

Liquid Phase Behavior of Imidazolium-Based Ionic Liquids with Alcohols

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Ionic liquids have been suggested as replacement solvents in reactions and separations since they have negligible vapor pressure; thus, they would reduce fugitive emissions that are common when organic solvents are used in these applications. To fully utilize ionic liquids in reactions and separations, a fundamental understanding of the factors that govern the phase behavior of ionic liquids with other common liquids is necessary. In this work, we present a systematic study of the impact of different factors on the phase behavior of imidazolium-based ionic liquids with alcohols. All systems examined showed upper critical solution temperature (UCST) behavior, with low solubility of the ionic liquid in the alcohol and high solubility of the alcohol in the ionic liquid. An increase in the alkyl chain length of the alcohol resulted in an increase in the UCST. Branching of the alcohol resulted in a higher solubility of the alcohol in the ionic-liquid-rich phase. By increasing the alkyl chain length on the cation, the UCST decreased, while replacement of the hydrogen at the C2 position of the ring with a methyl group resulted in an increase in the UCST. The choice of anion was shown to have a large impact on the UCST of the system. The relative alcohol affinity for the different anions observed was $(\text{CN})_2\text{N} > \text{CF}_3\text{SO}_3 > (\text{CF}_3\text{SO}_2)_2\text{N} > \text{BF}_4 > \text{PF}_6$.

Introduction

Room temperature ionic liquids have garnered increased interest recently as potential “green” replacements for volatile organic solvents due to their unique properties. Typically composed of organic cations with organic or inorganic anions, ionic liquids (ILs) have negligible vapor pressure and a wide liquidus range (i.e., over 300 K).¹ Although the definition of a room temperature ionic liquid has been expanded to include those compounds with melting points under 100 °C, all ILs examined in this study are those with melting points below 25 °C. Another characteristic of ionic liquids is the potential to tune the physical and chemical properties of the compound by varying different features of the ionic liquid, including the alkyl chain length on the cation and the anion. By changing these features of the ionic liquid, properties such as density, heat capacity, and viscosity are affected. For example, we have recently shown that the density of ionic liquids increases with a decrease in the alkyl chain length on the cation and an increase in the molecular weight of the anion.² With a detailed knowledge of the impact of different factors on the properties of ionic liquids, the use of ionic liquids as “designer solvents” for specific applications can be envisioned. One area where this knowledge will be of great importance is in the liquid phase behavior of ILs with common liquids, such as alcohols and water.

Liquid phase equilibrium for ILs and common solvents is very important for developing ILs for liquid–liquid extraction processes. Previous studies have shown this potential. Huddleston et al. showed that an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, or [bmim][PF₆], could be used to extract aromatic compounds from water.³ Fadeev and Meagher have shown that two imidazolium ionic liquids with the hexafluorophosphate anion could be used for the extraction

of butanol from aqueous fermentation broths.⁴ Other studies have shown that one can use ionic liquids for the extraction of aromatics from aromatic/alkane mixtures,⁵ alcohols from alcohol/alkane mixtures,⁶ and sulfur-containing aromatics from gasoline.⁷

Another potential application for ionic liquids where liquid phase equilibrium is important is as a solvent for reactions. Reviews by Welton⁸ and Wasserschied⁹ detail specific types of reactions where ionic liquids have been used successfully as a solvent. When a specific ionic liquid is chosen as a reaction solvent, an important aspect to consider is the solubility of the reactants and products in the ionic liquid. In addition, if one uses an extractant solvent to separate reactants and products, the phase behavior of the extractant with the ionic liquid must also be considered.

To aid in the development of ionic liquids for reactions and separations, liquid phase equilibria for a number of ionic liquids have been reported in a variety of different ways. These data include binary temperature–composition curves of ILs with alcohols,^{10–15} alkanes and aromatics,¹⁶ and water,^{11,17} ternary temperature–composition curves of ILs with alcohols and water,^{11,18} infinite dilution activity coefficients for a variety of organic compounds in ILs,^{19–22} and solubilities of some organics^{23–25} and water^{4,26–30} in ionic liquids. Although there is a general understanding of the liquid phase behavior trends for different classes of organics with ionic liquids, a complete understanding of the impact of different characteristics of the ionic liquid on the liquid phase behavior is lacking. This is because many of the individual studies have been conducted with few ionic liquids with little variation of the anion, alkyl chain length, or additional substituent groups on the ionic liquid.

