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Thermodynamic Phase Behavior of Ionic Liquids

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The phase diagrams of the following imidazolium ionic liquids, {1-ethyl-3-methylimidazolium tosylate [EMIM][TOS] + hexane or cycloheptane} and {1-ethyl-3-methylimidazolium ethylsulfate [EMIM][$EtSO_4$] + hexane or benzene}, have been measured. The (solid + liquid) (SLE) and (liquid + liquid) (LLE) phase equilibria of binary mixtures containing {hexyl(2-hydroxyethyl)dimethylammonium bromide (C_6Br) + hexane or benzene or an alcohol (ethanol or dodecan-1-ol)} and the salt with a different anion {hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate (C_6BF_4) + hexane or benzene or dodecan-1-ol} have been measured. The effect of anion type (Br^- vs BF_4^-) on the thermophysical properties of the IL and on the phase behavior is dependent on the strength of the cation−anion interaction in the investigated ILs and is noticeable. The phase diagrams for some novel ammonium ionic liquids, (2-decanoyloxyethyl)dimethylpentyloxymethylammonium trifluoro-acetate [$C_{10}OOEtC_5OMMMN$][CF_3COO] or (2-methyloyoxyethyl)dimethylpentyloxyammonium acesulfamate [$MOOEtC_5OMMMN$][Ace] or (2-hydroxyethyl)dimethylundecyloxymethylammonium dicyanamide [$C_{11}OMEtOHMMN$][$(CN)_2N$], with octan-1-ol are reported. The solvents were chosen as representatives of alkanes, cycloalkanes, aromatic hydrocarbons, and alcohols. The interaction between the most commonly studied ionic liquids and those chosen in this work with typical organic solvents was described. The solubilities were measured by a dynamic method from 250 K to the melting point of the ionic liquid or to the boiling point of water in the bath. The immiscibility of the liquid phase in {[EMIM][TOS] + cycloheptane} was observed. The observed upper critical solution temperature (UCST) in binary mixtures of {[EMIM][TOS] + cycloheptane} and {[EMIM][$EtSO_4$] + hexane or benzene} was limited by the boiling temperature of the solvent. The difference between the solubilities of the three ammonium ionic liquids, [$C_{10}OOEtC_5OMMMN$][CF_3COO] or [$MOOEtC_5OMMMN$][Ace] or [$C_{11}OMEtOHMMN$][$(CN)_2N$], in octan-1-ol is significant: a simple eutectic system was observed for [$C_{10}OOEtC_5OMMMN$][CF_3COO]; LLE was observed for [$MOOEtC_5OMMMN$][Ace]; and an eutectic system with immiscibility in the liquid phase was observed for [$C_{11}OMEtOHMMN$][$(CN)_2N$]. For the system {[$C_{11}OMEtOHMMN$][$(CN)_2N$] + octan-1-ol}, the upper critical solution temperature was determined to be 312.9 K. Characterization and purity of the compounds were obtained by water content (Fisher method) and differential scanning microcalorimetry (DSC) analysis. From DSC, melting points, enthalpies of fusion, temperatures, and enthalpies of the solid−solid phase transitions and the temperatures of glass transition of all the investigated ionic liquids were measured.

Introduction

During the past 10 years, ionic liquids (ILs) have been recognized as important novel entities showing specific properties including high heat capacities, high densities, extremely low volatilities, nonflammability, high thermal stability, a wide temperature range for the liquid state, and a large number of possible variations in cation and anion conformation.[1−18] A major reason for the interest in ILs is their negligible vapor pressure which decreases the risk of technological exposure and subsequent loss of solvent to the atmosphere. Ionic liquids with their promising physical and chemical properties are versatile electrolytes for diverse technologies such as batteries, photoelectrical cells, and other electrochemical devices.[11−15] The solid−liquid (SLE) and liquid−liquid phase equilibria (LLE) measurements of IL systems based on *N,N′*-dialkyl-substituted imidazolium cations or ammonium cations are attracting increasing attention for applications in liquid−liquid extraction.[10,16−19] Knowledge of SLE is of paramount importance for the design of separation processes especially cooling, evaporation, and antisolvent crystallization. There is a pressing need to develop better solvents for separation, especially in the case of nonideal complexing mixtures. There are numerous publications concerning the suitability of ionic liquids as entrainers for extractive distillation and as extraction solvents for liquid−liquid extraction.[10,18−24] Physical and thermodynamic properties and constants, transport properties, miscibility, and purity assessment have been highlighted as immediate needs. The SLE and LLE measurements of IL systems are attracting increasing attention for applications in liquid−liquid extraction.[19−34] Furthermore, ILs were found to be capable of breaking down a multitude of azeotropic systems.[18−20,23,24] With increasing knowledge of how the structure of an IL affects its physical properties, one should be able to utilize the advantages of ILs as opposed to the volatile organic solvents that are in current use. It has also been shown[35−42] that ILs may have much higher selectivities for the separation of aliphatic from the aromatic hydrocarbons hexane/benzene than sulfolane, NMP, or (NMP + water). This indicates that ILs are excellent solvents for the separation of aliphatic from aromatic hydrocarbons by extraction or by extractive distillation.

Many factors that control the phase behavior of ionic liquids with other liquids, especially with alcohols, have been discussed in recently published papers focusing on pyridinium ILs as opposed to imidazolium ILs[33] or ammonium ILs as opposed to

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imidazolium ILs.[34] The impact of different alcohol and IL characteristics including alcohol chain length, cation (alkyl or alkoxy) chain length, and cations with different substituent groups on the nitrogen in ammonium ILs has been discussed.[21,22,26,28,31−34]

This paper follows the discussion on room-temperature ionic liquids and is a continuation of our systematic study of ionic liquid solubility measurements.[26−29,31,32,34] In our latest work, the LLE of 20 binary systems containing 1-hexyloxymethyl-3-methylimidazolium tetrafluoroborate ([$C_6H_{13}OCH_2MIM$][BF_4]) and 1-hexyloxymethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([$C_6H_{13}OCH_2MIM$][Tf_2N]) with cyclohexane and aliphatic and aromatic hydrocarbons have been presented. SLE and LLE of binary systems comprising 1-hexyloxymethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [$C_6H_{13}OCH_2MIM$][Tf_2N], with alcohols, ketones, or water were measured as well as binary systems comprising 1-hexyloxymethyl-3-methylimidazolium tetrafluoroborate, [$C_6H_{13}OCH_2MIM$][BF_4], with alcohols, ketones, and water.[43]

