

Solubility of Ionic Liquid [emim][PF₆] in Alcohols[†]

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The solubility of 1-ethyl-3-methylimidazolium hexafluorophosphate, [emim][PF₆], in alcohols (methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, *tert*-butyl alcohol, and 3-methylbutan-1-ol) has been measured by a dynamic method from 290 K to the melting point of ionic liquid or to the boiling point of the solvent. The solubility of [emim][PF₆] in alcohols decreases with an increase of the molecular weight of the solvent and is higher in secondary alcohols than in primary alcohols. In every case, with the exception of methanol, the mutual liquid–liquid equilibrium was observed. The shape of the equilibrium curve is similar for [emim][PF₆] in every alcohol. The observation of the upper critical solution temperature was limited by the boiling temperature of the solvent. The liquidus curves were correlated by means of two modified nonrandom two-liquid and the UNIQUAC ASM equations utilizing parameters derived from the solid–liquid equilibrium.

Introduction

Ionic liquids (ILs) are a new generation of solvents for catalysis and synthesis which have been demonstrated as potential successful replacements for conventional media in chemical processes.^{1–13} They are generally salts based on a substituted imidazolium or pyridinium cation and an inorganic anion such as a halide, [AlCl₄][−], [BF₄][−], or [PF₆][−], and are very often liquids at room temperature. Room-temperature ILs are being investigated as cleaner replacements for volatile organic solvents. The important properties of ILs include high heat capacity, high density, extremely low volatility, nonflammability, high thermal stability, wide temperature range for liquid, many variations in compositions, and a large number of possible variations in cation and anion conformations, allowing fine-tuning of the IL properties for specific applications.^{14–28} A major reason for the interest in ILs is their negligible vapor pressure, which decreases the risk of technological exposure and the loss of solvent to the atmosphere. ILs, with their promising physical and chemical properties, are versatile electrolytes for diverse technologies, e.g., in batteries, photo-electrical cells, and other electrochemical devices.^{29–34} Of course the presence of water in the gas phase or in the IL has a considerable impact on the electrochemical properties of ILs.

To design any process involving ILs on an industrial scale, it is necessary not only to know a range of physical properties including viscosity, density, and interfacial tension but also to know heat capacity and other thermodynamic properties including phase equilibria as vapor–liquid equilibria, liquid–liquid equilibria (LLE), and solid–liquid equilibria (SLE).^{20,35–49}

This paper follows the measurements of a new generation of solvents for catalysis, synthesis, and extraction, room-temperature ILs, and is a continuation of our systematic study of the ILs solubility measurements.^{42–45} In our previous work, the

solubility of 1-ethyl-3-methylimidazolium hexafluorophosphate, [emim][PF₆], in aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene) and of 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], in the same aromatic hydrocarbons, in *n*-alkanes (pentane, hexane, heptane, and octane), and in cyclohydrocarbons (cyclopentane and cyclohexane) has been measured.⁴² We also determined the melting point, enthalpy of fusion, and enthalpies of solid–solid-phase transitions by the differential scanning calorimetry.⁴²

The solid–liquid and liquid–liquid measurements of IL systems based on *N,N'*-dialkyl-substituted imidazolium cations are attracting increasing attention for applications in liquid–liquid extraction.^{50–52}

The systematic investigations into the physicochemical properties and phase equilibria (SLE and LLE) of systems with simple imidazoles, benzimidazoles, phenylimidazoles, and their derivatives have been managed.^{53–59} The purpose of these measurements was to get basic information on the interaction of imidazoles with water and different organic solvents and octanol/water partitioning, having in mind a new class of low-melting *N,N'*-dialkylimidazolium salts. Experimental work with imidazoles is easier and not so costly as with ILs and may give very helpful indication for ILs. Up to now, the phase equilibrium behavior with ILs has not been investigated systematically.^{20,35–38,42–49} For a better understanding of their behavior and with a view to the application in chemical engineering or the development of thermodynamic models, reliable experimental data are required. It was shown that the large miscibility gap exists in the mixtures of 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide, [emim][CF₃SO₂)₂N], or 1-ethyl-3-methylimidazolium ethyl-sulfate, [emim][C₂H₅OSO₃], with aliphatic (cyclohexane) and aromatic (benzene) hydrocarbons.³⁵ The excess molar enthalpy for the benzene + [emim][CF₃SO₂)₂N] was highly negative (about −750 J mol^{−1}) and for the cyclohexane + [emim][CF₃SO₂)₂N] was positive (about 450 J mol^{−1}).³⁵ The large miscibility gap can directly be used for the separation of aromatic from aliphatic hydrocarbons by liquid–