In this work, we conduct a systematic study of the impact of different characteristics of the ILs and the alcohols on the liquid–liquid phase equilibrium of imidazolium-based ionic liquids and alcohols. Alcohol characteristics investigated include

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the effect of increasing the alkyl chain length of the alcohol (i.e., 1-propanol vs 1-butanol or 1-hexanol) and the effect of branching of the alcohol (i.e., 1-butanol vs 2-butanol or *tert*-butyl alcohol). Ionic liquid characteristics investigated include the effect of increasing the alkyl chain length of one chain on the cation (i.e., butyl compared to hexyl), the effect of methyl substitution on the C2 carbon on the ring of the cation, and the effect of different anions (i.e., PF₆, BF₄, (CF₃SO₂)₂N, CF₃SO₃, and (CN)₂N). In addition, we report ionic liquid–water mutual solubility data for a number of ionic liquids.

Experimental Section

Materials. The list of chemicals used in the synthesis of ionic liquids in this study, including CAS number, source, grade, and purification method (if any), is as follows: 1-methylimidazole (616-47-7, Aldrich, 99%, redistilled over KOH), 1-butylimidazole (4316-42-1, Aldrich, 98%, redistilled over KOH), 1-bromobutane (109-65-9, Aldrich, 99%, washed with concentrated sulfuric acid and distilled over P₂O₅³¹), 1-chlorobutane (109-69-3, Aldrich, 99.5%, redistilled), tetrafluoroboric acid (16872-11-0, 48 wt % solution in water, used without purification), ammonium tetrafluoroborate (13826-83-0, Aldrich, 97+%, used without purification), methyl trifluoromethanesulfonate (333-27-7, Aldrich, 99+%, used without purification), silver nitrate (7761-88-8, Aldrich, 99+%, used without purification), and sodium dicyanamide (1934-75-4, Aldrich, 96%, used without purification). Solvents used include deionized water from a Millipore purification unit and redistilled Fisher 99.9% grade dichloromethane.

The list of alcohols used in this study, including CAS number, source, grade, purification method (if any), and water content (determined by Karl Fisher titration, EM Science Aquastar V-200 titrator) is as follows: 1-propanol (71-23-8, Aldrich, 99.5%, distilled over MgSO₄, 860 ppm water), 2-propanol (67-63-0, Aldrich, 99.5%, anhydrous, used without purification, 1040 ppm water), 1-butanol (71-36-3, Aldrich, 99.5%, distilled over MgSO₄, 1020 ppm water, or Aldrich, 99.8%, anhydrous, used without purification, 250 ppm water), 2-butanol (78-92-2, Aldrich, 99.5%, anhydrous, used without purification, 1290 ppm water), isobutanol (78-83-1, Aldrich, 99.5%, anhydrous, used without purification, 930 ppm water), *tert*-butyl alcohol (75-65-0, Aldrich, 99.5+%, distilled over sodium, 360 ppm water), 1-hexanol (111-27-3, Aldrich, 98%, distilled over MgSO₄, 1000 ppm water, or Aldrich, 99+%, anhydrous, used without purification, 590 ppm water), 1-octanol (111-87-5, Aldrich, 99+%, anhydrous, used without purification, 70 ppm water), and 1-dodecanol (112-53-9, Aldrich, 98+%, used without purification, 1250 ppm water). As noted above, two different samples of 1-butanol and 1-hexanol were used in this work. For studies involving [bmim][BF₄], the nonanhydrous sample of both 1-butanol and 1-hexanol was used. For all other studies, the anhydrous sample of both alcohols was used.

Several ILs were purchased or received from commercial vendors and other research groups. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]), 2,3-dimethyl-1-ethylimidazolium bis(trifluoromethylsulfonyl)imide ([emmim][Tf₂N]), and 2,3-dimethyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide ([pmmim][Tf₂N]) were obtained from Covalent Associates, Inc. and are all electrochemical grade (>99% purity). All ionic liquids purchased or received were dried before use, and the water content was determined by Karl Fisher titration. The water contents of these ionic liquids were 820 ppm for [pmmim][Tf₂N] and 460

ppm for [bmim][Tf₂N]. The water contents of [emim][Tf₂N] and [emmim][Tf₂N] were not measured since these ionic liquids were used only for ionic liquid–water mutual solubility studies. It should be noted that although these ILs are electrochemical grade, they do contain some impurities, as determined by proton NMR spectroscopy. These impurities are most probably unreacted alkylimidazolium halides, and can affect the liquid phase behavior of the IL with both alcohols and water.

Synthesis. Five ionic liquids used in this study were synthesized along with the corresponding halide precursors, using previously published methods.^{26,32,33}

[bmim][Cl] and *[bmim][Br]*. 1-Methylimidazole was reacted with an excess of a butyl halide (1-chlorobutane or 1-bromobutane) in a round-bottom flask under a nitrogen atmosphere to produce the 1-butyl-3-methylimidazolium halide ([bmim][Cl] or [bmim][Br]).

[hmim][Br]. 1-Hexyl-3-methylimidazolium bromide was synthesized in the same manner as [bmim][Br] with the exception that 1-bromohexane was used instead of 1-bromobutane.

