Solubility of 1-Alkyl-3-ethylimidazolium-Based Ionic Liquids in Water and 1-Octanol

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The liquid–liquid phase equilibria (LLE) of the following imidazolium ionic liquids (ILs), {1-ethyl-3-ethylimidazolium, or 1-butyl-3-ethylimidazolium, or 1-hexyl-3-ethylimidazolium bis{(trifluoromethyl)sylfonyl}imide [EEIM][Tf_2N], or [BEIM][Tf_2N], or [HEIM][Tf_2N], + water or + 1-octanol}, and {1-butyl-3-ethylimidazolium hexafluorophosphate [BEIM][PF_6] + water or + 1-octanol}, have been measured. The effect of anion type ([Tf_2N]- compared to [PF_6]-) and the effect of structural components of an ionic liquid including alkyl chain length on the cation and the ethyl substituent instead of methyl at the cation on the physical-chemical properties of the IL and on the phase behavior were studied. An upper critical solution temperature (UCST) was observed in every system. An increase in the alkyl chain length increases the mutual solubility with 1-octanol and partly with water. Ionic liquids with the ethyl substituent on the cation [HEIM][Tf_2N] show higher solubility in 1-octanol in comparison with the methyl substituent. After the synthesis, the characterization and purity of the compounds were obtained by nuclear magnetic resonance (NMR), elemental analysis, water content (Fischer method), and differential scanning microcalorimetry (DSC). From DSC, the melting point, enthalpy of fusion, and the temperatures of glass transition of all the investigated ionic liquids were determined. The experimental LLE data were correlated by means of the NRTL equation.

Introduction

All popular imidazolium salts such as [C_nMIM][PF_6] or [C_nMIM][Tf_2N] present usually the phase split in water and 1-octanol at room temperature. A miscibility gap was observed for [EMIM][Tf_2N], [BMIM][Tf_2N], and [HMIM][Tf_2N] in water[1–5] and for [HMIM][Tf_2N] in 1-octanol[6,7] or for pyridinium ILs in alcohols.[8] Liquid–liquid equilibrium (LLE) were measured for [EMIM][PF_6] and [BMIM][PF_6] with water at the temperature range (315 to 323) K.[9] It was found that the mutual solubility increases with increasing temperature. An increase in the alkyl chain length from butyl- to octyl- for [BMIM][PF_6], [C_8MIM][PF_6], and [C_8MIM][BF_4] decreases mutual solubility of IL with water at $T = 295$ K.[10] Lengthening the alkyl chain length for [EMIM][Tf_2N], [BMIM][Tf_2N], and [HMIM][Tf_2N] imidazolium ILs also decreases mutual solubility.[2–4] As observed in the other properties, changing the anion from [PF_6]- to [BF_4]- increases the mutual solubilities substantially.[10] The solubility of the IL in water is mainly determined by the anion of the IL. Typical imidazolium ILs based on halide-, ethanoate-, nitrate-, and trifluoroacetate-based anions are fully water-soluble.[2,11] Salts with [BF_4]- and [CF_3SO_3]- anions are partly soluble in water. For more polar anions, like in [MMIM][CH_3SO_4] or [BMIM][CH_3SO_4], complete miscibility with water was observed.[12]

A systematic investigation of the mixtures of [BMIM][PF_6] with alcohols was presented very early.[13–15] Methanol was found completely miscible with [BMIM][PF_6] at temperatures above 273 K. A systematic decrease in solubility was observed with an increase of the alkyl chain length of an alcohol. The same conclusions resulted from the solubility measurements of [EMIM][Tf_2N] in alcohols (1-propanol, 1-butanol, and 1-pentanol)[16] and from those of [C_8MIM][BF_4] with alcohols (1-butanol, 1-pentanol)[17] and many other ILs with different anions and cations in alcohols.[5–7,18] As in many published results, the alkyl chain length increasing on the alcohol was found to cause an increase in the UCST of the system, and increasing the alkyl chain length on the cation results in a decrease in the UCST of the system. There are numerous publications concerning the suitability of ionic liquids as entrainers for separation of water and alcohols.[19–21] Ionic liquids based on the 1-alkyl-3-methylimidazolium cation, [C_nMIM]-, are among the most popular and commonly studied and can be largely exploited for liquid–liquid separation purposes using ILs in spite of traditional volatile organic liquids. As for the anions, bis{(trifluoromethyl)sulfonyl}imide [Tf_2N]- is superior compared to the more commonly investigated hexafluorophosphate, [PF_6]-, and tetrafluoroborate, [BF_4]-, because it is hydrolytically stable, is less viscous, and does not decompose to give HF.