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TABLE 1: Experimental Solid–Liquid Equilibrium Temperatures for $\{x_1$ [emim][PF₆] + (1 – x_1) Alcohol} Systems; γ_1 , Experimental Activity Coefficient of Solute (derived from eq 1)

x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
methanol																	
0.0125	292.13	10.11	0.2031	304.10	2.43	0.5294	313.45	1.33	0.0026	327.45		0.4638	327.45		0.7532	327.45	1.18
0.0170	295.50	10.00	0.2204	304.24	2.26	0.5706	315.05	1.30	0.0035	327.45		0.4877	327.45		0.7642	327.45	1.17
0.0236	298.02	9.58	0.2401	304.54	2.11	0.6235	316.85	1.26	0.0049	327.45		0.5142	327.45		0.7807	327.45	1.15
0.0312	299.46	8.95	0.2603	304.84	1.97	0.6554	318.60	1.24	0.0084	327.45		0.5358	327.45		0.8096	327.51	1.13
0.0389	300.42	8.28	0.2804	305.35	1.87	0.6819	319.90	1.22	0.0132	327.45		0.5549	327.45		0.8329	327.70	1.11
0.0466	300.86	7.64	0.3012	305.83	1.77	0.7146	321.42	1.20	0.0270	327.45		0.5690	327.45		0.8406	327.87	1.10
0.0575	301.26	6.83	0.3265	306.24	1.68	0.7537	323.15	1.17	0.0469	327.45		0.5789	327.45		0.8567	328.06	1.09
0.0740	301.83	5.79	0.3544	307.12	1.60	0.8033	325.10	1.13	0.0812	327.45		0.5953	327.45		0.8785	328.79	1.07
0.0846	302.17	5.25	0.3838	308.20	1.53	0.8203	326.05	1.12	0.1100	327.45		0.6184	327.45		0.8947	329.42	1.06
0.1042	302.50	4.43	0.4141	309.22	1.47	0.8395	326.92	1.11	0.1495	327.45		0.6250	327.45		0.9056	329.91	1.05
0.1229	302.76	3.84	0.4440	310.18	1.43	0.8636	328.08	1.09	0.1905	327.45		0.6397	327.45		0.9164	330.34	1.04
0.1403	303.10	3.40	0.4517	310.55	1.42	0.8736	328.47	1.08	0.2311	327.45		0.6598	327.45		0.9414	331.43	1.03
0.1557	303.37	3.09	0.4691	311.29	1.40	0.9236	330.47	1.05	0.2700	327.45		0.6651	327.45		0.9613	332.20	1.01
0.1714	303.54	2.83	0.4882	311.84	1.37	0.9301	330.90	1.04	0.3100	327.45		0.6817	327.45		0.9747	332.71	1.01
0.1855	303.66	2.64	0.5047	312.39	1.36	1.0000	332.80	1.00	0.3523	327.45		0.6980	327.45		0.9774	332.67	1.01
ethanol																	
0.0044	317.11		0.2188	317.11		0.5870	318.10	1.23	0.4345	327.45		0.7197	327.45		1.0000	332.80	1.00
0.0118	317.11		0.2419	317.11		0.6405	319.69	1.19				0.7428	327.45				
butan-2-ol																	
0.0185	317.11		0.2576	317.11		0.6861	320.78	1.17	0.0044	324.07		0.2811	324.07		0.6789	324.07	
0.0262	317.11		0.2840	317.11		0.7281	322.38	1.14	0.0077	324.07		0.3256	324.07		0.7107	324.35	1.21
0.0348	317.11		0.3151	317.11		0.7761	324.01	1.11	0.0164	324.07		0.3596	324.07		0.7355	325.21	1.19
0.0441	317.11		0.3254	317.11		0.8235	326.01	1.09	0.0169	324.07		0.3962	324.07		0.7743	325.95	1.14
0.0591	317.11		0.3765	317.11		0.8739	328.64	1.06	0.0352	324.07		0.4368	324.07		0.8127	327.70	1.11
0.0953	317.11		0.4024	317.11		0.9276	331.53	1.03	0.0510	324.07		0.4540	324.07		0.8483	329.48	1.08
0.0987	317.11		0.4362	317.11		0.9700	332.43	1.01	0.0784	324.07		0.5066	324.07		0.8946	330.62	1.04