[bmim][BF₄]. The 1-butyl-3-methylimidazolium halide was reacted with an excess of either ammonium tetrafluoroborate in a dichloromethane solution or HBF₄ in an aqueous/dichloromethane biphasic solution, and the ionic liquid [bmim][BF₄] was formed. The product ammonium halide and any residual ammonium tetrafluoroborate, or the hydrochloric acid and any residual tetrafluoroboric acid, were removed from the ionic liquid by washing with water.

[bmim][triflate]. 1-Butylimidazole was reacted directly with methyl trifluoromethanesulfonate in an ice bath, forming [bmim]-[trifluoromethanesulfonate], or [bmim][triflate].

[bmim][dca]. Equimolar amounts of sodium dicyanamide and silver nitrate were mixed in an aqueous solution, with solid silver dicyanamide precipitating from the solution. The solid was then filtered and washed with water to remove any sodium nitrate. Excess silver dicyanamide was reacted with 1-butyl-3-methylimidazolium bromide in aqueous solution to form the ionic liquid [bmim][dicyanamide], or [bmim][dca]. The aqueous solution was then filtered to remove all solid precipitate (silver bromide and excess silver dicyanamide).

[hmim][BF₄]. This ionic liquid was synthesized in the same manner as [bmim][BF₄] using [hmim][Br] and ammonium tetrafluoroborate to form 1-hexyl-3-methylimidazolium tetrafluoroborate, or [hmim][BF₄].

[bmim][BF₄], [hmim][BF₄], [bmim][triflate], and [bmim][dca] were cleaned with activated carbon to remove any colored compounds and dried under vacuum at 75 °C for 48 h to remove organic solvents (e.g., dichloromethane) and water. The water contents of [bmim][BF₄], [hmim][BF₄], [bmim][triflate], and [bmim][dca] were measured using Karl Fisher titration. All ionic liquids were analyzed by proton NMR spectroscopy to confirm the absence of any major impurities. Halide (Cl[−] and Br[−]) and ammonium ion contents were measured using an Oakton Ion 510 series pH/mV/ion/°C meter with Cole-Parmer ion-specific probes (27502-13 for Cl[−], 27502-05 for Br[−], and 27502-03 for NH₄⁺). Two different samples of [bmim][BF₄] were used for these investigations. For liquid phase equilibrium studies involving 1-propanol, 1-butanol, and 1-hexanol with [bmim][BF₄], the ionic liquid was synthesized via the acid route using [bmim][Cl]. Its halide content was less than 10 ppm chloride, and the water content was 1400 ppm. For the other studies involving [bmim][BF₄], the ionic liquid was synthesized via the ammonium tetrafluoroborate route using [bmim][Br]. It contained less than 8 ppm bromide, less than 18 ppm ammonium,

and 850 ppm water. The [bmim][triflate] contains neither halide nor ammonium impurities since it was synthesized by direct metathesis. The water content of this ionic liquid was 2800 ppm. The [bmim][dca] contains less than 290 ppm bromide and 5150 ppm water. The [hmim][BF₄] contains less than 18 ppm bromide and 410 ppm water. It was our experience that some of the ionic liquids (e.g., [bmim][triflate] and [bmim][dca]) were harder to dry than others and that further drying tended to result in discoloration of the ionic liquid. Therefore, this tradeoff between dryness and the formation of trace amounts of colored decomposition products is responsible for the relatively high water content in some of the ionic liquids.

Experimental Method. All experiments for determining the phase equilibrium of ionic liquid/alcohol systems were conducted using a "cloud point" method, similar to that described by Marsh.¹⁰ In this technique, a sample of known composition was placed in a viewcell and heated until it was one phase. The "cloud point temperature" is the temperature at which the sample initially changes from one phase to two phases. The phase transition is observed visually. In our apparatus, four solutions of ionic liquid and an organic liquid at different concentrations were prepared gravimetrically in 5 mL viewcells (3/8 in. o.d. Pyrex glass tubes) in a glovebox, sealed from the atmosphere, and placed in a water bath. The uncertainty in the compositions is estimated to be ± 0.0001 mole fraction. The samples were heated in the water bath using a 1000 W immersion heater (Vycor 16790-1L) to about 5 K above the highest expected cloud point temperature and maintained at that temperature for 10 min using an Omega CN 8500 temperature controller. The samples were cooled using a recirculating water chiller at a cooling rate of about 1 K/min. The temperature of each sample was measured individually using a T-type thermocouple (Eurotherm 2408i temperature indicator). The experiment (i.e., the heating and cooling cycle) was repeated four additional times to determine accurate and reproducible values (± 0.5 K) of each cloud point temperature. The reproducibility of the cloud point temperatures for replicate samples of the same composition and for different batches of ionic liquids and alcohols is within ± 0.5 K.