The solubility of two dialkoxy-imidazolium salts, 1,3-dihexyloxymethylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [$(C_6H_{13}OCH_2)_2IM$][Tf_2N], in alcohols, hydrocarbons, and water along with the systems 1,3-dihexyloxymethylimidazolium tetrafluoroborate, [$(C_6H_{13}OCH_2)_2IM$][BF_4], in alcohols and water have been previously determined in our laboratory.[43]

SLE of quaternary ammonium ILs in alcohols, hydrocarbons, and water have previously been measured.[28,34,44] The SLE phase diagrams investigated for four quaternary ammonium salts, ethyl(2-hydroxyethyl)dimethylammonium bromide, C_2Br, (2-hydroxyethyl)dimethylpropylammonium bromide, C_3Br, butyl-(2-hydroxyethyl)dimethylammonium bromide, C_4Br, and hexyl-(2-hydroxyethyl)dimethylammonium bromide, C_6Br, and alcohols and water have been published previously.[28,34,44] Other anions including [BF_4]$^-$, [PF_6]$^-$, [$(CN)_2N$]$^-$, and [Tf_2N]$^-$ have also been investigated.[34]

Ionic liquids based on the 1-alkyl-3-methylimidazolium cation, [C_nMIM]$^-$, or the tetraalkylammonium cation, [Alk_4N]$^-$, are among the most popular and commonly studied or used in technological improvements. As for the anions, bis{(trifluoromethyl)sulfonyl}imide [Tf_2N]$^-$ and methyl-, ethyl-, or octylsulfate, [C_nSO_4]$^-$, are more superior compared to the more commonly investigated hexafluorophosphate, [PF_6]$^-$, and tetrafluoroborate, [BF_4]$^-$, being hydrolytically stable and less viscous. In this work, we report the interaction of new untypical anions, [TOS]$^-$, [CF_3COO]$^-$, [Ace]$^-$, [$(CN)_2N$]$^-$, or the less known [$EtSO_4$]$^-$, with typical solvents such as alkanes (hexane), cycloalkanes (cycloheptane), aromatic hydrocarbons (benzene), and alcohols (ethanol, octan-1-ol, decan-1-ol). Comparing the results of the solubility of ILs in typical solvents from different publications, the conclusion can be stated that the miscibility gap in the liquid phase increases in the order alcohol < aromatic hydrocarbon < cycloalkane < alkane.[21,22,25,26,28,29,31−34,43−47]

As presented by us earlier, ILs [EMIM][PF_6], [BMIM][PF_6],[48,49] [MMIM][CH_3SO_4], [BMIM][CH_3SO_4],[31] [$C_6H_{13}OCH_2MIM$][BF_4],[26] [$C_6H_{13}OCH_2MIM$][Tf_2N],[26] [$(C_6H_{13}OCH_2)_2IM$][Tf_2N],[43] and [BMIM][$MDEGSO_4$][50] have shown immiscibility in the liquid phase in binary systems with alkanes. In these systems, the small free volume effects and the van der Waals interactions between alkane chains of cations and/or anions and alkanes can only explain the differences in solubilities of different ILs.

A similar very low solubility in alkanes was observed for the ammonium ionic liquids. For example, the solubility of C_4Br exhibits a simple eutectic system with immiscibility in the liquid phase,[34] and the other ammonium salt, (benzyl)dimethylalkylammonium nitrate, [BA][NO_3], shows a very large immiscibility gap in hexadecane and a slightly lower one in hexane.[51] Also, the ammonium salt with alkane substituents only (didecyldimethylammonium nitrate, [DDA][NO_3]) has a better solubility in hexane than in hexadecane.[52]

In all systems with imidazolium and ammonium salts, an increase in the alkyl chain length of the alkane (solvent) resulted in a decrease of solubility.

Generally, in cycloalkanes, the solubility is very similar to that in alkanes. The [EMIM][PF_6] and [BMIM][PF_6],[48,49] [MMIM][CH_3SO_4] and [BMIM][CH_3SO_4],[31][$C_6H_{13}OCH_2MIM$][BF_4] and [$C_6H_{13}OCH_2MIM$][Tf_2N],[26] [$(C_6H_{13}OCH_2)_2IM$][Tf_2N],[43] and [BMIM][$MDEGSO_4$][50] have shown immiscibility in cycloalkanes in the whole IL mole fraction. Sometimes, a similarity of the molecule, the imidazolium ring and the cycloalkane ring, results in better solubility in cycloalkane than in alkane. The opposite reaction is observed for ammonium salts; for example, C_4Br is much less soluble in the liquid phase in cyclohexane than in hexane.[34]

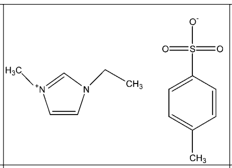
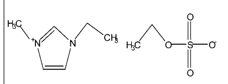
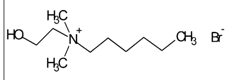
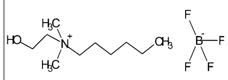
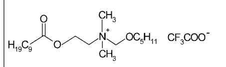
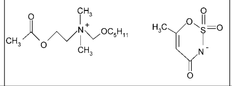
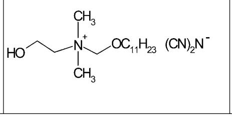
The phase diagrams of ILs with benzene and benzene derivatives differ from those with alkanes. The solubility of ILs is much higher, which is the result of stronger $n-\pi$ or $\pi-\pi$ interaction with the solvent.

Liquid-phase equilibrium for ILs and common solvents such as alcohols is very important for developing ILs for liquid−liquid extraction processes. Previous studies in many laboratories have shown this potential.[21,22,26,28,31−34,43,44,45−47,50−52] Most of the solubility measurements of ILs were made in short chain alcohols. It is well-known that an increase in the alkyl chain length of the alcohol resulted in an increase in the upper critical solution temperature (UCST).

This paper reports the latest developments in our investigations into imidazolium and quaternary ammonium salts. Some new results with [EMIM][TOS] and [EMIM][$EtSO_4$] with the representatives of alkane (hexane) and cycloalkane (cycloheptane) are presented. The more complicated organic anion tosylate was chosen to compare with our previous study.