0.1244	317.11		0.4709	317.15		1.0000	332.80	1.00	0.1125	324.07		0.5509	324.07		0.9425	331.65	1.02
0.1619	317.11		0.4947	317.09					0.1524	324.07		0.5869	324.07		1.0000	332.80	1.00
0.1919	317.11		0.5432	317.29	1.27				0.1954	324.07		0.6194	324.07				
propan-1-ol																	
			0.2296	323.81		0.6060	323.79		0.2396	324.07		0.6542	324.07				
tert-butyl alcohol																	
0.0048	323.81		0.2675	323.81		0.6559	323.93		0.0000	297.32		0.3173	323.82		0.7156	323.82	1.15
0.0071	323.81		0.2894	323.81		0.7057	324.08		0.0047	323.82		0.3603	323.82		0.7502	324.15	1.13
0.0116	323.81		0.3102	323.81		0.7517	324.70	1.12	0.0060	323.82		0.4032	323.82		0.7746	324.75	1.11
0.0220	323.81		0.3359	323.81		0.7817	325.32	1.11	0.0098	323.82		0.4432	323.82		0.8094	325.88	1.09
0.0356	323.81		0.3568	323.81		0.8041	326.08	1.09	0.0206	323.82		0.4856	323.82		0.8507	327.70	1.07
0.0530	323.81		0.3741	323.81		0.8454	327.31	1.07	0.0512	323.82		0.5038	323.82		0.8804	329.09	1.05
0.0865	323.81		0.3927	323.81		0.8796	328.64	1.05	0.0849	323.82		0.5200	323.82		0.9185	330.54	1.03
0.1135	323.81		0.4212	323.81		0.9111	330.34	1.04	0.1100	323.82		0.5540	323.82		0.9389	331.50	1.02
0.1456	323.81		0.4732	323.81		0.9356	331.26	1.02	0.1500	323.82		0.5914	323.82		0.9715	332.43	1.01
0.1785	323.81		0.5108	323.81		0.9661	332.51	1.01	0.1870	323.82		0.6186	323.82		1.0000	332.80	1.00
0.1987	323.81		0.5499	323.81		1.0000	332.80	1.00	0.2335	323.82		0.6507	323.82				
propan-2-ol																	
0.0022	322.37		0.2305	322.37		0.6800	322.37					0.6852	323.82				
3-methylbutan-1-ol																	
0.0035	322.37		0.2687	322.37		0.7081	322.76	1.15	0.0067	329.06		0.4285	329.06		0.7260	329.06	
0.0053	322.37		0.3102	322.37		0.7152	322.93	1.15	0.0120	329.06		0.4709	329.06		0.7517	329.06	
0.0057	322.37		0.3451	322.37		0.7409	323.55	1.14	0.0214	329.06		0.5169	329.06		0.7742	329.06	
0.0076	322.37		0.3865	322.37		0.7569	324.30	1.13	0.0485	329.06		0.5614	329.06		0.8050	329.06	
0.0098	322.37		0.4213	322.37		0.7787	324.95	1.11	0.0980	329.06		0.6001	329.06		0.8423	329.28	
0.0132	322.37		0.4522	322.37		0.8038	325.95	1.10	0.1500	329.06		0.6360	329.06		0.8821	330.05	
0.0185	322.37		0.4710	322.37		0.8113	326.65	1.09	0.2082	329.06		0.6468	329.06		0.9106	330.78	
0.0246	322.37		0.4882	322.37		0.8472	328.00	1.07	0.2587	329.06		0.6679	329.06		0.9267	331.29	
0.0463	322.37		0.5146	322.37		0.8572	328.89	1.07	0.3178	329.06		0.6833	329.06		0.9593	332.15	
0.0795	322.37		0.5347	322.37		0.8853	329.75	1.05	0.3719	329.06		0.7067	329.06		1.0000	332.80	
0.1025	322.37		0.5616	322.37		0.9209	331.35	1.03									
0.1268	322.37		0.5918	322.37		0.9265	331.60	1.03									
0.1548	322.37		0.6181	322.37		0.9553	332.12	1.01									
0.1987	322.37		0.6518	322.37		1.0000	332.80	1.00									