For ionic liquid/water systems, a direct phase composition measurement method was used, as described in-depth previously by Anthony et al.³⁰ Volumes of ionic liquid and water were mixed vigorously and then allowed to separate into two phases, an ionic-liquid-rich phase and a water-rich phase. Each phase was then analyzed to determine the mutual solubilities of the liquids. The solubility of water in the ionic-liquid-rich phase was determined by Karl Fischer titration, and the solubility of ionic liquid in the water-rich phase was determined by UV-vis spectroscopy (Varian Cary 1). The reproducibility of the mutual solubility data for replicate samples is within 0.1 wt %. As stated previously, the Tf₂N ionic liquids contain some impurity. The reproducibility of the mutual solubility using different batches of ionic liquid was determined using a sample (<10 ppm Br) of [bmim][Tf₂N] that was synthesized in our laboratory. The reproducibility between these two different batches of IL is within 0.3 wt %.

Results and Discussion

For this study, the liquid-liquid phase equilibria for a number of binary ionic liquid/alcohol systems were determined. The alcohols investigated for each IL are as follows: ([bmim][BF₄]) 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, *tert*-butyl alcohol, 1-hexanol; ([bmim][Tf₂N]) 1-butanol, 1-hexanol, water; ([pmmim][Tf₂N]) 1-butanol, 1-hexanol, water; ([hmim]-

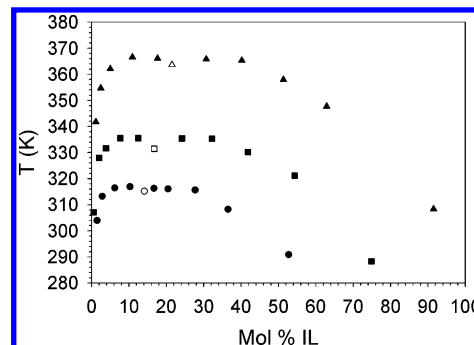


Figure 1. T - x diagram for [bmim][BF₄] with 1-propanol (●), 1-butanol (■), and 1-hexanol (▲). Comparison is made with the data of Wagner et al. for [bmim][BF₄] with 1-propanol (○), 1-butanol (□), and 1-hexanol (+).¹⁵

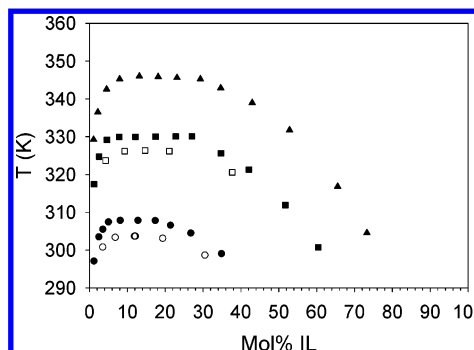


Figure 2. T - x diagram for [hmim][BF₄] with 1-butanol (●), 1-hexanol (■), and 1-octanol (▲). Comparison is made to the data of Wagner et al. for [hmim][BF₄] with 1-butanol (○) and 1-hexanol (□).¹⁵

[BF₄]) 1-butanol, 1-hexanol, 1-octanol; ([bmim][triflate]) 1-butanol, 1-hexanol, 1-octanol, 1-dodecanol; ([bmim][dca]) 1-hexanol, 1-octanol, 1-dodecanol; ([emim][Tf₂N]) water; ([emmim]-[Tf₂N]) water.

Results in the form of T - x data for each binary system investigated are shown in the Supporting Information. Similar characteristics were observed for all of the liquid-liquid equilibrium systems examined. For example, upper critical solution temperature (UCST) behavior was observed in all systems. In addition, the alcohol-rich phase typically contained only a small amount (e.g., 1–2 mol %) of ionic liquid, while the ionic-liquid-rich phase frequently contained a large concentration of alcohol, sometimes in excess of 50 mol %. Using the systems listed above, the impact of different alcohol and ionic liquid characteristics was determined.

Influence of Alcohol Characteristics. Alcohol Chain Length. Figure 1 shows the liquid phase behavior for the ionic liquid [bmim][BF₄] with the alcohols 1-propanol, 1-butanol, and 1-hexanol, along with a comparison to data for this system from Wagner et al.¹⁵ [bmim][BF₄] is totally miscible with ethanol and methanol at room temperature. From the figure, it is clear that the UCST increases as the chain length of the alcohol increases. The same trend is observed in Figure 2 for the ionic liquid [hmim][BF₄] with the alcohols 1-butanol, 1-hexanol, and 1-octanol, as well as the systems examined for [bmim][Tf₂N], shown in Figure 3, and [pmmim][Tf₂N], shown in Figure 4. This trend is observed for not only primary alcohols but also secondary alcohols, as shown in Figure 5, where we compare the phase behavior of 2-propanol and 2-butanol with [bmim]-[BF₄]. This trend is consistent with observations for other ionic liquid systems, such as in the study by Heintz et al. of [emim]-[Tf₂N] with a series of primary alcohols,¹⁴ the study of solid-liquid equilibrium of [C₁₂mim][Cl] with a series of alcohols,¹²