Processes that currently involve homogeneous mixtures of water and volatile organic compounds might be improved by substitution of organic solvent with hydrophilic IL. It has been shown previously that water can decrease the viscosity and density of ILs, which can be satisfactorily used in new technologies.

This paper is a continuation of our systematic study of ionic liquid solubility measurements.[12,18,22,23] In this work, we report the mutual solubility of ILs with an ethyl substituent instead of methyl on the cation: [EEIM][Tf_2N], or [BEIM][Tf_2N], or [HEIM][Tf_2N] and [BEIM][PF_6] with water and 1-octanol. Some of these ILs were studied earlier in various fields: [EEIM][Tf_2N] in electrochemistry,[24] [HEIM][Tf_2N][25] and [HEIM][PF_6][26] as lubricants for the contact of steel/steel. These ILs have showed excellent tribiological performance and were superior to the ionic liquids of alkylimidazolium tetrafluoroborate and the conventional high-temperature lubricants.[25] Unfortunately, the ILs with the [Tf_2N]-anion indicate the occurrence

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Table 1. List of Investigated Ionic Liquids, Names, Structure, and Abbreviations of Names

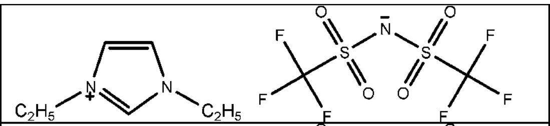
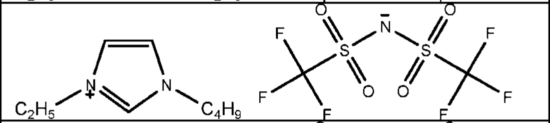
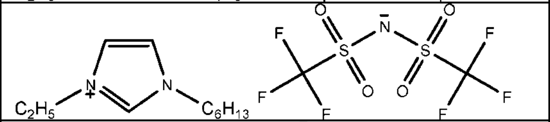
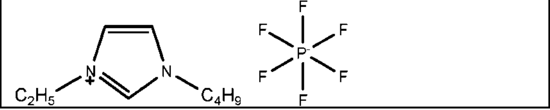
1-ethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide		[EEIM][Tf_2N]
1-butyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide		[BEIM][Tf_2N]
1-hexyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide		[HEIM][Tf_2N]
1-butyl-3-ethylimidazolium hexafluorophosphate		[BEIM][PF_6]

Table 2. Thermophysical Constants of Pure Salts Determined from DSC Data

	$T_{\mathrm{fus},1}$	$\Delta_{\mathrm{fus}}H_1$	$T_{\mathrm{tr},1(\mathrm{g})}$	$\Delta_{\mathrm{tr}}Cp_{(\mathrm{g})}$
compound	K	$\mathrm{kJ \cdot mol^{-1}}$	K	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
[EEIM][Tf_2N]	262.6 ± 0.1	20.4 ± 0.3	205.9 ± 0.1	19.5 ± 0.5
[BEIM][Tf_2N]	–	–	180.9 ± 0.1	154 ± 0.5
[HEIM][Tf_2N]	–	–	184.8 ± 0.1	153 ± 0.5
[BEIM][PF_6]	–	–	192.9 ± 0.1	87 ± 0.5

of a complicated tribiochemical reaction with iron with the formation of FeS, organic fluoride, and others[25] and that with [PF_6]- with the formation of $FePO_4$ and FeF_2 surface compounds.[26] It was interesting to check the other possibilities of these ethyl analogues in extraction and separation processes, for example.

The melting point, glass transition temperature, and enthalpy of fusion were determined by differential scanning calorimetry (DSC) for each ionic liquid investigated. Density was measured by an Anton-Paar (type DMA 602) apparatus.