liquid extraction. Our LLE measurements of [emim][PF₆] or [bmim][PF₆] have shown mutual solubilities with aliphatic, cyclic, and aromatic hydrocarbons as a function of the chain length of the alkyl substituent at the imidazole ring.⁴² Basic [emim][PF₆] IL can act as both a hydrogen bond acceptor ([PF₆][−]) and donor ([emim]⁺) and would be expected to interact with solvents with both accepting and donating sites. On the other hand, alcohols are very well known to form hydrogen-bonded solvents with both high enthalpies and constants of association. Hence, they would be expected to stabilize with hydrogen-bond donor sites.

Experimental Procedures and Results

Materials. The [emim][PF₆] sample was obtained from Solvent Innovation GmbH, Köln, Germany. The sample purity was ≥ 98 mass percent, and it was used without any purification. The substance was packed under nitrogen.

All alcohols were delivered from Sigma–Aldrich Chemie GmbH, Stenheim, Germany. Before direct use, they were fractionally distilled over different drying reagents to the mass fraction purity ≥ 99.8 mass percent. The solvents were stored over freshly activated molecular sieves of type 4 Å (Union Carbide). Analysis for the water contamination using the Karl

TABLE 2: Experimental Liquid–Liquid Equilibrium Temperatures for $\{x_1 [\text{emim}][\text{PF}_6] + (1 - x_1) \text{Alcohol}\}$ Systems

x_1	T/K	x_1	T/K
ethanol			
0.0044	321.27	0.2840	346.95
0.0118	330.75	0.3151	343.80
0.0185	338.05	0.3254	342.89
0.0262	343.51	0.3765	337.03
0.0348	347.53	0.4024	333.46
0.0441	350.23	0.4362	329.47
0.2188	351.43	0.4709	325.05
0.2419	349.85	0.4947	321.80
0.2576	348.61		
propan-1-ol			
0.0048	342.65	0.5108	355.85
0.0068	354.15	0.5499	350.58
0.0071	356.45	0.6060	342.98
0.0116	364.65	0.6559	333.13
0.4212	368.03	0.7057	325.45
0.4732	360.05		
propan-2-ol			
0.0022	334.47	0.5347	346.21
0.0035	342.45	0.5616	342.45
0.0053	350.45	0.5918	338.15
0.0057	352.85	0.6181	334.15
0.4710	354.41	0.6518	328.55
0.4882	352.46	0.6800	324.30
0.5146	348.65		
butan-1-ol			
0.0026	368.15	0.6184	376.15
0.0035	373.55	0.6250	374.95
0.0049	381.15	0.6397	371.15
0.5142	389.65	0.6598	364.75
0.5358	387.31	0.6651	363.35
0.5549	385.35	0.6817	358.55
0.5690	383.65	0.6980	350.15
0.5789	382.25	0.7197	339.65
0.5953	379.95	0.7428	328.15
butan-2-ol			
0.4540	371.04	0.6194	356.75
0.5066	368.48	0.6542	352.26
0.5509	364.85	0.6789	346.03
0.5869	361.15		
tert-butyl alcohol			
0.5200	354.35	0.6186	338.52
0.5540	350.15	0.6507	332.37
0.5914	344.15	0.6852	326.15
3-methylbutan-1-ol			
0.6468	403.20	0.7260	370.95
0.6679	395.85	0.7517	358.65
0.6833	390.19	0.7742	347.95
0.7067	381.79	0.8050	332.18

Fischer technique for the alcohols showed that the impurity in each of the solvents was <0.02 mol percent.

Solid–Liquid and Liquid–Liquid Equilibria Apparatus and Measurements. SLE and LLE temperatures were determined using a dynamic method described in detail previously.⁶⁰ Appropriate mixtures of solute and solvent placed under the nitrogen in drybox into a Pyrex glass cell were heated very slowly (less than 2 K h^{-1} near the equilibrium temperature) with continuous stirring inside a cell that was placed in a glass thermostat filled with silicone oil or water. The temperature of the liquid bath was varied slowly until the last crystals disappeared. This temperature was taken as the temperature of the (solid–liquid) equilibrium in the saturated solution. The crystal disappearance temperatures were detected visually. In LLE measurements, two phases' (foggy mixture) disappearance in the middle of the liquid phase was observed as increasing temperature. The observation of the "cloud point" with decreasing temperature was very difficult. The temperature was measured with an electronic thermometer P 550 (DOSTMANN

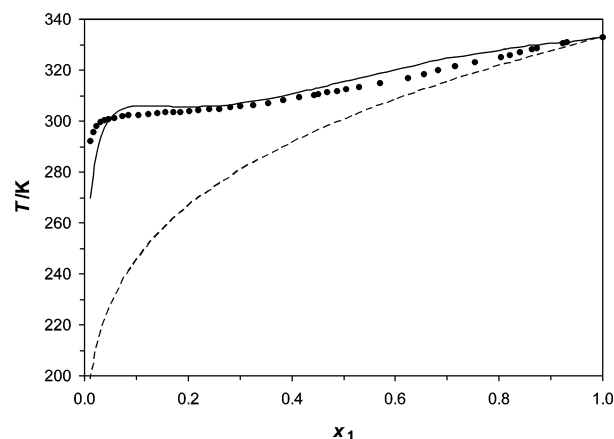


Figure 1. Solid–liquid diagram for $\{x_1 [\text{emim}][\text{PF}_6] + (1 - x_1) \text{methanol}\}$: ●, experimental points; solid line, calculated by the NRTL 1 equation; dashed line, ideal solubility.