As for the ammonium salts, two quaternary ammonium salts such as hexyl(2-hydroxyethyl)dimethylammonium bromide, C_6Br, and hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate, C_6BF_4, were investigated with different solvents ({C_6Br + hexane or benzene or ethanol or dodecan-1-ol} and {C_6BF_4 + hexane or benzene or dodecan-1-ol}). Some novel ILs with new anions [CF_3COO]$^-$, [Ace]$^-$, and [$(CN)_2N$]$^-$ were chosen for the comparison. Normally, salts based upon halide anions have higher melting points than salts with larger, more complex anions. In this study, the cation of the IL was made more complex with the addition of alkoxy groups, hydroxyl groups, or carbonyl groups. These new results were compared to other ionic liquids in the same solvent as previously published.[25,26,31,34,43] Characteristics investigated here include the effect of the anion in imidazolium ILs {[TOS]$^-$ vs [$EtSO_4$]$^-$}; the effect of the anion in ammonium ILs {[Br]$^-$ vs [BF_4]$^-$}; the effect of polar substituents on cations such as alkoxy-, hydroxyl-, and carbonyl groups [$C_{10}OOEtC_5OMMMN$]$^+$, [$MOOEtC_5OMMMN$]$^+$, or [$C_{11}OMEtOHMMN$]$^+$; and the effect of polar anions such as [CF_3COO]$^-$, [Ace]$^-$, or [$(CN)_2N$]$^-$. The names of substances under study, chemical formulas, and the abbreviations are presented in Table 1. The melting point, glass transition temperature, enthalpy of fusion, and enthalpies of different solid−solid phase transitions were determined by differential scanning calorimetry (DSC) and thermogravimetric techniques/differential thermal analysis (TG/DTA) for each ionic liquid investigated.

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

1-ethyl-3-methyl-imidazolium tosylate		[EMIM][TOS]
1-ethyl-3-methyl-imidazolium ethylsulfate		[EMIM][EtSO$_4$]
hexyl(2-hydroxyethyl)dimethyl-ammonium bromide		C$_6$Br
hexyl(2-hydroxyethyl)dimethyl-ammonium tetrafluoroborate		C$_6$BF$_4$
(2-decanoyloxyethyl)dimethyl-pentyloxymethylammonium trifluoroacetate		[C$_{10}$OOEtC$_5$OMMMN] [CF$_3$COO]
(2-methyloyoxyethyl)dimethyl-pentyloxyammonium acesulfamate		[MOOEtC$_5$OMMMN][Ace]
(2-hydroxyethyl)-dimethyl-undecyloxymethylammonium dicyanamide		[C$_{11}$OMEtOHMMN] [(CN)$_2$N]

Experimental Section

Materials. The 1-ethyl-3-methylimidazolium tosylate, [EMIM][TOS], and 1-ethyl-3-methylimidazolium ethylsulfate, [EMIM][EtSO$_4$], samples were obtained from Solvent Innovation GmbH (Köln, Germany). The mass fraction purity was ≥ 98 %, dried under a vacuum at 300 K for 48 h to remove organic solvents and water. Investigated compounds C$_6$Br and C$_6$BF$_4$ were prepared using the *N*,*N*-dimethylethanolamine (Sigma-Aldrich, CAS number 108-01-0) and the appropriate haloalkane, hexyl bromide (Sigma-Aldrich, CAS number 111-25-1), as described in our previous work.[28] The synthesis of hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate was performed via metathesis reactions: an equivalent of bromide salt reacts with sodium tetrafluoroborate (NaBF$_4$) in water. Solvent should be used in as small quantity as possible to dissolve bromide salt. Reactions were performed in a round-bottom flask at (343 to 353) K under reflux with strong stirring for at least 24 h. After reaction, mixtures were transferred to the separator, and dichloromethane was added in equal volume as the reaction mixture. After shaking, the organic layer was collected and solvent was removed under vacuum with a rotary evaporator. Washing by dichloromethane was repeated at least 4 times. After the last wash, the flask with ionic liquid was placed under a high vacuum with stirring at 343 K. After 24 h, water (Karl Fischer) content was measured. The ammonium ILs (2-decanoyloxyethyl)dimethylpentyloxymethylammonium trifluoroacetate, [C$_{10}$OOEtC$_5$OMMMN][CF$_3$COO], (2-methyloyoxyethyl)dimethylpentyloxyammonium acesulfamate [MOOEtC$_5$OMMMN][Ace],[53] and (2-hydroxyethyl)dimethylundecyloxymethylammonium dicyanamide, [C$_{11}$OMEtOHMMN][(CN)$_2$N], were synthesized. Chloride salts were prepared by the nucleophilic substitution reaction of deanol or its esters by alkyl chloromethyl ethers with varying numbers of carbon atoms in the alkoxy group, under anhydrous conditions;[54] this permitted a specific type of Menschutkin reaction involving a S_N1 mechanism.[55] The prepared ILs were characterized by their ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectra were recorded on a Varian model XL 300 spectrometer at 300 MHz with tetramethylsilane as the standard, and the ^{13}C NMR spectra were recorded on the same instrument at 75 MHz to detect any impurities. These ionic liquids were cleaned with activated carbon to remove any colored compounds and dried under vacuum at 340 K for 48 h to remove organic solvents and water.

All solvents (hexane, cycloheptane, benzene, ethanol, octan-1-ol, dodecan-1-ol) were acquired from Sigma-Aldrich Chemie GmbH, Stenheim, Germany. Prior to use, they were fractionally distilled over several drying reagents to ensure a mass fraction purity ≥ 99.8 %. The solvents were stored over freshly activated molecular sieves of type 4 Å (Union Carbide).

Samples of ionic liquids used in the experiment have been checked regularly concerning water content using Karl Fischer titration. In all cases, the content of water was less than 180 ppm.

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 $K\cdot min^{-1}$, with a power sensitivity of 16 $mJ\cdot s^{-1}$ 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 thermophysical properties are shown in Table 2.