Experimental Section

Materials. Four imidazolium-based ILs were synthesized. The list of chemicals used in the synthesis of ILs in this study, including CAS number, source and grade, and purification method (if any) is as follows: 1-*H*-imidazole (288-32-4, Koch-Light Laboratory, 99 %), bromoethane (74-96-4, Aldrich 98 %), 1-chlorobutane (109-69-3, Aldrich 99.5 % redistilled), 1-chlorohexane (544-10-5 Aldrich 99 %), lithium bis{(trifluoromethyl)-sulfonyl}imide (90076-65-6, Aldrich 97 %). 1-*H*-Imidazole was reacted with an excess of an alkyl halide (ethylbromide) in a round-bottom flask under a nitrogen atmosphere to synthesize the 1-ethylimidazole. Chloride salts were prepared by the nucleophilic substitution reaction of 1-ethylimidazole by alkyl chloride with varying numbers of carbon atoms in a round-bottom flask under a nitrogen atmosphere to produce 1-alkyl-3-ethylimidazolium chloride, [EEIM]Cl, [BEIM]Cl, and [HEIM]Cl. These substances were purified by mixing with activated carbon to remove colored compounds. 1-Alkyl-3-ethylimidazolium chloride was reacted with lithium bis{(trifluoromethyl)sulfonyl}imide ($LiTf_2N$) in water in a round-bottom flask at 343 K under reflux with strong stirring for at least 3 h. After reaction, mixtures were transferred to the separator where the organic phase was washed by water until the mass fraction of chloride was less than $3 \cdot 10^{-6}$. The aqueous phases were tested for the presence of chloride ion using aqueous 0.1 M silver nitrate solution.

Next, the organic layer was collected and solvent was removed under vacuum with a rotary evaporator. Later, a flask with ionic liquid was placed under high vacuum with stirring at 343 K. After 24 h, the water content was measured using Karl Fischer titration. In all cases, the mass fraction of water was less than $2.3 \cdot 10^{-4}$. 1-Butyl-3-methylimidazolium chloride was reacted with potassium hexafluorophosphate with equimolar proportions in water during 2 h. Next, the same procedures were used as described above. The prepared ILs were characterized by their ^{1}H NMR and elemental analysis. The ^{1}H NMR spectra were recorded on a Varian model XL 300 spectrometer at 300 MHz with tetramethylsilane as the standard. Finally, the ILs were dissolved in the water–methanol solution (1:1) to test the chloride ion with the Mohr method (titration with aqueous silver nitrate solution in the presence of 5 % K_2CrO_4). The ILs were found to contain from (0 to 0.02) mass % with an accuracy ± 0.005.

Twice distilled and degassed water was used for solubility measurements. 1-Octanol was acquired from Sigma-Aldrich Chemie GmbH, Stenheim, Germany. Prior to use, it was

Table 3. Molar Mass and Experimental and Calculated Densities of Ethyl- and Methyl-Substituted ILs at 298.15 K

		ρ(298.15 K)	ρ(298.15K)	ρ(298.15K)
		$[C_nEIM]^{\mathrm{exptl}}$	$[C_nEIM]^{\mathrm{calcd}}$	$[C_nMIM]^{\mathrm{lit}}$
compound	*M*	$\mathrm{g \cdot cm^{-3}}$	$\mathrm{g \cdot cm^{-3}}$	$\mathrm{g \cdot cm^{-3}}$
[EEIM][Tf_2N]	405.12	1.4760, 1.452[a]	1.470[b]	1.519[c], 1.5174[d]
[BEIM][Tf_2N]	433.14	1.4018	1.402[e]	1.436[c], 1.4442[d], 1.43704[f]
[HEIM][Tf_2N]	461.16	1.3454, 1.343[g]	1.344[b]	1.373[c], 1.3715[d], 1.37081[f]
[BEIM][PF_6]	298.21	1.3276	1.328[e]	1.369[c], 1.3674[d], 1.3603[h]

[a] Density at ambient temperatures (291 to 303) K from ref 24. [b] Densities calculated from ref 27. [c] Densities of 1-alkyl-3-methylimidazolium-based ILs from ref 29. [d] Densities of 1-alkyl-3-methylimidazolium-based ILs from ref 30. [e] Densities calculated from ref 28. [f] Densities of 1-alkyl-3-methylimidazolium-based ILs from ref 31. [g] Density at ambient temperature from ref 25. [h] Densities of 1-alkyl-3-methylimidazolium-based ILs from ref 32.

Table 4. Experimental Liquid−Liquid Phase Equilibrium Temperatures, T^{LLE}, in Function of the IL Mole Fraction, x_1, for {IL (1) + Water (2)} Binary Systems