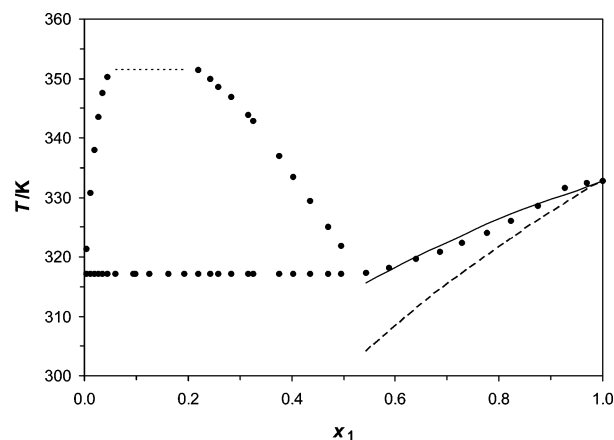


Figure 2. Solid–liquid and liquid–liquid equilibrium diagrams for $\{x_1 [\text{emim}][\text{PF}_6] + (1 - x_1) \text{ethanol}\}$: ●, experimental points; solid line, calculated by the NRTL 1 equation; dashed line, ideal solubility; dotted line, boiling temperature of a solvent.

electronic GmbH) with the probe totally immersed in the thermostating liquid. The accuracy of the temperature measurements was judged to be $\pm 0.01 \text{ K}$. Mixtures were prepared by mass, and the errors did not exceed $\delta_{x_1} = 0.0002$ and $\delta_{T_1}/\text{K} = 0.1$ in the mole fraction and temperature, respectively. It was found that the solution-crystallization procedure was quite slow and difficult, thus the solubility measurements were very time consuming. The LLE measurements were limited at the upper temperature by the boiling point of the solvent.

Results. The solubility of $[\text{emim}][\text{PF}_6]$ in alcohols are shown in Tables 1 and 2 and in Figures 1–5. The tables include the direct experimental results of the SLE temperatures, T (stable crystalline form) or LLE temperatures vs x_1 , the mole fraction of the $[\text{emim}][\text{PF}_6]$ in the saturated solution for the investigated systems. The activity coefficient presented as well in Table 1 was calculated by using eq 1. As we can see from Figure 1, methanol was completely miscible with $[\text{emim}][\text{PF}_6]$ at temperatures above 290 K. Figures 1–5 present the liquidus curve from the melting point to the eutectic point (Figure 1) or the area of the binary liquids. The liquidus curve at the area of binary liquids is at stable temperature. The curves of LLE are typical for a partially miscible two-component system with an upper critical solution temperature. The maximum of the curves was not observed because the boiling temperature of the solvent was lower. It is presented by the upper dotted line in Figures 2–5. The dashed line in Figures 1–5 presents the "ideal

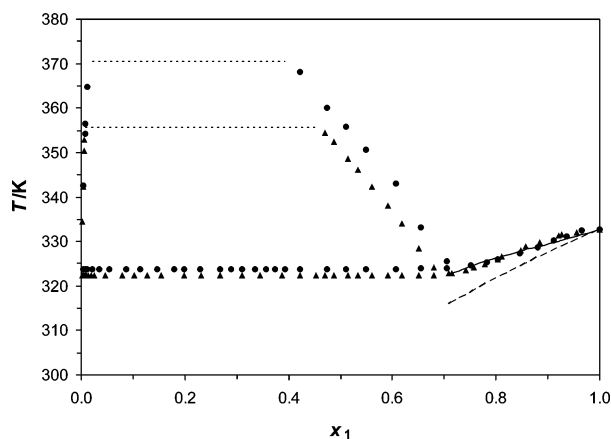


Figure 3. Solid-liquid and liquid-liquid equilibrium diagrams for $\{x_1 [\text{emim}][\text{PF}_6] + (1 - x_1) \text{ an alcohol}\}$: \blacktriangle , propan-1-ol; \bullet , propan-2-ol; solid line, calculated by the NRTL 1 equation; dashed line, ideal solubility; dotted line, boiling temperature of a solvent.

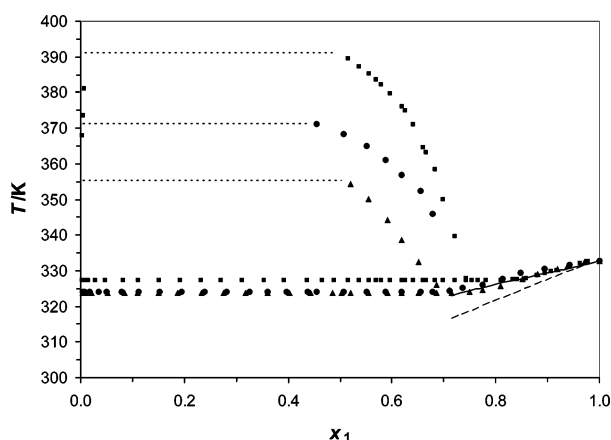


Figure 4. Solid-liquid and liquid-liquid equilibrium diagrams for $\{x_1 [\text{emim}][\text{PF}_6] + (1 - x_1) \text{ an alcohol}\}$: \blacksquare , butan-1-ol; \bullet , butan-2-ol; \blacktriangle , *tert*-butyl alcohol; solid line, calculated by the NRTL 1 equation; dashed line, ideal solubility; dotted line, boiling temperature of a solvent.

solubility", described by eq 1, when the activity coefficient γ_1 is equal to 1.

