

Ionic Fluids Containing Both Strongly and Weakly Interacting Ions of the Same Charge Have Unique Ionic and Chemical Environments as a Function of Ion Concentration

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Liquid multi-ion systems made by combining two or more salts can exhibit charge ordering and interactions not found in the parent salts, leading to new sets of properties. This is investigated herein by examining a liquid comprised of a single cation, 1-ethyl-3-methylimidazolium ($[C_2mim]^+$), and two anions with different properties, acetate ($[OAc]^-$) and bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$). NMR and IR spectroscopy indicate that the electrostatic interactions are quite different

from those in either $[C_2mim][OAc]$ or $[C_2mim][NTf_2]$. This is attributed to the ability of $[OAc]^-$ to form complexes with the $[C_2mim]^+$ ions at greater than 1:1 stoichiometries by drawing $[C_2mim]^+$ ions away from the less basic $[NTf_2]^-$ ions. Solubility studies with molecular solvents (ethyl acetate, water) and pharmaceuticals (ibuprofen, diphenhydramine) show nonlinear trends as a function of ion content, which suggests that solubility can be tuned through changes in the ionic compositions.

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1. Introduction

Over the past 20 years, ionic liquids (ILs, defined as liquids consisting entirely of ions,^[1] commonly with the arbitrary criterion that they melt below 100 °C) have received much attention as interesting new solvents that can offer unique properties often unavailable in traditional molecular solvents.^[2] Depending on the choice of ions, these may include negligible vapor pressure; high chemical, thermal, and electrochemical stabilities; and unique solvation properties. Perhaps even more interest-

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	Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.201402894.

ing is the fact that the physicochemical properties of these "designer solvents"^[3] can be tuned by the independent selection of the cation and anion to obtain the optimal solvent for a specific application.^[4]

One fundamental reason that the properties of ILs deviate from those of molecular solvents is due to their nanoscale ordering. ILs are composed of ions, and hence, experience interionic interactions that yield long-lived associations.^[5] Coulombic interactions (i.e. electrostatic interactions) are considered to be the major source of attraction in ILs, mainly depending on the ion charges, the interionic distances, and the coordination number,^[6] but other interactions, such as van der Waals interactions, dipole–dipole interactions, π – π stacking interactions, and hydrogen bonding, may also be present.^[7] In combination, these interactions are responsible for organized ionic networks and nanostructural segregation in IL media,^[8] whereas delocalization of the charges on the ions can reduce cation-anion interactions and result in less charge ordering and nano-segregation.^[9] Even if not all of the parameters affecting this domain segregation are understood in detail yet,^[10] the degree of charge ordering is mainly governed by the nature of the cation and anion, as well as the length/steric bulkiness of substituents on the ions.[11]

Perhaps because of the tunability and structural complexity already present in binary ILs, relatively little attention has been paid to ILs with three or more ions. Such systems can be prepared easily by combining two or more ILs or by dissolving solid salts in an IL. The combinations of ILs that have been studied so far tend to show near ideal mixing behavior,^[12] this



makes it possible to predict certain properties of these systems, such as density.^[13] Such simple behavior may seem surprising in light of the importance of nanostructuring on the properties of ILs, and indeed other properties, such as spectroscopy and solvating power, often show dramatic, nonlinear changes as a function of composition.^[14] We have advocated considering these combinations as new compounds rather than mixtures [specifically, molten analogues of crystalline double salts or "double salt ionic liquids" (DSILs)] because the new interactions that form between the ions of different ILs upon mixing are ionic bonds; a form of chemical bonding.^[15] Regardless of issues with nomenclature, the ability to predict certain physical properties, while dramatically changing the chemical properties, makes these multi-ion IL systems very useful for all kinds of chemical processes.