x_1	T_1^{LLE}/K	x_1	T_1^{LLE}/K
[EEIM][Tf$_2$N]			
0.8797	268.8	0.3496	377.1
0.8154	284.5	0.3137	388.2
0.6991	320.3	0.2838	397.8
0.6707	323.0	0.2307	407.4
0.6483	325.9	0.2173	410.6
0.6019	333.2	0.1815	417.0
0.5771	338.4	0.1640	424.5
0.5487	340.7	0.1468	432.6
0.4937	345.3	0.1335	437.1
0.4613	347.5	0.1193	441.9
0.4131	349.9	0.0321	446.6
0.3958	354.6	0.0247	372.5
0.3699	364.8		
[BEIM][Tf$_2$N]			
0.7764	298.75	0.4945	366.75
0.7531	305.04	0.00033	353.35
0.6983	320.05	0.00027	343.55
0.6496	332.2	0.00023	332.25
0.5955	343.79	0.00019	319.65
0.5437	355.71	0.00015	308.35
[HEIM][Tf$_2$N]			
0.8327	300.85	0.5877	367.95
0.8171	306.65	0.000131	368.65
0.7716	321.05	0.000088	349.45
0.7365	331.05	0.000072	340.35
0.7196	335.95	0.000054	331.05
0.6796	345.45	0.000041	321.05
0.6334	356.75		
[BEIM][PF$_6$]			
0.9086	294.9	0.5368	363.3
0.8340	303.8	0.4896	374.3
0.7814	318.9	0.4355	384.6
0.6735	331.6	0.3758	409.6
0.5953	343.6	0.3245	426.0

fractionally distilled to ensure that the water content was $1.6 \cdot 10^{-4}$ in mass fraction. The solvent was stored over freshly activated molecular sieves of type 4 Å (Union Carbide).

The names of substances under study, chemical formulas, and the abbreviations are presented in Table 1.

Differential Scanning Calorimetry (DSC). The enthalpy of fusion, melting temperature, and glass transition temperatures were measured by DSC (Perkin-Elmer Pyris 1). Measurements were carried out at a scan rate of 10 $\mathrm{K \cdot min^{-1}}$, with a power sensitivity of 16 $\mathrm{mJ \cdot s^{-1}}$ and with a recorder sensitivity of 5 mV. The DSC was calibrated with a 99.9999 % purity indium sample. The uncertainty of the calorimetric measurements was estimated to be ± 1.5 %. The uncertainty of the enthalpy of melting was ± 0.3 $\mathrm{kJ \cdot mol^{-1}}$, of measured temperatures $T_{\mathrm{fus},1}$ and $T_{\mathrm{tr},1(\mathrm{g})}$ was ± 0.1 K, and of half the C_p of glass transition was ± 0.5 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The thermophysical properties are shown in Table 2.

Density Measurements. The densities of all ILs were measured using an Anton Paar DMA 602 vibrating-tube densimeter thermostatted at $T = (298.15 \pm 0.01)$ K. The densimeter's calibration was performed at atmospheric pressure using doubly distilled and degassed water, specially purified benzene (CHEMIPAN, Poland 0.999), and dried air. The vibrating-tube temperature was measured by an Anton Paar DM 100-30 digital thermometer and was regulated to better than ± 0.01 K using a UNIPAN 60 thermostat and 202 Temperature Control System (UNIPAN, Poland). The densities of ILs are listed in Table 3.

Table 5. Experimental Liquid−Liquid Phase Equilibrium Temperatures, T^{LLE}, in Function of the IL Mole Fraction, x_1, for {IL (1) + 1-Octanol (2)} Binary Systems

x_1	T_1^{LLE}/K	x_1	T_1^{LLE}/K
[EEIM][Tf$_2$N]			
0.9269	293.5	0.3133	380.8
0.8247	310.8	0.2873	381.3
0.7600	328.4	0.2611	381.9
0.6051	358.2	0.2195	382.2
0.5227	367.3	0.1893	382.0
0.4546	373.8	0.1456	381.8
0.4053	376.7	0.1035	381.1
0.3502	379.9	0.0392	335.4
[BEIM][Tf$_2$N]			
0.7780	284.6	0.3273	349.1
0.7100	299.6	0.2785	350.9
0.6442	317.9	0.2231	352.3
0.5756	329.6	0.1695	353.2
0.5198	336.1	0.1176	353.3
0.4961	338.5	0.0689	350.8
0.4240	343.4	0.0376	346.3
0.3690	346.7		
[HEIM][Tf$_2$N]			
0.6898	259.6	0.3314	323.6
0.6494	282.5	0.2911	325.1
0.6355	293.0	0.2658	326.1
0.6165	302.0	0.2420	326.5
0.5653	309.1	0.1988	327.5
0.5058	313.5	0.1275	328.4
0.4578	316.4	0.0766	327.8
0.4268	318.5	0.0557	327.0
0.3667	321.9	0.0467	325.1
[BEIM][PF$_6$]			
0.9181	270.1	0.2935	356.1
0.8724	289.3	0.2341	356.0
0.8163	310.9	0.1564	354.5
0.7049	330.4	0.1232	353.3
0.6406	336.8	0.1074	351.9
0.5674	344.2	0.0866	350.4
0.5005	349.7	0.0659	348.3
0.4383	353.0	0.0503	346.3
0.3870	354.6	0.0395	342.7
0.3385	355.3		

Elemental Analysis. Elemental analysis was carried out using the Perkin-Elmer Series II model 2400 CHNS/O Analyzer. Elementary analysis results are presented in Table 1S of the Supporting Information.