Discussion

ILs can be considered, in the majority of cases, as polar phases with their solvent properties being mainly determined by the ability of the salt to act as a hydrogen-bond donor and/or acceptor and the degree of localization of the charges on the anions. In most cases, imidazolium-based ILs are highly ordered hydrogen-bonded solvents and can have strong effects on chemical reactions and processes. Thus the ability of a solute to form hydrogen bonds or other possible interactions with potential solvents is an important feature of its behavior. Additionally, ILs are such good hydrogen-bond donors/acceptors because they are charged, as already mentioned above. Alcohols used in this work are also good hydrogen-bond donors/acceptors but not as good as ILs, which will be shown in our work. The molecules in the crystal very often occur as more complex structures, such as ILs formed with aid of the hydrogen bonds. Dissolution of such a crystal in a nonpolar solvent may be supposed to involve the transfer of lattice-born multimers into the solution.^{61,62} Thus the crystal structure of ILs is very important and is responsible for the phase diagrams in binary mixtures of hydrogen-bonded ILs with different solvents. For our knowledge, the structure of the [emim][PF₆] is not known.

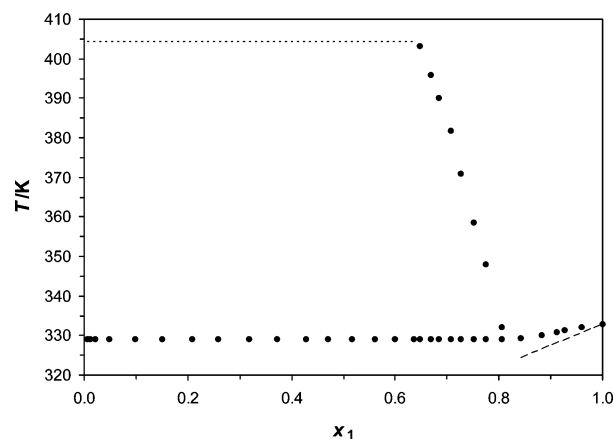


Figure 5. Solid-liquid and liquid-liquid equilibrium diagrams for $\{x_1 [\text{emim}][\text{PF}_6] + (1 - x_1) 3\text{-methylbutan-1-ol}\}$: \bullet , experimental points; dashed line, ideal solubility; dotted line, boiling temperature of a solvent.

Only the unit cell of the [C₁₂mim][PF₆] salt was described as having a spoon-shaped structure,⁶³ a result of strong interaction between the nitrogens of the imidazole ring and special order of the alkyl chain. In polar solvents such as alcohols one can expect stronger interaction with the solvent and possible ruin the hydrogen bonded net.

Experimental phase diagrams of SLE and LLE investigated in this work are characterized mainly by the following: (1) in all cases, with the exception of methanol, there were huge miscibility gaps observed; (2) the mutual solubility of [emim][PF₆] in alcohols decreases with an increase of the molecular weight of an alcohol (see Figures 1–3); (3) the mutual liquid-liquid solubility for primary alcohols decreases in the order ethanol > propan-1-ol > butan-1-ol > 3-methylbutan-1-ol and for secondary alcohols decreases in the order propan-2-ol > butan-2-ol (see Figures 3 and 4); (4) the liquidus curves of the primary, secondary, and tertiary alcohols exhibit similar shapes (see Figure 4); (5) the mutual solubility of [emim][PF₆] in alcohols decreases in the following order tertiary alcohols > secondary alcohols > primary alcohols. Solubility of [emim][PF₆] in methanol and ethanol is higher than that in aromatic hydrocarbons, measured by us previously.⁴² The miscibility gap for C₃ alcohols is higher than that in benzene but comparable with solubility in toluene. Solubility in 3-methyl-butanol-1 is very similar to ethylbenzene and *o*-, *m*-, and *p*-xylene. Unfortunately, the solubility of [emim][PF₆] in aliphatic hydrocarbons was not measured in our previous work.