We are interested in better understanding how competition between ions of the same charge for the most favorable coun-



Figure 1. Structures of the ions $[C_2mim]^+$, acetate ($[OAc]^-$), and bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$).

terion interactions leads to new chemical environments that might be used for specific separations applications. To study this effect, we have conducted an investigation into the spectroscopic properties (¹H NMR, ¹³C NMR, and FTIR spectroscopy) and solubility of molecular solvents (ethyl acetate and water) in a system composed of 1-ethyl-3-methylimidazolium ([C₂mim]⁺) cations and both acetate ([OAc]⁻) and bis(trifluoromethylsulfonyl)imide ([NTf₂]⁻) anions (Figure 1) in varying concentrations. Notably, due to the great difference in basicity of the two anions, the two-ion "parent" ILs, [C₂mim][OAc] and [C₂mim][NTf₂], have dramatically different solvent properties with Kamlet–Taft β parameters (representing hydrogen-bond basicity) of 1.06 for [C₂mim][OAc] and 0.23 for $[\mathsf{C}_2\mathsf{mim}][\mathsf{NTf}_2].^{[16]}$ The former is totally miscible with water, poorly miscible with EtOAc,^[17] and can dissolve biopolymers, such as cellulose and chitin,^[18] whereas the latter has very low miscibility with water, is totally miscible with EtOAc, and cannot dissolve the biopolymers,^[19] and yet the two ILs are totally miscible with each other. We have also investigated the solubility of two active pharmaceutical ingredients (APIs; ibuprofen and diphenhydramine) to understand how tuning the hydrogen-bond basicity of the DSIL can lead to control over solubility and the separation of industrially relevant compounds, as well as the separation of [C₂mim][OAc] from [C₂mim][NTf₂]. These are in keeping with interest in applying these systems to industrial processes, such as separations, in which recycling of the IL is important.

2. Results and Discussion

[C₂mim][OAc] and [C₂mim][NTf₂] were purchased from lonic Liquids Technologies, Inc. (lolitec Inc., Tuscaloosa, AL) and dried under high vacuum at 60 °C for 48 h (to reduce the water content to 1604.1 and 651.2 ppm, respectively), as described in the Experimental section. The DSILs $[C_2 \text{mim}][OAc]_x[NTf_2]_{(1-x)}$ (in which x is the $[OAc]^-/[C_2 \text{mim}]^+$ molar ratio) were prepared as approximately 6 g samples by mass addition of the corresponding amount of each IL with x=0.10, 0.20, 0.33, 0.50, 0.67, 0.80, and 0.90. After 1 h of magnetic stirring, the samples were dried under high vacuum at 60 °C for 24 h and stored under argon. All of the samples were homogeneous with water contents below 1600 ppm. The density and viscosity of the DSILs were measured, and the results (Figure S1 in the Supporting Information) showed that density decreased with increasing acetate concentration and viscosity increased with increasing [OAc]⁻/[C₂mim]⁺ molar ratio. During the preparation of this manuscript, two reports were published by Stark et al. in which the physical properties and ¹H NMR spectra of the [C₂mim][OAc]_x[NTf₂]_(1-x) system were also described.^[13,14] The density and viscosity data shown in this study are in good agreement with those reported by Stark et al.

2.1. NMR Spectroscopy

¹H NMR chemical shifts in imidazolium ILs reflect interionic interactions and are proportional to the strength of such interactions.^[20] By comparing the magnitude and direction of chemical shifts in the NMR spectra of the DSILs to those of the parent ILs as a function of the molar ratio of the ions (*x*), one can suggest the probable nature, type, and strength of the interionic interactions.^[21] ¹H NMR data for $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ were collected by loading neat samples in capillaries with CDCl₃ as the external lock and were compared with those of $[C_2mim][OAc]$ and $[C_2mim][NTf_2]$. The spectra are shown in Figure S2 in the Supporting Information, and the chemical shifts of the imidazolium ring protons (H-2, H-4, and H-5, see Figure 1 for the numbering scheme) and the $[OAc]^-$ methyl protons as a function of $[OAc]^-/[C_2mim]^+$ molar ratio (*x*) are illustrated in Figure 2.