Water Content. Water content was analyzed by the Karl Fischer titration technique (method TitroLine KF). Samples of all compounds were dissolved in methanol and titrated with a step of 2.5 μL. The results are presented in Table 2S of the Supporting Information.

Liquid–Liquid Equilibria Measurements. Liquid–liquid equilibrium temperatures were determined using a dynamic method previously described.[12,22,23] Appropriate mixtures of IL and solvent were placed, under nitrogen in a drybox, into a Pyrex glass cell and heated slowly (less than 2 $\mathrm{K \cdot h^{-1}}$ near the equilibrium temperature). The mixture was continuously stirred within the cell and was placed in a glass thermostat filled with water. The temperature of the liquid bath was varied slowly until the one phase was obtained. The equilibrium temperature was observed visually over an increasing temperature range, although the observation of the "cloud point" with decreasing temperature proved to be very difficult. The effect of precooling and the kinetics of the phenomenon of binary phase creation were probably the reasons that the temperature of the cloud point was not repeatable during our analysis. The total mass and volumes of sample were different from point to point, and they were from about (1 to 20) g in the Pyrex cell. Mixtures were prepared by mass ratio, and the uncertainty in the mole fraction was estimated to be ± 0.0005. The experiment (i.e., the heating

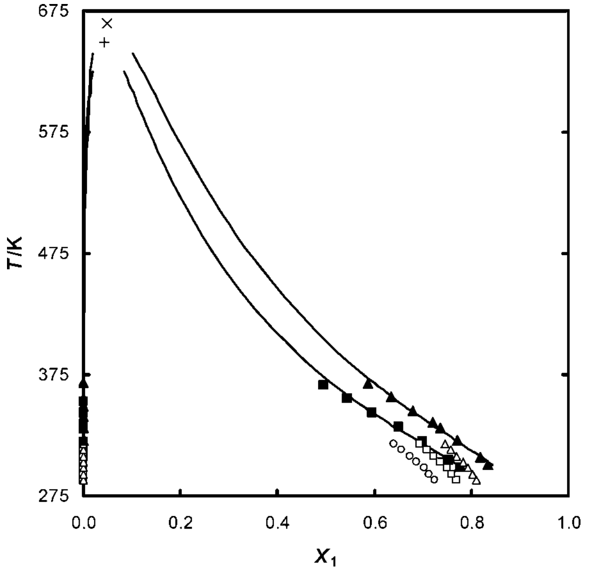


Figure 1. Liquid–liquid phase equilibria diagrams for binary systems.{IL (1) + water (2)}: ■, [BEIM][Tf_2N]; ▲, [HEIM][Tf_2N]; ○, [EMIM][Tf_2N], ref 3; □, [BMIM][Tf_2N], ref 3; △, [HMIM][Tf_2N], ref 3; +, UCST for [BEIM][Tf_2N]; and ×, UCST for [HEIM][Tf_2N] calculated from NRTL parameters. Solid line, NRTL equation.

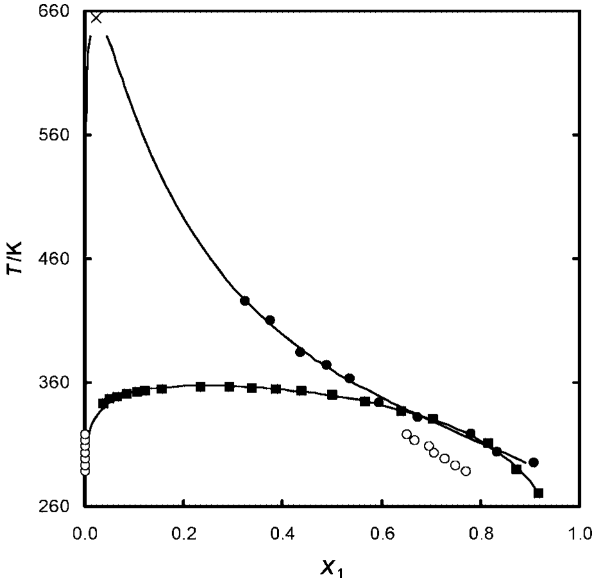


Figure 3. Liquid–liquid phase equilibria diagrams for binary systems. {[BEIM][PF_6] (1) + solvent (2)}: ●, water; ■, 1-octanol; ×, UCST for water calculated from NRTL parameters. Solid line, NRTL equation; ○, [BMIM][PF_6] + water.[3]