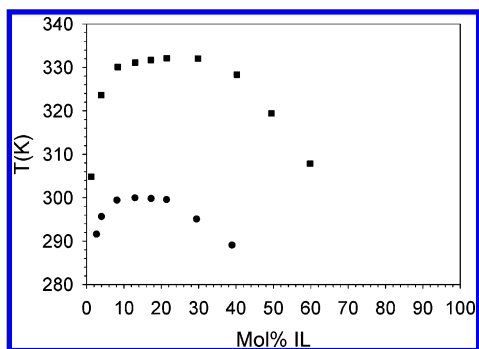


Figure 3. T - x diagram for [bmim][Tf₂N] with 1-butanol (●) and 1-hexanol (■).

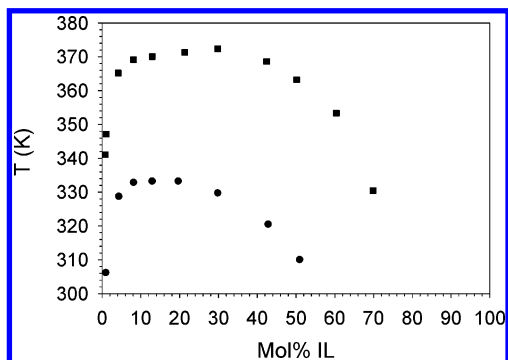


Figure 4. T - x diagram for [pmmim][Tf₂N] with 1-butanol (●) and 1-hexanol (■).

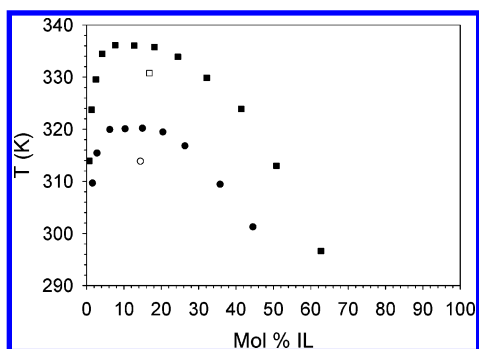


Figure 5. T - x diagram for [bmim][BF₄] with 2-propanol (●) and 2-butanol (■). Comparison is made to the data of Wagner et al. for [bmim][BF₄] with 2-propanol (○) and 2-butanol (□).¹⁵

and the study of BF₄ and PF₆ ionic liquids with alcohols by Wagner et al.¹⁵ By making the alcohol more aliphatic, the UCST of the system increases.

Comparison of our data with data from Wagner et al.¹⁵ for the [bmim][BF₄] and [hmim][BF₄] systems with alcohols reveals the same general trend of increasing UCST with increasing alcohol chain length. However, the values of the phase transition temperatures from Wagner et al.¹⁵ are always lower than the values observed in this study by 2–6 K. It should be noted that although a full curve is available from Wagner et al.¹⁵ for [hmim][BF₄] systems with alcohols, only one composition is available for each of the [bmim][BF₄] systems. The differences in phase transition temperatures may be due to different water contents of the ionic liquids and/or alcohols used. In the work of Wagner et al.¹⁵ the ionic liquids were dried for 3 days at 60 °C, but no water contents for the alcohols were mentioned, except that the solvents were of the highest quality and used without purification. We would anticipate that the presence of higher water impurity levels than those used here would cause a decrease in the phase transition temperature. Conversely, less

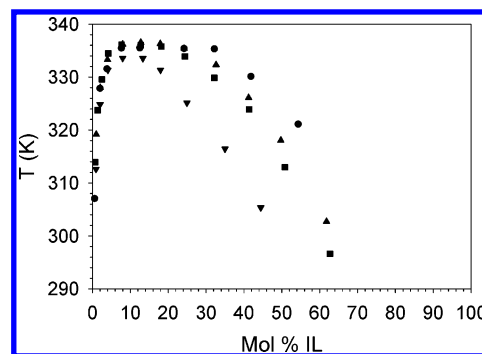


Figure 6. T - x diagram for [bmim][BF₄] with 1-butanol (●), 2-butanol (■), isobutanol (▲), and *tert*-butyl alcohol (▼).

