −1152.65	−3116.82 4581.23	2634.44 −1186.72	3186.05 −2218.13	1429.67 −964.09	1.12	0.95	0.92	1.07	1.14
benzene	3366.40 −1836.73	−6609.37 9738.92	−1560.77 −1483.48	5379.14 −5097.62	2963.77 −1638.04	2.32	1.46	3.08	2.22	2.40
toluene	241.19 359.71	4088.83 1233.05	−1424.54 5397.99	1406.17 4945.97	252.59 352.86	0.99	1.00	1.00	0.60	0.99
ethylbenzene	438.29 410.69		−38.09 6405.58	2637.69 5174.25	438.30 419.37	1.63		1.48	3.36	1.63
propylbenzene	1114.21 −117.08		667.39 9372.85	2775.03 4611.19	1101.44 −109.20	0.91		0.45 ^b	1.06	0.92

^a Obtained values of parameters and root-mean-square deviations (rmsd) of temperature (σ_T) are a measure of goodness of the correlation.

^b Calculated with nonrandomness parameter $\alpha = 0.5$.

presented in Tables 1S and 2S of the Supporting Information. Tables 1S and 2S include direct experimental results of the SLE equilibrium temperatures, T^{SLE} , and of the LLE equilibrium temperatures, T^{LLE} , versus IL mole fraction, x_1 , for the system {B₄PTOS + solvent, or *n*-propylbenzene}.

Results

The data (temperature versus mole fraction of the IL) regarding binary systems with alcohols and benzene or alkylbenzenes are presented in Figures 1–5. LLE data for the system {B₄PTOS + *n*-propylbenzene} is given in Table 2S of the Supporting Information and in Figure 5 in comparison with B₄PCH₃SO₃.

On the basis of the investigated phase diagrams, 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 carbon chain of the alcohol increases. In the case of each alcohol, solubilities of the IL are remarkably lower in comparison to those determined for tetra-*n*-butylphosphonium methane-sulfonate in the same system. This is unquestionably the influence of the anion of the IL on its phase behavior with the same solvent when the melting temperature of the compound (335.35 K for B₄PCH₃SO₃ in comparison with 335.25 K for B₄PTOS) is close to the same. Only enthalpy of melting is significantly lower for B₄PCH₃SO₃ (11.10 kJ·mol^{−1}) in comparison with that for B₄PTOS (17.98 kJ·mol^{−1}). Lower solubility of B₄PTOS in alcohols may follow from differences in shapes of anions in both considered ILs and thus much weaker interactions of the tosylate-based anion with alcohol molecules than the methanesulfonate-based anion. Steric effects seem to prevail here over possible molecular interactions, such as *H*-bond between lone pairs of the oxygen atoms of the anion and hydrogen atom of the OH group present in the solvent molecule. The phase diagrams of the binary systems of IL with 1-octanol, 1-decanol, and 1-dodecanol have been completed (see Figure 2), i.e., solubilities of appropriate alcohol in the IL were measured, and obtained liquidus curves are nearly the same as

those for the methanesulfonate-based IL. Eutectic points for those mixtures were detected graphically. Table 3 presents determined values of eutectic compositions and temperatures. Eutectic point shifts to the higher mole fraction of the IL ($x_{1,e}$), and eutectic temperature (T_e) increases as the length of carbon chain of an alcohol increases.

It was observed that the solubilities of B₄PTOS phosphonium salt in alcohols were higher than the ideal solubility (see activity coefficients in Table 1S of the Supporting Information). This interaction with the solvent can be explained by stronger interaction with an OH group of an alcohol or aromatic ring of benzene and of toluene with the anion of the IL than IL–IL or alcohol–alcohol interactions in the solution. These play an important role in controlling LLE phase behavior of the investigated salt. However, the existence of the LLE in *n*-propylbenzene is evidence that the interaction between the IL and the solvent is not significant. On the other hand, the IL under study is much more soluble in benzene and alkylbenzene, as expected (Figures 3 and 4). Differences in shapes and electronic structure are not so big, as in the case of the alcohols. The phase diagrams differ totally from those of the alcohols, and for *n*-propylbenzene, the immiscibility gap in the liquid phase appears in the range of low IL's mole fraction. For benzene and toluene, simple eutectic diagrams with total miscibility in the liquid phase occurs (Figure 3). Aromatic hydrocarbons demonstrate that the interaction is most likely due to π – π interactions between the benzene ring of the IL (from the tosylate anion) and that from the solvent, contrary to hydrogen bonding, which was observed for many mixtures previously.^{21–23,45,46} Although LLE has been clearly detected only in (IL + *n*-propylbenzene) systems (Figure 5), one may suspect that, in the case of (IL + ethylbenzene), low sensitivity of applied dynamic method of measurements (visual method), or kinetics of second phase formation have not allowed one to notice LLE in this system. However, the noticeable inflection on the liquidus curve was observed. On the other hand, in analogous systems with methanesulfonate-based IL, the mutual immiscibility of IL and ethylbenzene was observed. Moreover,