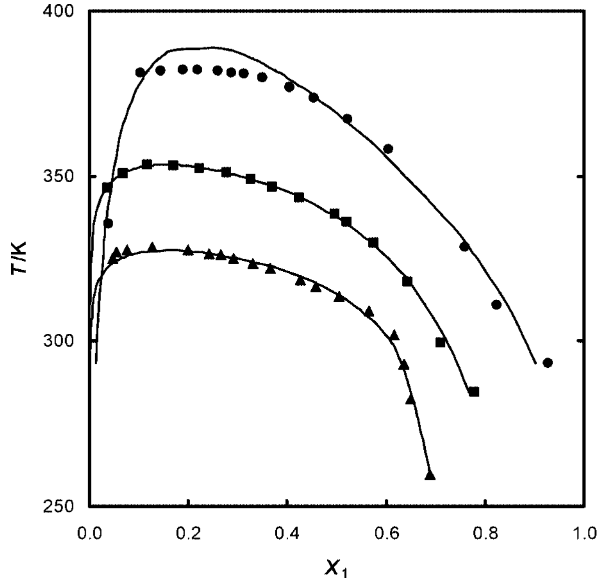


Figure 2. Liquid–liquid phase equilibria diagrams for binary systems. {IL (1) + 1-octanol (2)}: ●, [EEIM][Tf_2N]; ■, [BEIM][Tf_2N]; ▲, [HEIM]-[Tf_2N]. Solid line, NRTL equation.

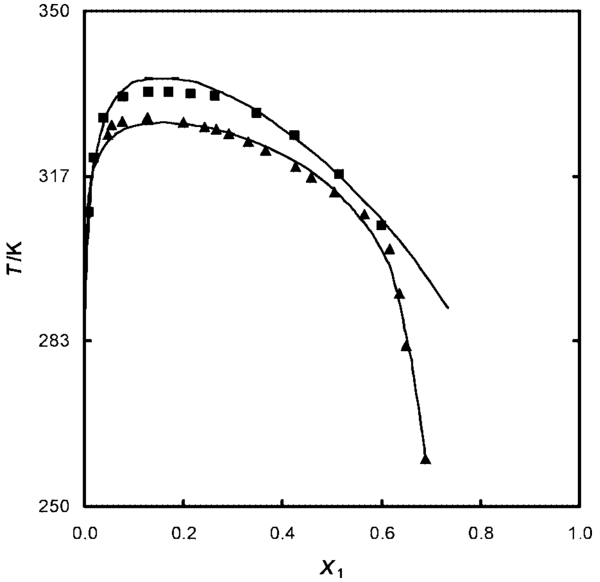


Figure 4. Liquid–liquid phase equilibria diagrams for binary systems. {IL (1) + 1-octanol (2)}: ■, [HMIM][Tf_2N], refs 6 and 8; ▲, [HEIM][Tf_2N]. Solid line, NRTL equation.

and cooling cycle) was repeated three to four times to determine accurate and reproducible values of each solubility point. The uncertainty of the data taken on the disappearance of two phases was ± 0.1 K, and that for the cloud point was ± 0.5 K. The differences of the two temperatures of disappearance of the two phases and the cloud point were about 0.5 K. Temperatures were measured with a P550 electronic thermometer (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostatting liquid.

Results and Discussion

The quick and trivial method of synthesis permit us to receive the ethylimidazolium-based ILs with a unique feature. The NMR technique of ^1H NMR of the pure salts does not have unexpected signals, i.e., from unremoved solvents or unreacted intermediates (see general remarks, GRS 1 of Supporting Information and Figures 1S to 4S of Supporting Information showing the spectra of investigated ILs).

Elemental analysis results verify a high purity of the compounds because they are similar to the calculated values. The difference between found and calculated values is the highest for [EEIM][Tf_2N] and is equal to 3.05 % for the hydrogen. The smallest difference is for [BEIM][PF_6] for hydrogen, and it is equal to 0.01 %.