Correlation of Solid-Liquid Equilibrium. The solubility of a solid 1 in a liquid may be expressed in a very general manner by eq 1⁶⁴

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

where x_1 , γ_1 , $\Delta_{\text{fus}} H_1$, $\Delta_{\text{fus}} C_{p,1}$, $T_{\text{fus},1}$, and T stand for mole fraction, activity coefficient, enthalpy of fusion (17.86 kJ mol⁻¹ for [emim][PF₆]),⁴² difference in solute heat capacity between the solid and liquid at the melting temperature (this value is unknown), melting temperature of the solute (1) ($T_{\text{fus},1} = 332.80$ K),⁴² and measured equilibrium temperature, respectively. The

TABLE 3: Characteristic Parameters of the Pure Compounds: Molar Volumes V_m and the Association Constant K_A Used for NRTL 1, NRTL 2, and UNIQUAC ASM Models Calculations at $T = 298.15$ K

compound	V_m cm ³ mol ⁻¹	K_A
methanol	40.72 ^a	986 ^a
ethanol	58.66 ^a	317 ^a
propan-1-ol	75.12 ^a	197 ^a
propan-2-ol	76.96 ^b	131 ^b
butan-1-ol	91.98 ^a	175 ^a
butan-2-ol	92.39 ^b	68 ^b
tert-butyl alcohol	94.90 ^c	120 ^d

^a From ref 71. ^b From ref 72. ^c From ref 73. ^d From ref 74.

melting point of [emim][PF₆] was reported to be 331–333 K⁶⁵ or 335.15 K.²² The experimental activity coefficients, calculated from eq 1 and presented in Table 1, may have smoothed values when they are obtained from the ideal solubility equation and correlated by the chosen equation liquidus curve. For the liquid–liquid equilibria, the data obtained for the very small values of the mole fraction of IL does not authorize any calculations in the area of LLE.

In this study, three methods were used to fit the solute activity coefficients, γ_1 to the so-called correlation equations that describe the Gibbs excess free energy of mixing, (G^E), the nonrandom two-liquid 1 (NRTL 1),⁶⁶ nonrandom two-liquid 2 (NRTL 2),⁶⁶ and UNIQUAC ASM⁶⁷ models. The exact mathematical forms of the equations have been presented in our previous paper.⁶⁸ Two modified forms of the NRTL equations proposed by Renon were presented by Nagata and co-workers⁶⁶ by substituting local surface fraction for local mole fraction and further by including Guggenheim's combinatorial entropy for athermal mixtures whose molecules differ in size and shape. The resultant equations involve three adjustable parameters and are extended to multicomponent systems without adding ternary parameters. The final description of the activity coefficient in the NRTL 2 equation comes from Gibbs excess free energy of mixing, G^E , expression with different equation for the internal energy, U^E .⁶⁶ The internal energy of mixing, U^E , for a binary mixture of components 1 and 2 was derived by using Scott's two-liquids theory and the local composition concept using the

local mole fractions and later local volume fractions. The NRTL 2 equation adopted the local surface fractions. The UNIQUAC-associated solution theory has been proposed to reproduce the vapor–liquid, liquid–liquid, and solid–liquid equilibria of the binary-alcohol-unassociated component or alcohol mixtures as well as for ternary mixtures of two alcohols with one nonpolar component. The model postulates the formation of linear multisolvated complexes from i -mers of one or two alcohols. The association equilibrium constants was assumed to be independent of the degree of association and solvation.

The parameters of the equations were fitted by an optimization technique. The objective function was as follows

$$F(A_1A_2) = \sum_{i=1}^n w_i^{-2} \{ \ln[x_{1i}\gamma_{1i}(T_i, x_{1i}, A_1A_2)] - \ln(a_{1i}) \}^2 \quad (2)$$

where $\ln(a_{1i})$ denotes an “experimental” value of the logarithm of the solute activity, taken as the right-hand side of the eq 1, w_i is the weight of an experimental point, A_1 and A_2 are the two adjustable parameters of the correlation equations, i denotes the i th experimental point, and n is the number of experimental data. The weights were calculated by means of the error propagation formula

$$w_i^2 = (\partial \ln(x_1\gamma_1) - \partial \ln(a_i)/\partial T)_{T=T_i}^2 (\Delta T_i)^2 + (\partial \ln(x_1\gamma_1)/\partial x_1)_{x_1=x_{1i}}^2 (\Delta x_{1i})^2 \quad (3)$$

where ΔT and Δx_1 are the estimated errors in T and x_{1i} , respectively.

According to the above formulation, the objective function was obtained by solving the nonlinear equation (eq 1), using the Marquardt's method of minimization.⁶⁹ The root-mean-square deviation of temperature (σ_T defined by eq 4) was used as a measure of the goodness of the solubility correlation

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

where n is the number of experimental points (including the melting point) and 2 is the number of adjustable parameters.