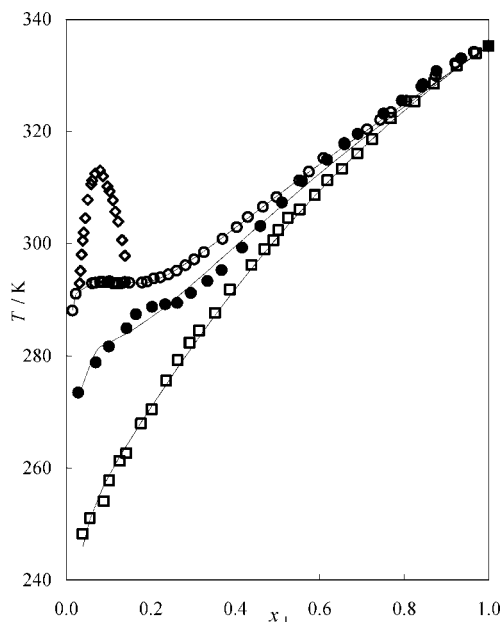


Figure 4. Experimental and calculated SLE and LLE of {B₄PTOS (1) + *n*-alkylbenzene (2)} binary systems: (□) toluene, (●) ethylbenzene, (○) *n*-propylbenzene, (◇) LLE temperatures of the system with *n*-propylbenzene. Solid lines (—) have been designated by the NRTL equation.

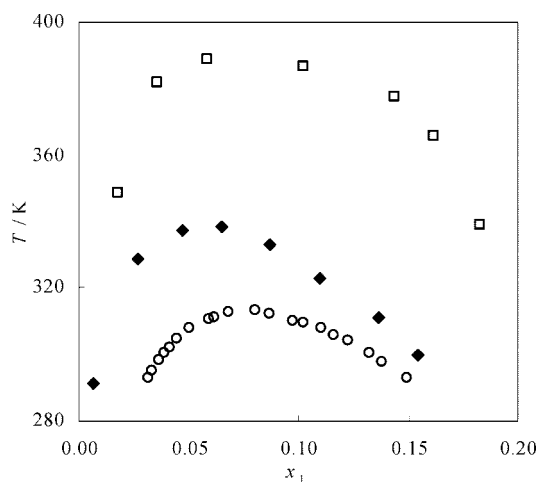


Figure 5. Experimental LLE of {Bu₄PX (1) + *n*-alkylbenzene (2)} binary systems: (○) X = tosylate, *n*-propylbenzene (this work); (◆) X = methanesulfonate, ethylbenzene (ref 38); (□) X = methanesulfonate, *n*-propylbenzene (ref 38).

for the tosylate-based IL, the consolute temperatures are lower, or undetectable, as mentioned earlier (see Figure 5). Figure 5 shows the LLE diagram with the UCST. The maximum of the binodal curve was at 313 K and at a low IL mole fraction $x_1 = 0.08$. Generally, the trend observed in the solubility changes of a phosphonium salt with respect to the alkyl chain length and benzene substitution is the same as that observed previously for ammonium salts. The increase of the alkyl chain of the substituent decreases the solubility of the IL.