Solid−Liquid and Liquid−Liquid Equilibria Measurements. Solid−liquid equilibrium and liquid−liquid equilibrium temperatures were determined using a dynamic method previously described.[26,28,31,32] Appropriate mixtures of solute and solvent were placed, under nitrogen in a drybox, into a Pyrex glass cell and heated slowly (less than 2 $K\cdot h^{-1}$ near the equilibrium temperature). The mixture was continuously stirred, with the cell being placed in a glass thermostat filled with water. The temperature of the liquid bath was varied slowly until the last crystals disappeared, this point being taken as the temperature of the solid−liquid equilibrium in the saturated solution. The crystal disappearance temperatures were detected visually. In LLE measurements, a sample of known composition was placed in a view cell and heated until 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 pre-cooling 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. For the investigated mixtures, it was impossible to detect visually the mutual solubility of ILs in the solvent-rich phase. These data were calculated previously for some ILs by COSMO-RS[31,32] with $x_1 \approx 1\cdot 10^{-4}$. The total mass and volumes of the sample were different from point to point, and they were from about (1 to 20) g in the Pyrex cell.

Temperatures were measured with a P550 electronic thermometer (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostating liquid. The accuracy of the temperature measurements was judged to be ± 0.01 K. Mixtures were prepared by mass ratio; the uncertainty was estimated to be ± 0.0005 for the mole fraction and ± 0.1 K (LLE) or 0.05 K (SLE) for temperature, respectively. It was found that the solution crystallization procedure was quite slow and difficult; hence, the solubility measurements were very time-consuming. For many systems, the LLE measurements were

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

compound	$T_{fus,1}$ / K	$\Delta_{fus}H_1$ / kJ·mol^{-1}	$T_{tr,1}$ / K	$\Delta_{tr}H_1$ / kJ·mol^{-1}	M / g·mol^{-1}
[EMIM][TOS]	322.9	27.83	214(g)[a]	–	282.35
[EMIM][EtSO$_4$]	–	–	187(g)[b]	–	236.29
C$_6$Br	355.3[c]; 355.5	3.78	184 (g)[d]	–	254.23
C$_6$BF$_4$	–	–	172(g)[e]	–	261.11
[C$_{10}$OOEtC$_5$OMMMN][CF$_3$COO]	279.8	7.83	252; 244; 236; 209(g)[f]	2.38; 7.16; 7.71	457.57
[MOOEtC$_5$OMMMN][Ace]	–	–	219(g)[g]	–	394.49
[C$_{11}$OMEtOHMMN] [(CN)$_2$N]	283.5	7.15	258.35*;* 195.40(g)[h]	10.028	340.51

[a] ΔC_p at the glass transition is equal to 61.0 J·mol^{-1}·K^{-1}. [b] ΔC_p at the glass transition is equal to 107 J·mol^{-1}·K^{-1}. [c] Data for C$_6$Br were published earlier.[28] [d] ΔC_p at the glass transition is equal to 59.7 J·mol^{-1}·K^{-1}. [e] ΔC_p at the glass transition is equal to 114.6 J·mol^{-1}·K^{-1}. [f] ΔC_p at the glass transition is equal to 301 J·mol^{-1}·K^{-1}. [g] ΔC_p at the glass transition is equal to 163 J·mol^{-1}·K^{-1}. [h] ΔC_p at the glass transition is equal to 200 J·mol^{-1}·K^{-1}.

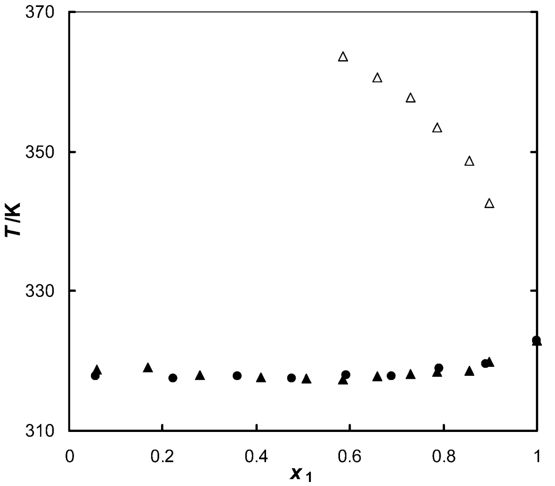


Figure 1. $T-x$ diagram for [EMIM][TOS] (1) in ●, hexane; or ▲, cycloheptane SLE experimental points; and Δ, cycloheptane LLE experimental points.

limited at the upper temperature by the boiling point of the liquid bath medium (water).

Results and Discussion

The half C_p extrapolated temperatures of glass transition were in the range from (174 to 214) K for the measured salts. It is a typical result for ILs. Only [EMIM][EtSO$_4$], C$_6$BF$_4$, and [MOOEtC$_5$OMMMN][Ace] were liquid at room temperature, with the other salts being solid at room temperature. The ammonium salts exhibit very low enthalpy of melting in comparison with [EMIM][TOS], although they do show solid−solid phase transitions. From DSC diagrams, three phase transitions for [C$_{10}$OEtC$_5$OMMMN][CF$_3$COO] and one for [C$_{11}$OMEtOHMMN][(CN)$_2$N] were observed.

In this discussion, the liquid−liquid equilibria for new binary ionic liquid−organic solvent systems were determined. The solubilities of two imidazolium ionic liquids, [EMIM][TOS] in hexane and cycloheptane and [EMIM][EtSO$_4$] in hexane and benzene, were measured. The results of LLE in hexane were compared with the previously measured [MMIM][CH$_3$SO$_4$], [BMIM][CH$_3$SO$_4$], or [BMIM][OcSO$_4$] data.[31,56] The results are shown in Figure 1 and Figures 2a and 2b. The solubilities are listed in Tables 1S and 2S of the Supporting Information (SI), for [EMIM][TOS] and [EMIM][EtSO$_4$], respectively. The tables include direct experimental results of the equilibrium temperatures, T_1^{SLE} and/or T_1^{LLE}, vs x_1, the mole fraction of the IL in equilibrium, for the investigated systems.