TABLE 4: Correlation of the Solid–Liquid Equilibria Data of the [emim][PF₆](1) + Alcohol Mixtures by the NRTL 1, NRTL 2, and UNIQUAC ASM Equations: Values of Parameters and Measures of Deviations

alcohol	parameters			deviations		
	NRTL 1 ^a	NRTL 2 ^a	UNIQUAC ASM	NRTL 1	NRTL 2	UNIQUAC ASM
	Δg_{12} Δg_{21} J mol ⁻¹	Δg_{12} Δg_{21} J mol ⁻¹	Δu_{12} Δu_{21} J mol ⁻¹	σ_T^b K	σ_T^b K	σ_T^b K
methanol	1866.29 −4375.97			5.33		
ethanol	3419.80 −4480.27	1445.16 −1867.78	2437.78 −2698.23	1.11	1.90	1.90
propan-1-ol	3117.32 −3995.66	1515.93 −1884.35	2523.19 −2719.43	0.55	0.58	0.58
propan-2-ol	−3270.44 −2562.60	−3248.13 −851.83	−3785.80 −379.08	0.73	0.72	0.72
butan-1-ol	2538.58 −3039.82	998.01 −1172.17	1663.00 −1743.46	0.67	0.71	0.71
butan-2-ol	−5456.64 764.83	−1220.49 933.70	−2102.26 2521.64	0.95	0.95	0.95
tert-butyl alcohol	2627.63 −3381.45	1205.92 −1483.72	2022.36 −2173.79	0.62	0.67	0.67

^a Calculated with the third nonrandomness parameter $\alpha = 0.95$. ^b According to eq 4 in the text.

The pure component structural parameters r (volume parameter) and q (surface parameter) in the UNIQUAC ASM equation were obtained by means of the following simple relationships⁷⁰

$$r_i = 0.029281V_m \quad (5)$$

$$q_i = \frac{(z-2)r_i}{z} + \frac{2(1-l_i)}{z} \quad (6)$$

where V_m is the molar volume of pure component i at 298.15 K (for our solute, [emim][PF₆], $V_m = 242.6 \text{ cm}^3 \text{ mol}^{-1}$),⁴² z is the coordination number, assumed to be equal to 10, and l_i is the bulk factor; it was assumed that $l_i = 1$ for cyclic molecules. The calculations were carried out by the use of the data set of molar volumes and associating data of alcohols presented in Table 3. The enthalpy of the alcohol association was taken as $-25.1 \text{ kJ mol}^{-1}$.⁷¹ In this work, the parameter α_{12} , a constant of proportionality similar to the nonrandomness constant of the NRTL equation ($\alpha_{12} = \alpha_{21} = 0.95$), was taken into account in the calculations.

Table 4 lists the results of fitting the solubility curves by the three equations used, UNIQUAC ASM, NRTL 1 and NRTL 2.

For the systems presented in this table, the description of solid–liquid equilibrium for alcohols given by the three two-parameters equations was in the same range with the average standard deviation $\sigma_T = 0.77$, 0.92, and 0.92 for the NRTL 1, NRTL 2, and UNIQUAC ASM equations, respectively. The results of calculations presented in Table 4 are missing for 3-methylbutan-1-ol mainly because of the lack of the associating data for that alcohol. Unfortunately, the solubility of [emim][PF₆] in alcohols was very small. The miscibility gap in the liquid phase increases with the increase of the molecular weight of the alcohol (excluding methanol). The immiscibility in the liquid phase was possible to observe only for the increasing temperatures, and the observations were closed to the upper critical point for the ethanol, with the lowest boiling temperature, only. The other alcohols have shown too low boiling temperature compared with the upper critical solution temperature and the observation was impossible. The liquid–liquid equilibrium upper critical point may be expected for the higher temperatures and also to increase with the increase of the molecular weight of the alcohol. The correlation of the LLE using the same parameters from the same models is quite difficult in this work because of the lack of the experimental points in the solvent rich region. Parameters shown in Table 4 may be helpful for the describing activity coefficients for any concentration, temperature and multicomponent systems. They are also useful for the full thermodynamic description of the solution.

Concluding Remarks

The (IL + methanol) binary mixture exhibited a simple eutectic system. The liquid–liquid phase diagrams for the mixtures under study exhibited upper critical solution temperatures (UCST). The area of two liquid phases increases with an increase in the chain length of the alcohol. The observations of UCST were limited by the boiling temperature of the solvent. It was impossible to detect by the visual method the mutual solubility of ILs in the solvent-rich phase for every mixture. The crystal disappearance even in a very diluted solution was possible to observe, but the observation of the liquid–liquid demixing was destructed by the permanent foggy solution. Such an observation in the solvent-rich region was not possible for the [emim][PF₆] in butan-2-ol, *tert*-butyl alcohol, and 3-methylbutan-1-ol alcohols. The spectroscopic or other techniques are

necessary in the mentioned mixtures. The existence of the liquid–liquid equilibria in these mixtures is the evidence that the interaction between the IL and the solvent is not significant. From our work, we can conclude that even such polar solvents as alcohols do not destruct the net of the IL after dissolution. The interactions A–A and B–B were stronger than A–B in the observed mixtures.

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