The results of our ¹H NMR spectroscopy measurements show that all proton signals on the imidazolium ring (H-2, H-4, and H-5) shift downfield with increasing [OAc]⁻/[C₂mim]⁺ molar ratio, whereas the [OAc]⁻ methyl protons shift upfield. The largest shift is associated with the imidazolium H-2 proton (downfield shift $\Delta\delta$ of ca. 2 ppm), and this shift has a nonlinear dependence on acetate concentration. There is a corresponding nonlinear upfield $\Delta\delta$ of the methyl protons in the [OAc]⁻ anions as the [OAc]⁻ concentration increases. On the contrary, $\Delta\delta$ for the H-4 and H-5 proton signals is smaller and more linearly dependent on [OAc]⁻ concentration with a downfield shift of about 1 ppm. Lastly, the rate of change of the H-2 proton chemical shift becomes smaller at a 1:1 ratio of [OAc]⁻/[NTf₂]⁻, before which H-2 shifts downfield at a rate more than three times that of H-4 or H-5, and after which it is approximately as sensitive to the addition of [OAc]⁻ as the C-4 and C-5 protons.



Figure 2. ¹H NMR chemical shifts of A) the imidazolium ring protons (\bullet : H-2, ∇ : H-4, \blacksquare : H-5) and B) [OAc]⁻ methyl protons (\bullet : H-9) in [C₂mim][OAc]_x[NTf₂]_(1-x) (zero on the x axis corresponds to [C₂mim][NTf₂] and 1.0 to [C₂mim][OAc]).



Figure 3. Ion packing environments showing contacts less than the sum of the van der Waals radii. Dashed lines indicate short contacts to imidazolium ring hydrogen and carbon atoms (α -hydrogen atom contacts excluded) with donor–acceptor distances in Å. From top to bottom: [C₂C₂im][OAc] (cation and anion), [C₁mim][NTf₂], [C₂mim][*cis*-NTf₂], and [C₂mim][*trans*-NTf₂] (cations only). Redrawn by using coordinates from Refs. [22–24].

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A comparison of the known crystal structures of small dialkylimidazolium [OAc]⁻ and [NTf₂]⁻ salts (Figure 3) offers insight into the spectroscopic changes observed by NMR spectroscopy. Crystal structures for 1,3-diethylimidazolium acetate ([C₂C₂im] [OAc]),^[22] 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide $([C_1mim][NTf_2])$ ^[23] and [C₂mim][NTf₂] have been reported.^[24] The [C₂mim]⁺ cations (and dialkylimidazolium cations in general) are considered to have five sites for interactions with anions.^[20, 25] The crystal structures of both [NTf₂]⁻ and [OAc]⁻ salts

have a fairly isotropic distribution of anions around the imidazolium cations and interactions that are typical of dialkylimidazolium salts, with anions occupying Coulombic and hydrogenbonding sites (ring and α -hydrogen atoms). However, owing to differences in the basicity of the ions and charge localization, the contacts representative of hydrogen bonds in the $[NTf_2]^-$ salts are much longer than those in $[C_2C_2im][OAc]$, whereas the out-of-plane Coulombic interactions are slightly shorter. The greater strength of the interactions in [C₂C₂im][OAc] also appears to result in overall shorter cationanion contacts, and there are typically more [NTf₂]⁻ anions surrounding each cation than [OAc]⁻ ions, despite the fact that the [NTf₂]⁻ ions are much larger. These structural features suggest that, in addition to differences in interaction strength, there are chemical differences in the nature of the interactions preferred by [NTf₂]⁻ and [OAc]⁻ ions.

In $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$, there will be competition between the anions for the most favorable interaction sites on the cations. Because the $[OAc]^-$ anion is more basic and has higher cohesive energy and stronger ion packing^[26] than that of the charge-diffuse $[NTf_2]^{-},^{[27]}$ stronger hydrogen-bonding and Coulombic interactions are expected between the $[C_2mim]^+$ cation and $[OAc]^{-}.^{[28]}$ As the $[OAc]^-$ concentration increases (i.e. upon going from x=0 to 1.0), each $[C_2mim]^+$ cation can hydrogen bond to or interact with more $[OAc]^$ anions. In any compositional range other than pure $[C_2mim]$ [OAc], the molar ratios of $[C_2mim]^+$ and $[OAc]^-$ are not 1:1, and this preferential interaction of $[C_2mim]^+$ ions with $[OAc]^$ ions should lead to structures that cannot be formed in the neat IL.