Figure 1 presents the results of the solubility of [EMIM][TOS] in hexane and cycloheptane. Both solvents are nonpolar, and there is no interaction between the IL and the solvent. The form of the phase diagram produced can be attributed to packing effects, as the hexane molecule can pack closer to the ethyl or methyl group of the cation than the cyclic molecule of cycloheptane. It was noticed previously that [EMIM][TOS] showed the immiscibility in the liquid phase of the binary system with cyclohexane.[57] The upper critical solution temperature increases with an increasing number of carbon atoms in the cyclic hydrocarbon. On occasion, it was impossible to detect visually the mutual solubility of ILs with the solvent in the solvent-rich phase. Such an observation in the solvent-rich

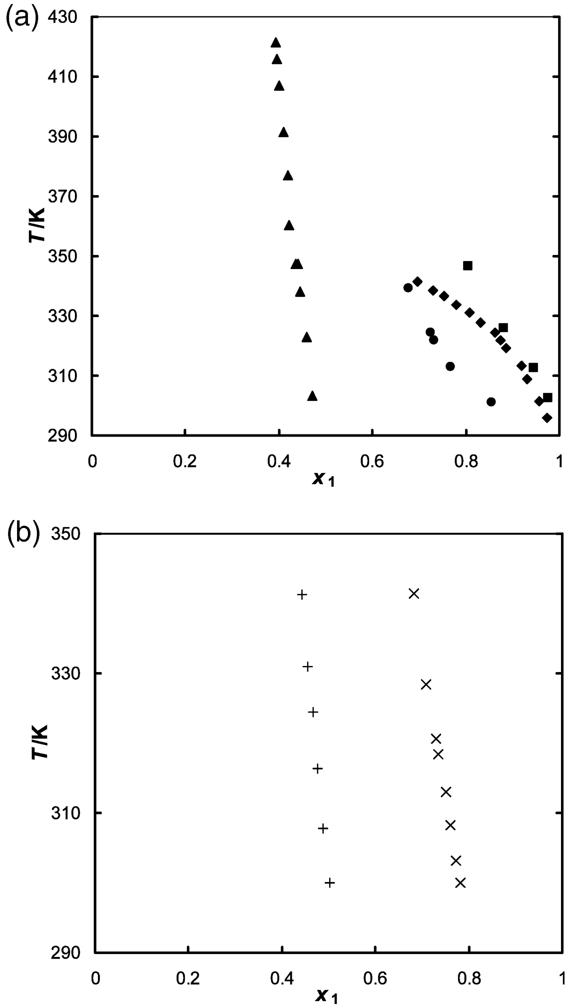


Figure 2. (a) Liquid−liquid equilibrium diagrams for different ILs (1) in hexane: ■, [BMIM][CH$_3$SO$_4$];[31] or ◆, [MMIM][CH$_3$SO$_4$];[31] or ●, [EMIM]-[EtSO$_4$] [this work]; ▲, [BMIM][OcSO$_4$].[55] (b) Liquid−liquid equilibrium diagrams for different ILs (1) in hexane: ×, [C$_6$H$_{13}$OCH$_2$MIM][Tf$_2$N];[26] +, [(C$_6$H$_{13}$OCH$_2$)$_2$ IM][Tf$_2$N].[43]

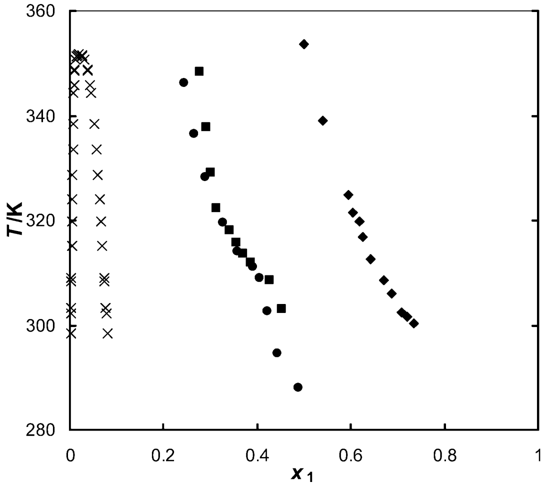


Figure 3. Liquid−liquid equilibrium diagrams for different ILs (1) in benzene: ◆, [MMIM][CH_3SO_4];[31] ■, [BMIM][CH_3SO_4];[3] ●, [EMIM]-[$EtSO_4$] [this work]; ×, [$C_6H_{13}OCH_2MIM$][Tf_2N].[26]

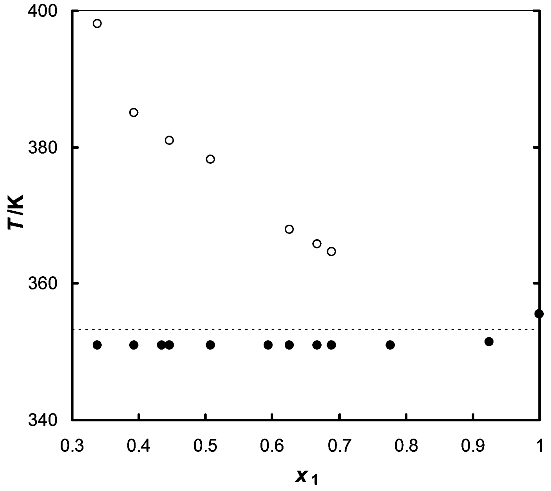


Figure 4. (Solid + liquid) phase equilibria of (C_6Br + benzene): ●, SLE experimental points; ○, LLE experimental points; dotted line, the boiling temperature of solvent.

region was not possible, for example, with [EMIM][TOS] in cycloheptane, all salts in hexane, and most of the mixtures in benzene. Spectroscopic or other techniques are necessary for the aforementioned mixtures.

With reference to Figures 2a and 2b, the difference between the solubilities of different ionic liquids in hexane may be discerned. The data presented herein for [EMIM][$EtSO_4$] are of a similar order as that for 1-hexyloxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [$C_6H_{13}OCH_2MIM$]-[Tf_2N].[26] Lower solubilities were noted for [BMIM][CH_3SO_4] and for [MMIM][CH_3SO_4].[31] A much lower immiscibility gap in hexane (greater solubility) was observed for [BMIM]-[$OcSO_4$][56] and for 1,3-dihexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide, [$(C_6H_{13}OCH_2)_2IM$][Tf_2N].[43] Generally, the dihexyloxy salt showed increased solubility in many polar solvents as compared to the hexyloxy salt, possibly because of stronger hydrogen bonding.[43] A similar order of solubilities was also observed for hexane. The better packing effects and the van der Waals interactions between two of the same alkane chains of IL and hexane have to be assumed.