The temperatures of glass transition were in the range from (180 to 205) K for the measured ILs. This is a typical result for ILs. ILs synthesized by us were liquid at room temperature. Only the [EEIM][Tf_2N] IL exhibits very low melting temperature (262.6 K) and enthalpy of melting 20.46 $kJ\cdot mol^{-1}$ (see Table 2). For all ILs under study, the characteristic peak of the "relaxation" just before the glass transition effect was noted

Table 6. 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 Deviation σ_x

	NRTL parameters[a]				
	$g_{12} - g_{22}$ (J·mol^{-1})		$g_{21} - g_{11}$ (J·mol^{-1})		
system	a_{12}	b_{12}	a_{21}	b_{21}	σ_x
[BEIM][Tf$_2$N] + water	19030	−61.95	−430.0	72.78	0.0084
[HEIM][Tf$_2$N] + water	20295	−60.91	6923	57.79	0.0064
[BEIM][PF$_6$] + water	28435	−85.50	89.12	−215.2	0.0149
[EEIM][Tf$_2$N] + 1-octanol	17126	−50.65	661.8	27.88	0.0569
[BEIM][Tf$_2$N] + 1-octanol	21740	−73.86	61565	−136.13	0.0090
[HEIM][Tf$_2$N] + 1-octanol	18238	−67.70	76112	−194.84	0.0181
[BEIM][PF$_6$] + 1-octanol	15220	−47.76	33428	−66.11	0.0253

[a] $\alpha = 0.2$.

(see Figure 5S of Supporting Information, DSC diagram for [HEIM][Tf$_2$N], as an example).

The measured densities of the new compounds are compared with those predicted by the Ye and Shreeve Group Contribution Method[27] and with the experimental data from the literature of 1-alkyl-3-methyl-substituted imidazolium-based salts in Table 3. A modified model, presented recently by Gardas and Coutinho,[28] provides excellent predictions for our experimental data. The new model[28] predicts the measured densities within less than 0.2 %. All ethylimidazolium bis{(trifluoromethyl)sylfonyl}imides and [BEIM][PF$_6$] have revealed lower densities than those ILs with a methyl substituent.[29–32]

The liquid–liquid equilibria for four new ionic liquids, [EEIM][Tf$_2$N], [BEIM][Tf$_2$N], [HEIM][Tf$_2$N], and [BEIM][PF$_6$], in water and 1-octanol have been determined. The solubilities are listed in Tables 4 and 5, for water and 1-octanol, respectively. The tables include direct experimental results of the equilibrium temperatures, T_1^{LLE}, as a function of x_1, the mole fraction of the IL in equilibrium for the investigated systems.

The phase diagrams of the three 1-alkyl-3-ethylimidazolium bis{(trifluoromethyl)sulfonyl}imides {IL + water} are shown in Figure 1 and those of {IL + 1-octanol} in Figure 2. A comparison between the measured data and the data recently published for the equivalent methylimidazolium compounds in water is presented in Figure 1 and Figure 3. The effect of ethyl vs methyl group on the hydrophobicity and on the temperature dependence of the solubility in water is similar for all compounds studied, and in general, the higher hydrophobicity of the new ethyl-substituted ILs makes them less soluble in water than the corresponding methyl-substituted compounds (see Figure 1 for bis{(trifluoromethyl)sulfonyl}imides[2,3] + water and Figure 3 for hexafluorophosphates[3] + water). In water, the influence of alkyl chain is not the same as for 1-octanol. The shape of the equilibrium curve of ILs in water (see Figure 1) is not unusual for the imidazolium salts. It is similar to the results of LLE for [MMIM][CH$_3$SO$_4$] and [BMIM][CH$_3$SO$_4$] in different solvents.[12,23]

In 1-octanol, the upper critical solution temperature decreases with an increase of the alkane chain of the cation exactly in the same pattern as was observed for the 1-alkyl-3-methylimidazolium-substituted cation[6,8] or pyridinium cation with different substituent groups (in alcohols).[7] On occasion, it was impossible to detect visually the mutual solubility of ILs with the solvent in the solvent-rich phase. Spectroscopic or other techniques are necessary for the aforementioned mixtures. The solubility curves of ILs in the solvent were detected only by few experimental points (see Table 5).

With reference to Figure 3, the difference between the solubilities of [BEIM][PF$_6$] in water and 1-octanol may be discerned. The solubility of IL is much higher in 1-octanol. The comparison is also presented with the solubility of [BMIM][PF$_6$] in water,[4] and for the [PF$_6$]- anion, the solubility of ethylimidazolium IL is lower. Replacing the [Tf$_2$N]- anion by the [PF$_6$]- anion significantly increases the solubility in water at any particular temperature. The mole fraction of the UCST point for the [PF$_6$]- anion is shifted to the higher IL mole fraction in water and to the lower mole fraction in 1-octanol.