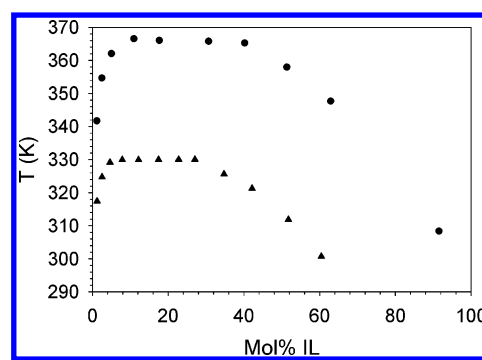


Figure 7. T - x diagram for [bmim][BF₄] (●) and [hmim][BF₄] (▲) with 1-hexanol.

water contamination should result in slightly higher phase transition temperatures, as observed experimentally for the ethanol/[bmim][PF₆] and 2-methylpropanol/[bmim][Tf₂N] systems.³⁴

Alcohol Branching. Figure 6 shows the liquid phase behavior for [bmim][BF₄] with 1-butanol and a series of branched alcohols, 2-butanol, isobutanol, and *tert*-butyl alcohol. Although the UCST of these systems are almost identical, significant differences are observed in the compositions of the ionic-liquid-rich phase. For a given composition on the ionic-liquid-rich side of the diagram, the phase transition temperature is decreased for the more highly branched alcohols. In other words, at a given temperature the solubility of the alcohol in the ionic-liquid-rich phase is higher for branched alcohols than it is for linear alcohols. It is interesting to note that this trend of higher affinity for branched alcohols is also observed by Heintz et al. in their studies of infinite dilution activity coefficients of solutes in imidazolium- and pyridinium-based ionic liquids.^{21,22} The increase in solubility of the alcohol in the ionic liquid could be due to the greater basicity of the branched alcohols, as quantified by the Kamlet-Taft β parameter.³⁵ β is a measure of the ability of a compound to accept a hydrogen bond. β values are 0.45 for 1-butanol, 0.45 for isobutanol, 0.51 for 2-butanol, and 0.57 for *tert*-butyl alcohol.³⁵ The more basic alcohols are able to dissolve more readily in the ionic liquid, perhaps through specific hydrogen-bonding interactions with acidic hydrogens on the imidazolium cation ring.

Influence of Ionic Liquid Characteristics. Length of the Alkyl Chain on the Cation. Figure 7 shows the liquid phase behavior for the ionic liquids [bmim][BF₄] and [hmim][BF₄] with 1-hexanol. The UCST is significantly higher for the ionic liquid with the shorter alkyl chain. The same trend is observed with 1-butanol, comparing [bmim][Tf₂N] from our work and [emim][Tf₂N] from Heintz et al.,¹⁴ as shown in Figure 8. Wu et al. showed this trend clearly in their study of 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids (butyl,

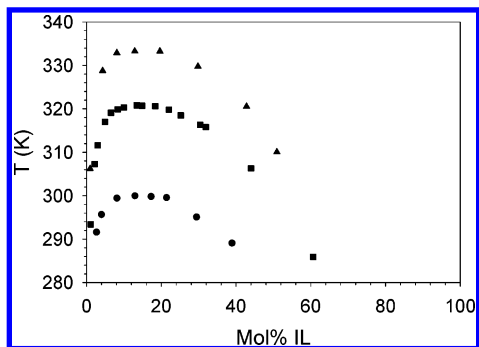


Figure 8. T - x diagram for [bmim][Tf₂N] (●) and [pmmim][Tf₂N] (▲) with 1-butanol. Comparison is made with data for [emim][Tf₂N] (■) from Heintz et al.¹⁴

pentyl, hexyl, heptyl, and octyl) with 1-butanol.¹⁰ By extending the alkyl chain from an ethyl group to a butyl group to a hexyl group, the UCST decreases and the ionic liquid–alcohol mutual solubilities increase at any particular temperature below the UCST. The enhancement in solubility with increased alkyl chain length is most likely due to the increased ability of the longer alkyl chain on the cation to interact with the alkyl portion of the alcohol via van der Waals interactions.

C2 Substitution. Figure 8 shows the liquid phase behavior for 1-butanol with [bmim][Tf₂N] and [pmmim][Tf₂N]. The data from Heintz et al.¹⁴ for 1-butanol with [emim][Tf₂N] are included for comparison. From the previous section, an ionic liquid with a longer alkyl chain length on the cation is expected to have a lower UCST with a particular alcohol than a similar ionic liquid with a short chain. Therefore, even though we did not study 3-methyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide, or [pmim][Tf₂N], we can be confident that the cloud point curve and UCST for this ionic liquid would be between the curves for [emim][Tf₂N] and [bmim][Tf₂N]. However, the cloud point curve and UCST for 1-butanol with [pmmim][Tf₂N], which is similar to [pmim][Tf₂N] with the exception that the C2 hydrogen has been replaced by a methyl group, occur at much higher temperatures than what we would have expected for [pmim][Tf₂N]. In fact, the cloud point curve for 1-butanol with [pmmim][Tf₂N] is at significantly higher temperatures than the [emim][Tf₂N]/1-butanol curve. By substituting a methyl group at the C2 position for a hydrogen, the mutual solubilities of the ionic liquid and alcohol are lessened substantially. It is widely known that the hydrogen at the C2 position on the imidazolium cation is the most acidic hydrogen on the ring.³⁶ This hydrogen is able to interact with alcohols via hydrogen bonding. Replacing the hydrogen with a methyl group eliminates the possibility of interaction between the cation at the C2 position and the alcohol through hydrogen bonding, causing a decrease in the mutual solubilities of the ionic liquid and alcohol and an increase in the UCST of the system. Thus, we have shown that hydrogen bonding between alcohols and acidic hydrogens on the imidazolium ring plays a key role in determining phase behavior.