Correlation of SLE. Since no solid–solid phase transitions were observed and change of heat capacity at 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 solvents has been fitted to all the sets of experimental SLE data:⁴⁷

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

where $T_{\text{fus},1}$, $\Delta_{\text{fus}} H_1$, T^{SLE} , x_1 , and γ_1 stand for the melting temperature for the pure IL, enthalpy of melting for the pure IL, 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 free energy (G^E) by using the Gibbs–Duhem equation. In this work, five equations were used to describe the experimental data: the UNIQUAC equation proposed by Abrams and Prausnitz,⁴⁸ the Wilson equation,⁴⁹ the NRTL equation proposed by Renon,⁵⁰ and its further modifications made by Nagata et al.: the NRTL1 and NRTL2 equations.⁵¹ Molar volumes of solvents utilized in the equations are presented in Table 2 (literature, experimental data). In the case of the studied IL, molar volume $V_{m,1}$ (298.15) as a hypothetical subcooled liquid was calculated by the group contribution method described by Barton.³⁹ The calculations yield $458.7 \text{ cm}^3 \cdot \text{mol}^{-1}$. Parameters r_i and q_i (number of segments and external contacts of the molecule of type i , respectively) occurring in every equation, except Wilson, are related with molar volumes by the following expressions:

$$r_i = 0.029281 V_{m,1} Z q_i = (Z - 2) r_i + 2 \quad (2)$$

where Z denotes the coordination number (it was assumed that $Z = 10$), and the bulk factor l_i was assumed to be equal to 0 for the linear molecule. All applied equations have two adjustable parameters, P_1 and P_2 (for NRTLs equations, the α parameter is fixed), which are determined by minimization of the objective function $\text{OBJ}(P_1, P_2)$, defined as follows:

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

where n denotes the number of experimental points. The Marquardt algorithm for solving nonlinear least-squares problem has been here successfully applied. As a measure of goodness of the correlations, the root-mean-square deviation (rmsd) of temperature, σ_T , has been proposed, 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 corresponding RMSDs are showed in Table 4 and the resulting curves are presented together with the experimental points in Figures 1–4.

On the basis of obtained results, one can state that the equations used are appropriate to provide a reliable description of SLE in the systems (phosphonium IL + alcohol, benzene, or alkylbenzene). The average value of rmsd for systems with alcohols and benzene or alkylbenzene is 1.52 and 1.50 K. In particular, the UNIQUAC and Wilson equations yield the best fitting in systems containing alcohols (average rmsd is 1.51 K), and benzene or alkylbenzenes (average rmsd is 1.18 K), respectively. All the NRTL equations give slightly higher average rmsd values, but on the other hand, they correlate much better with systems with partial miscibility in the liquid phase, as can be easily noticed in Table 4. However, the specific shape

of the area of the binary liquid phases in the {B₄PTOS + *n*-propylbenzene} binary systems causes the problem of possible joint correlation of SLE and LLE with the same parameters.

In comparison with ideal solutions, those investigated in this work are positively or negatively deviated from ideality in different solvents. For each mixture, it is described in detail by the experimental activity coefficients 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 solution ranged from 0.5 to about 24 for different experimental points. The highest values of activity coefficients were calculated for the solvent-rich phase in *n*-propylbenzene.

Concluding Remarks

Phase equilibrium data, including SLE and LLE, for mixtures of tetra-*n*-butylphosphonium tosylate IL and 1-alcohol, or benzene, or alkylbenzene have been presented. The results were compared to analogous study of tetra-*n*-butylphosphonium methanesulfonate in systems with the same solvents. The anion influence on phase behavior was discussed. The correlation of the data was carried out by means of five commonly known G^E equations. Obtained phase diagrams indicate that exchange of the anion, from methanesulfonate to *p*-toluenesulfonate, decreases solubility of the IL in alcohols and increases solubility of the IL in benzene and alkylbenzenes (*similia similibus solvuntur*). The applied salt has been surprisingly soluble in benzene. The immiscibility gap in the liquid phase was at low mole fraction of the IL only in the system with *n*-propylbenzene, but the UCST was at low temperature (<313 K). Moreover, as it has been showed many times, the solubility of IL decreases as size (length of the carbon chain of an alcohol or substituent at the benzene ring) of molecules of the solvent increases.

The solid–liquid phase diagrams have shown simple eutectic mixtures. The results of the correlation of SLE and LLE were acceptable with all equations with rmsd of temperature $\sigma_T < 2$ K.

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Supporting Information Available: GRS 1: DSC diagram; Table 1S: experimental SLE data and the activity coefficients in the saturated solutions; Table 2S: experimental LLE data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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