The results of LLE of [HEIM][Tf$_2$N] in 1-octanol were compared with that previously measured for [HMIM][Tf$_2$N] data in Figure 4.[6,8] The results presented by Łachwa et al.[7] are similar. A comparison of the solubility of these two ILs in 1-octanol exhibits higher UCST for the methyl analogue; the effect of the ethyl vs methyl group on the IL solubility shows the same trend in the interaction with alcohol as was observed previously for the alkyl substituent in position 1.

It is noticed that the lengthening of the aliphatic chain at the 1 or 3 position on the cation results in the same effects of interaction with solvent and/or has the same influence on packing effects.

Experimental phase diagrams of LLE investigated in this work are not easy to interpret. These ILs are complicated and highly interacting molecules, especially with water and alcohols. The solubility of ILs in 1-octanol is much higher than in water. It was observed for many systems previously. By extending the alkyl chain from the ethyl group to a hexyl group in the ethyl-substituted imidazolium cation, the UCST decreases and the ionic liquid−alcohol mutual solubilities increase. Different kinds of interactions between the IL and an alcohol are responsible for the solubility, but the dominate are the increasing van der Walls forces of the longer alkyl chain on the cation with alkyl portion of the alcohol.[2,5–8]

Liquid–Liquid Equilibrium Correlation. For liquid–liquid equilibrium, the results were correlated with the NRTL model.[33] The experimental data were correlated using the binary parameter NRTL model with the equations described by us earlier.[18,22] The NRTL α parameter was set to a value of $\alpha = 0.2$. The temperature-dependent model adjustable parameters ($g_{12} - g_{22} = a_{12} + b_{12}T$) and ($g_{21} - g_{11} = a_{21} + b_{21}T$) were found by minimization of the objective function OF

$$\mathrm{OF} = \sum_{i=1}^{n} \left[(\Delta x_1)_i^2 + (\Delta x_1^*)_i^2 \right] \tag{1}$$

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

$$\Delta x = x - x_{\mathrm{exptl}} \tag{2}$$

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

$$\sigma_x = \left(\frac{\sum_{i=1}^{n} (x_{\mathrm{exptl}} - x)_i^2}{n - 1} \right)^{1/2} \qquad (3)$$

For the investigated mixtures, it was very difficult to detect visually the mutual solubility of ILs in the solvent-rich phase. These data were calculated previously for some ILs by COSMO-RS[23] within $x_1 \approx 1 \cdot 10^{-4}$. From the experimental data of the methyl-substituted imidazolium IL solubility in water, the average solute mole fraction was $x_1 \approx 8.3 \cdot 10^{-4}$ for [EMIM][Tf_2N];[3] $x_1 \approx 3.2 \cdot 10^{-4}$ for [BMIM][Tf_2N];[3] $x_1 \approx 9.7 \cdot 10^{-5}$;[3] and $x_1 \approx 1.4 \cdot 10^{-3}$ for [BMIM][PF_6].[4] It was assumed that the solubility in the dilute IL region was in the range of a few experimental points measured in our experimental work (see Tables 4 and 5). The NRTL parameters and the corresponding standard deviations are reported in Table 6. The UCSTs, calculated by the NRTL, are presented in Figures 1 and 3. For the systems presented in this work, the average root-mean-square deviation, σ_x, is 0.0198. The results of the correlations are plotted in Figures 1 to 4. 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.

Conclusions

The ethyl-substituted imidazolium ionic liquids revealed lower densities and are less soluble in water and more soluble in 1-octanol than the corresponding methyl compounds. The temperature dependences are similar for all compounds studied. The higher hydrophobicity of the ethyl-substituted ILs was observed as expected for the longer alkane chain. It is interesting to note here the observed trend of solubilities for IL−alcohol binary systems, where the ILs−alcohols mutual solubilities increase with the cation alkyl chain length. This behavior is due to an increase in extension of the van der Waals interactions between the alkyl chains of both alcohols and ILs.

The ILs incorporating the ethyl substituent on the cation lead to lower densities than the one with the methyl substituent. From a practical standpoint, this means that normally high dense and viscous 1-alkyl-3-methylimidazolium-based ionic liquids can be circumvented simply by changing the alkane chain on the cation.

Supporting Information Available:

Elemental analysis, water content, general remarks regarding nuclear magnetic resonance (GRS 1), DSC diagram, and tables including liquid–liquid equilibrium data (Tables 3S and 4S). This material is available free of charge via the Internet at http://pubs.acs.org.

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