Changing the solvent from an aliphatic hydrocarbon to an aromatic hydrocarbon demonstrates that the interaction is most likely due to $n-\pi$ interactions between the oxygen atom of the IL and the benzene ring. The liquid−liquid equilibria for binary mixtures of [MMIM][CH_3SO_4], [BMIM][CH_3SO_4], or [EMIM]-[$EtSO_4$] in comparison with [$C_6H_{13}OCH_2MIM$][Tf_2N] in benzene are presented in Figure 3. Replacing the hexane by benzene significantly increases the solubility at any particular temperature. For [MMIM][CH_3SO_4], changes are from complete immiscibility in hexane to a much smaller immiscibility gap in benzene. Among these four salts, the lower UCST of the system was observed for [$C_6H_{13}OCH_2MIM$][Tf_2N] in benzene; this clearly indicates the influence of an increased interaction with the IL. The influence of a different cation on the solubility of [XMIM][CH_3SO_4], where X = [methyl] or [butyl] in benzene, has shown that the two liquid−liquid phase area decreases in the order [BMIM][CH_3SO_4] < [MMIM][CH_3SO_4].[31] The [EMIM][$EtSO_4$] measured in this work has an immiscibility similar to [BMIM][CH_3SO_4] (see Figure 3). It can be noticed that the lengthening of the aliphatic chain at the cation or the anion results in the same effects of interaction with solvent and/or has the same influence on packing effects. A sharp bend observed on the equilibrium curve of [EMIM][$EtSO_4$] in Figure 3 is not unusual for the imidazolium salts. That effect was also observed for many systems of [MMIM][CH_3SO_4] and [BMIM][CH_3SO_4] in different solvents.[31,32] It can be the result of sharp changing of viscosity or density of the solution with increasing temperature.

A greater interaction was observed for [$C_6H_{13}OCH_2MIM$]-[Tf_2N] with benzene than for [EMIM][$EtSO_4$] with benzene. We believe that this is due to the stronger interaction of the [Tf_2N]$^-$ anion and of the alkoxy group of the cation with the solvent. The specific interaction with the solvent between the nitrogen atoms of the imidazole ring and the oxygen of the alkoxymethyl group of the cation [$C_6H_{13}OCH_2MIM$]$^+$ and the benzene ring diminishes the area of immiscibility below 0.2 IL mole fraction (in benzene), as shown in Figure 3.

The solubility of C_6Br in benzene is usually much lower than in the alcohols (see Figure 4 and Table 3S of the SI). The results mainly depended on the temperature of melting of C_6Br. The UCST was shifted to the low mole fraction of C_6Br and was much higher than 400 K (not measured). The eutectic point was expected also at very low IL mole fraction. For short and one long alkyl substituents at the cation of the IL, it is also the result of an uncomfortable packing effect in the solution with the benzene molecule. Similar effects were observed in the liquid−liquid equilibrium measurements in the system {C_6Br + hexane}. Unfortunately, the numerical data are not presented because the experimental points were not repeatable in three series. The miscibility gap was observed for the whole mole fraction of the IL. The melting temperature of C_6Br is higher than the boiling temperature of hexane, thus the measurements at temperatures higher than 360 K were very difficult.

SLE diagrams of C_nBr (n = 2, 3, 4, 6) with 1-octanol and water[28] and of C_2Br with alcohols[44] were presented as simple eutectic systems. The solubilities of C_6Br in ethanol and dodecan-1-ol are presented in Figures 5 and 6 and in Tables 4S and 5S of the SI.

Experimental phase diagrams of SLE investigated in this work are not easy to interpret. The solutes are complicated and highly interacting molecules, especially in alcohols. The solubility of C_6Br in ethanol is much higher than in dodecan-1-ol and in octan-1-ol,[28] no doubt the result of intermolecular hydrogen bonding by the hydroxyl side group. The liquidus curve goes vertically down to the ethanol melting point. The eutectic point presumably is at a very low IL mole fraction. By increasing the alkyl chain of an alcohol, the immiscibility in the liquid was observed between IL mole fractions x_1 = 0.47 and x_1 =

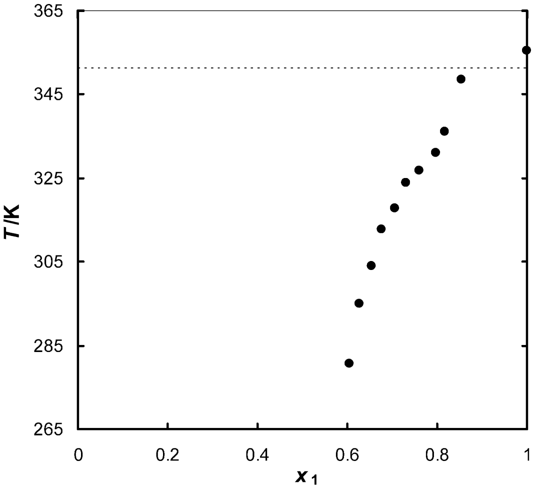


Figure 5. (Solid + liquid) phase equilibria of (C_6Br + ethanol): ●, experimental points; dotted line, boiling temperature of solvent.

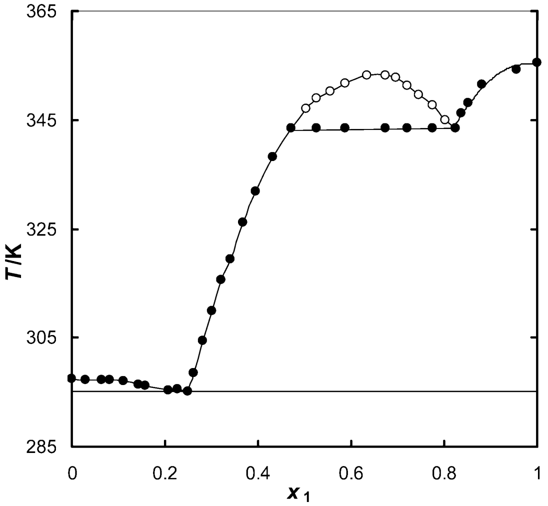


Figure 6. (Solid + liquid) and (liquid + liquid) phase equilibria of (C_6Br + dodecan-1-ol): ●, SLE experimental points; ○, LLE experimental points; full lines, drawn to guide the eye.