Anion. The influence of the anion can be examined by comparing the cloud point curves of several different [bmim] ionic liquids with a single alcohol, 1-butanol. Our data for [bmim][BF₄] and [bmim][Tf₂N] are compared with the data of Wu et al.¹⁰ for [bmim][PF₆] in Figure 9. The UCST is lowest for 1-butanol with [bmim][Tf₂N] (~300 K). However, the UCST increases to over 335 K for 1-butanol with [bmim][BF₄]. The UCST for the [bmim][PF₆] system is clearly over 373 K.¹⁰ Thus, the choice of anion has a dramatic effect on the phase behavior of imidazolium-based ionic liquids with alcohols.

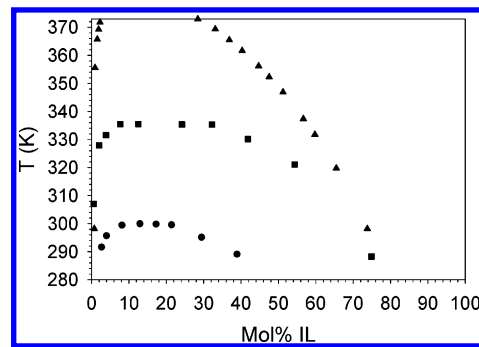


Figure 9. T - x diagram for [bmim][Tf₂N] (●) and [bmim][BF₄] (■) with 1-butanol. Comparison is made with data for the 1-butanol/[bmim]-[PF₆] system (▲) from Wu et al.¹⁰

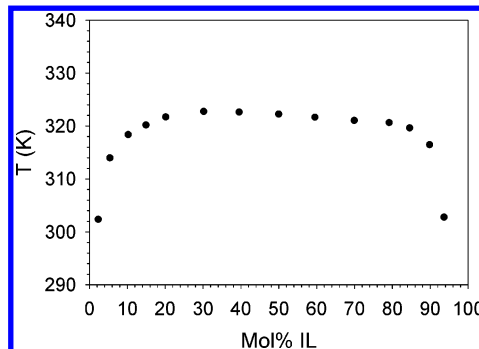


Figure 10. T - x diagram for [bmim][triflate] (●) with 1-dodecanol.

Other anions investigated include [triflate] and [dca]. [bmim]-[triflate] and [bmim][dca] are both totally miscible with 1-butanol at room temperature. In fact, [bmim][triflate] is completely miscible with 1-hexanol and 1-octanol at room temperature (295 K), as well. The shortest alcohol we tested for which we observed a phase split with [bmim][triflate] was 1-dodecanol, and this cloud point curve is shown in Figure 10. [bmim][dca] is completely miscible at room temperature with all alcohols we tested, including 1-dodecanol. Thus, changing the anion is the easiest way to adjust the liquid–liquid equilibrium with alcohols. The relative alcohol affinity of the various anions is dca > triflate > Tf₂N > BF₄ > PF₆. This trend is the same as observed by Cammarata et al. in terms of the strength of the hydrogen bonding between the anion and water.³² Increasing the hydrogen bond strength between the anion and the alcohol leads to higher mutual solubilities and a lower UCST.

It may be possible to model the phase behavior of ionic liquids with alcohols using any of a variety of excess Gibbs energy models, although that is not the primary goal of this work. One such model that has been proposed previously³⁴ for IL/alcohol systems is a Flory–Huggins-type lattice model. This model predicts that the composition at the UCST (x_c) should be related to the ratio of the IL/alcohol molar volumes (r) by $x_c = 1/(1 + r^{3/2})$. While the composition at the UCST for the dodecanol/[bmim][triflate] system is certainly greater than the others and there is some pattern for a particular ionic liquid with the linear alcohols, this relationship does not hold in general for the full range of systems investigated here. Thus, we conclude that a Flory–Huggins lattice model is insufficient to describe the complex range of specific and nonspecific interactions that are taking place in the IL/alcohol systems.

Ionic Liquid–Water Mutual Solubility. Water can be considered to be the alcohol with the shortest alkyl chain, i.e., where the R group is simply a hydrogen atom. Therefore, we measured the mutual solubilities of several Tf₂N ionic liquids with water at room temperature, and the results are shown in

TABLE 1: IL–Water Mutual Solubilities for Selected Imidazolium-Based Ionic Liquids at Ambient Conditions

IL	H ₂ O in IL phase		IL in H ₂ O phase	
	wt %	mol %	wt %	mol %
[bmim][PF ₆]	2.30 ± 0.3	27	1.96 ± 0.3	0.13
[emim][Tf ₂ N]	2.02 ± 0.3	31	1.71 ± 0.3	0.08
[bmim][Tf ₂ N]	1.58 ± 0.3	27	0.73 ± 0.3	0.032
[emim][Tf ₂ N]	1.50 ± 0.3	26	1.16 ± 0.3	0.052
[pmmim][Tf ₂ N]	1.33 ± 0.3	24	0.75 ± 0.3	0.033

Table 1. We have found that the mutual solubilities of ILs with water do not increase very much with increasing temperature,³⁰ so we report only the room temperature mutual solubility values, rather than full cloud point curves. The solubility of water in [bmim][PF₆] is within the range of reported values (1.2–2.67 wt %)^{4,11,18,26–30} and agrees well with values reported by Fadeev and Meagher (2.12 wt %),⁴ Najdanovic-Visak et al. (2.2 wt %),¹¹ and Anthony et al. (2.3 ± 0.2 wt %).³⁰ For [bmim][Tf₂N], our measurement of the water solubility in the ionic liquid agrees with the value reported by Bonhote et al. (1.4 ± 0.1 wt %),²⁶ but is significantly greater than the value reported by Huddleston et al. (0.328 wt %).²⁸ For [emim][Tf₂N], our value for the solubility of water in the ionic liquid is greater than that reported by Bonhote et al. (1.4 ± 0.1 wt %).²⁶

Unlike the ionic liquid/alcohol systems, the mutual solubility with water for [bmim][PF₆] is greater than for [bmim][Tf₂N]. This is why Tf₂N ionic liquids are sometimes called “hydrophobic”. The reason for the difference in the influence of anion on the phase behavior with water versus alcohols may be due to the fact that Tf₂N has a greater opportunity for van der Waals interactions with the alcohol or water compared to PF₆. With alcohols, these van der Waals interactions are more important than they are with water because of the alkyl chains on the alcohols. Conversely, PF₆ has a greater charge density than Tf₂N because it is smaller, so it can have stronger Coulombic or hydrogen-bonding interactions, which are more important with water than with alcohols. Clearly, phase behavior is the result of several competing interactions in the solution. Similarly, the effect of cation alkyl chain length on the liquid phase behavior for ionic liquid/water systems is also opposite of that observed for ionic liquid/alcohol systems, with the ionic liquid–water mutual solubility decreasing with increasing cation alkyl chain length. This trend has been observed in other ionic liquid systems³⁰ and is expected since there is no alkyl chain in water with which to interact through van der Waals interactions. However, the same trend is observed for C2 substitution of the cation for both water and alcohols, i.e., decreased affinity when the acidic hydrogen is replaced with a methyl group. This trend is also expected since hydrogen bonding between the cation and water is a very important interaction, as it is with alcohols.

Conclusions

Knowledge of the impact of different factors on the liquid phase behavior of ionic liquids with other liquids is useful for developing ionic liquids as designer solvents. From this work, we determined how liquid phase behavior of imidazolium-based ionic liquids with alcohols is affected by characteristics of both the alcohol and ionic liquid. An increase in the alkyl chain length of the alcohol results in an increase in the UCST, since the alcohol becomes more aliphatic and less able to interact with the IL through hydrogen-bonding, dipolar, and Coulombic forces. Increased branching of the alcohol did not affect the UCST but resulted in an increase in the solubility of the alcohol in the ionic-liquid-rich phase, which correlates with increasing

basicity of the alcohols. An increase in the length of one of the alkyl chains on the cation resulted in a decrease in the UCST, likely due to greater dispersion interactions between the alkyl chain on the cation and the chain of the alcohol. The replacement of the most acidic hydrogen on the imidazolium ring (attached to the C2 carbon) with a methyl group causes an increase in the UCST due to a decrease in hydrogen bonding of the alcohol with the cation. The effect of anion on the UCST was observed to be related to the ability of the anion to accept a hydrogen bond. The UCST of the ILs with alcohols decreased with increasing hydrogen bond strength with the following trend observed for alcohol affinity: dca > triflate > Tf₂N > BF₄ > PF₆. The effect of alkyl chain length on the cation and the choice of anion have significantly different effects on the mutual solubilities of ILs with water than with alcohols. This is due to the relative importance of Coulombic and van der Waals interaction with water compared to alcohols.

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Supporting Information Available: List of imidazolium-based ionic liquids investigated and *T*–*x* data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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