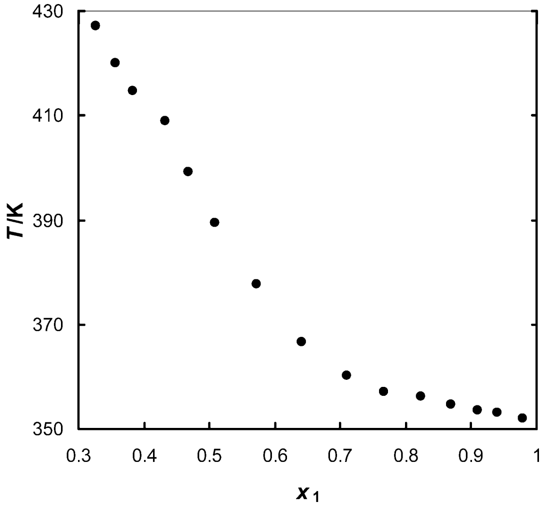


Figure 7. (Liquid + liquid) phase equilibria of (C_6BF_4 + hexane): ●, experimental points.

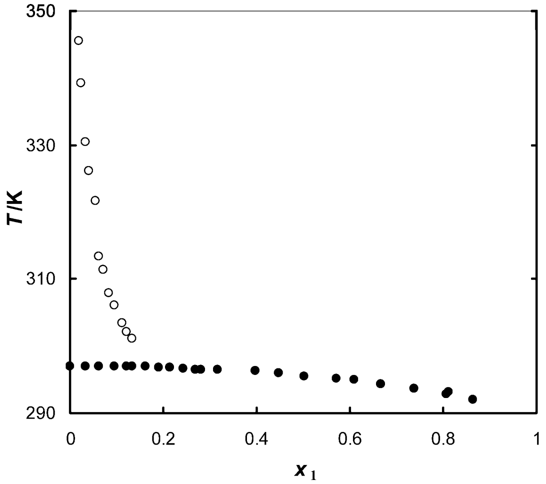


Figure 8. (Solid + liquid) and (liquid + liquid) phase equilibria of (C_6BF_4 + dodecan-1-ol): ●, SLE experimental points; ○, LLE experimental points.

0.82. The upper critical solution temperature was at 353 K. Due to the complete phase diagram of {C_6Br + dodecan-1-ol}, the eutectic point was found graphically. Table 5S (SI) lists the temperature and composition of the eutectic point for the investigated mixture.

As in all systems with ILs, the solubility of C_6BF_4 in hexane is much lower than in benzene and dodecan-1-ol. The miscibility gap in the whole mole fraction range is from 0 to 1. For the IL mole fraction from $x_1 = 1{\cdot}10^{-4}$ to $x_1 = 0.67$, the miscibility gap was observed at temperatures higher than 360 K. The UCST was higher than 430 K. The results are shown in Figure 7 and in Table 6S of the SI.

The binary system {C_6BF_4 + benzene} has a similar diagram with a wider miscibility gap in the liquid phase. Unfortunately, for this system also, the experimental points were not repeatable and the numerical data cannot be presented. The observation of the binary phase's disappearance was made impossible by the permanent foggy solution. We assume that water from the air could be the reason, even though the water content for the IL and the solvent was checked. Actually, it surprises us that no one author mentioned, in the discussion of the experimental results, the difficulties in experimental work with ionic liquids. Usually, the influence of water is discussed but not the difficulties of getting the results in different physicochemical methods working with ionic liquids.

The liquidus curve of C_6BF_4 in the system with dodecan-1-ol has shown a very flat shape completely different from the system {C_6Br + dodecan-1-ol}. The solid−liquid phase transition temperatures depended mainly on the melting temperature of dodecan-1-ol (see Figure 8 and Table 7S of the SI). The immiscibility in the liquid phase was observed at a very low IL mole fraction with an UCST of about 350 K (not measured) and with the eutectic point shifted to the high IL mole fraction, and for C_6Br in the binary system with 1-dodecanol, the eutectic point was $x_{1,e} = 0.248$. The upper critical solution temperatures in these two systems are similar, but the phase diagrams are completely different.

The phase diagrams for the novel ammonium ionic liquids [$C_{10}OOEtC_5OMMMN$][CF_3COO] or [$MOOEtC_5OMMMN$][Ace] or [$C_{11}OMEtOHMMN$][$(CN)_2N$] in octan-1-ol are presented in Figures 9a, 9b, and 9c and are listed in Table 8S of the SI.

The ability of a polar cation or anion of an IL to create a hydrogen bond with an alcohol is widely recognized and significantly increases the solubility of an IL in an alcohol. The interaction of the methylsulfate, $[CH_3SO_4]^-$, anion with alcohols is so strong that complete miscibility was observed for [BMIM]-

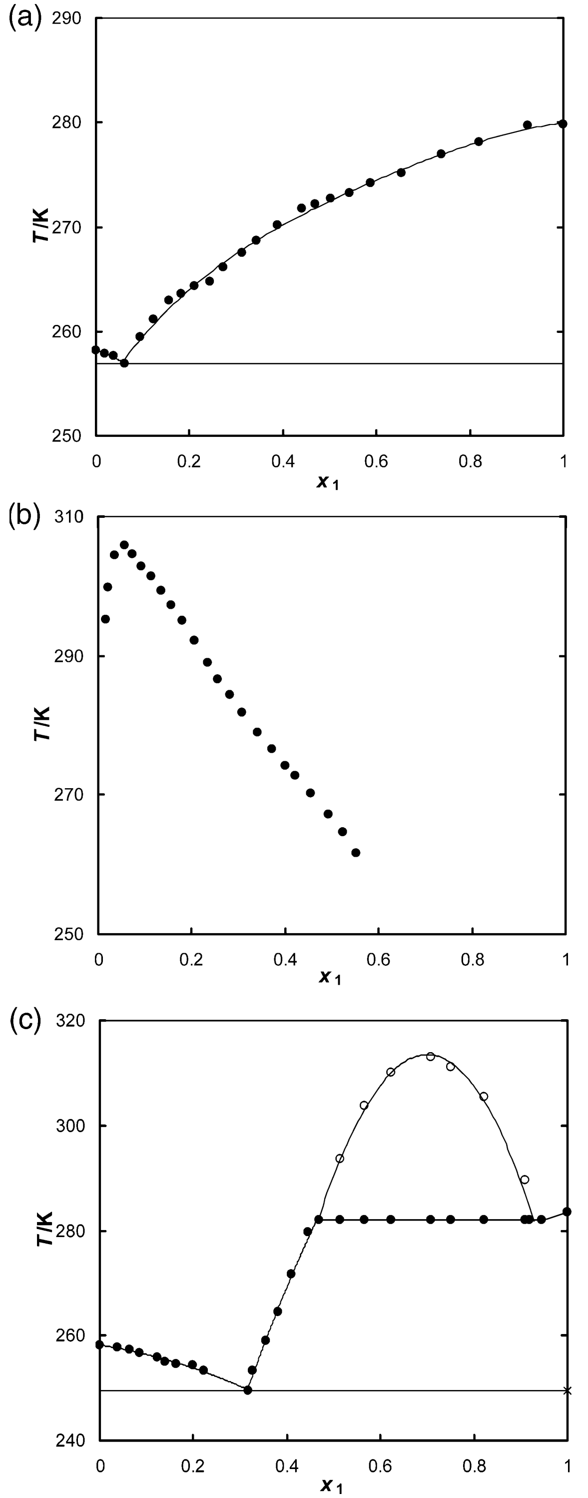


Figure 9. (a) Solid−liquid equilibrium diagram for [$C_{10}OOEtC_5OMMMN$]-[CF_3COO] (1) in octan-1-ol: ●, experimental points; full lines, drawn to guide the eye. (b) Liquid−liquid equilibrium diagram for [$MOOEtC_5$-$OMMMN$][Ace] (1) in octan-1-ol. (c) Solid−liquid and liquid−liquid equilibrium diagram for [$C_{11}OMEtOHMMIMN$][$(CN)_2N$] (1) in octan-1-ol: ●, experimental SLE points; ○, experimental LLE points; full lines, drawn to guide the eye.

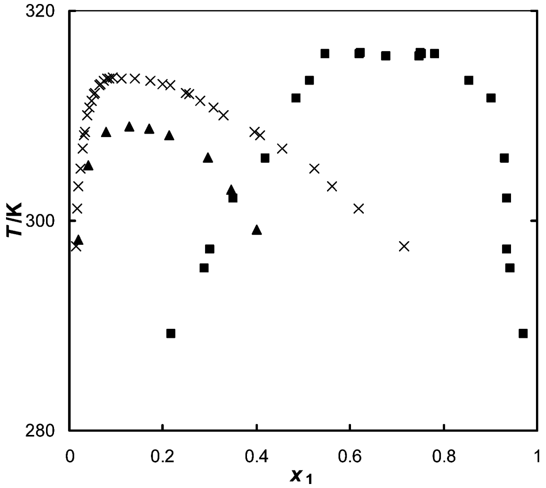


Figure 10. Liquid−liquid equilibrium diagrams for different ILs (1) in octan-1-ol: ■, [OMIM][Cl];[45] ×, [$C_6H_{13}OCH_2MIM$][Tf_2N];[43] ▲, [OMIM]-[Tf_2N].[25]

[CH_3SO_4] in alcohols ranging from methanol to undecan-1-ol and for [MMIM][CH_3SO_4] in alcohols ranging from methanol to pentan-1-ol at room temperature.[32] Only the binary systems of [MMIM][CH_3SO_4] with alcohols from hexan-1-ol to undecan-1-ol exhibit upper critical solution temperature behavior.[32] Figure 9a shows the solid−liquid equilibria with complete miscibility in the liquid phase for [$C_{10}OOEtC_5OMMMN$][CF_3COO]; many polar groups in this salt are responsible for the strong interaction with the solvent. The {[$C_{10}OOEtC_5OMMMN$][CF_3COO] + octan-1-ol} binary mixture exhibits a simple eutectic system. The [$MOOEtC_5OMMMN$][Ace] is liquid at room temperature and is not miscible in the liquid phase with octan-1-ol (see Figure 9b). The aromatic anion is responsible for no miscibility. The miscibility gap was observed also for [$C_{11}OMEtOHMMMN$]-[$(CN)_2N$] in octan-1-ol (see Figure 9c). The liquid−liquid phase diagram for {[$C_{11}OMEtOHMMMN$][$(CN)_2N$] + octan-1-ol} shows a miscibility gap in the liquid phase with an upper critical solution temperature. For this IL, the UCST is 312.9 K. The ammonium salt [$C_{11}OMEtOHMMMN$][$(CN)_2N$] has a hydroxyl group and a hexyloxy group or carbonyl group. There is no doubt, however, that those oxygen atoms in the cation are responsible for strong hydrogen bond formation with an alcohol.

A comparison of the solubility of three different ILs in octan-1-ol is presented in Figure 10, the least soluble being 1-octyl-3-methylimidazolium chloride, [OMIM][Cl].[45] Two other salts with a similar anion [Tf_2N]$^-$, [$C_6H_{13}OCH_2MIM$][Tf_2N][43] (UCST = 316 K) and [OMIM][Tf_2N][25] (UCST = 309 K), exhibit an UCST with the maximum shifted to the solvent-rich mole fraction. Better solubility (lower UCST) was observed for [OMIM][Tf_2N].

Conclusions

In most cases, imidazolium- and ammonium-based ionic liquids are highly ordered hydrogen-bonded substances that can assert strong effects on chemical reactions and processes. The solid−liquid phase diagrams show simple eutectic mixture behavior. The van der Waals interaction between the alkane chains on the cation and the solvent has much less influence than the hydrogen bonding between the polar group of the cation and an alcohol.

The salts studied here are soluble in alcohols with a small immiscibility gap for a longer chain alcohol (C_6Br in dodecan-1-ol) or for a larger cation of IL ([$C_{11}OMEtOHMMMN$][$(CN)_2N$] in octan-1-ol). For two investigated alcohols, an increase in the alkyl chain of the alcohol resulted as usual in a decrease in the solubilities (C_6Br).

Clearly, hydrogen bonding, $n-\pi$, or any other interactions of the polar groups on the cation or anion of an IL with the solvent play an important role in controlling the liquid−liquid and the solid−liquid phase behavior of imidazolium or ammonium-based ILs. However, the existence of the liquid−liquid phase equilibria in these mixtures shows that the interaction between the IL and the solvent in spite of many polar groups in the IL molecule is not significant.

Acknowledgment

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Supporting Information Available:

Solid−liquid and liquid−liquid equilibrium data (Tables 1S to 8S). This material is available free of charge via the Internet at http://pubs.acs.org.

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