The ¹H NMR chemical shifts observed for the H-2, H-4, and H-5 protons (Figure 2 A) are indicative of increased interactions between $[C_2mim]^+$ and $[OAc]^-$ as the abundance of the $[OAc]^-$ increases, in accordance with literature reports that the ¹H NMR chemical shifts for the imidazolium cation generally shift downfield with increasing cation–anion interaction strength.^[29] Nonlinearity observed (Figure 2) for the ¹H NMR spectroscopy signals of the cation H-2 proton and the $[OAc]^-$ anion methyl protons can be attributed to the presence of



both hydrogen-bonding and Coulombic interactions around the acidic C-2 position. In this case, the chemical shift of the H-2 proton is not only affected by directional hydrogen bonding, but also by anion associations in either of the two most favorable Coulombic sites above and below the imidazolium ring.^[30] We believe the greater change in chemical shift for proton H-2 at low $[OAc]^-$ concentrations (x < 0.5) is because [OAc]⁻ ions are initially more likely to occupy sites near C-2 than the hydrogen-bonding sites at C-4 and C-5. This is in accordance with predicted and measured cation-anion pair distribution functions in liquid imidazolium $[\mathsf{OAc}]^{-[31]}$ and $[\mathsf{NTf}_2]^-$ ILs.^[32] The chemical shifts of H-4 and H-5 are not as sensitive to the Coulombic interaction and are likely to be only affected by greater hydrogen bonding with $[OAc]^-$. At x = 0.5, which corresponds to a 1:2 $[OAc]^{-}/[C_2mim]^+$ ratio, the downfield shift in the H-2 proton begins to change at the same rate as the H-4 and H-5 protons. At x=0.5 (1 acetate for every 2 cations), there is one [OAc]⁻ oxygen atom for every C2 position, so any [OAc]⁻ ions added above this concentration are equally likely to hydrogen bond to any of the three ring protons.

The spectroscopic discussion by Stark et al. also noted the nonideality of the spectra (the difference between the NMR chemical shifts of each DSIL versus the linear weighted average).^[13,14] The authors concluded that based on large deviations for the C-2 hydrogen atom $[C_2mim]^+$ cations preferentially interacted with $[OAc]^-$ due to hydrogen bonding. This was also in agreement with their previous findings that weakly basic ILs, such as $[C_2mim][NTf_2]$, prevent biomass dissolution on $[C_2mim][OAc]$ by tying up the basic anions.^[33]

The ¹³C NMR spectra (Figure S3 in the Supporting Information) provide additional support for the interactions discussed above. The chemical shifts of the imidazolium ring carbon atoms (C-2, C-4, and C-5) move downfield for all three carbon atoms with increasing $[OAc]^{-}/[C_2mim]^+$ molar ratios (Figure 4). It has been shown through a combination of ¹³C NMR and Xray photoelectron spectroscopy (a more direct measurement of electron density) that an increase in electron density on the carbon atoms due to stronger interactions with more basic anions is correlated with a downfield shift of imidazolium



Figure 4. ¹³C NMR chemical shifts of the imidazolium ring carbon atoms (\odot : C-2, \bigtriangledown : C-4, \Box : C-5) in [C₂mim][OAc]_x[NTf₂]_(1-x) (zero on the *x* axis corresponds to [C₂mim][NTf₂] and 1.0 to [C₂mim][OAc]).

¹³C NMR signals, although the authors did acknowledge that this was the opposite of what was expected.^[21] In agreement with the ¹H NMR spectroscopy trends noted above, the chemical shift of C-2 changes more dramatically (with a slope of ca. 5) up to x=0.5 (1 acetate for every 2 cations, or as noted above, 1 oxygen atom per cation) than the modest shift observed for the C-4 and C-5 carbon atoms. From x=0.5 to 1.0, the downfield shift of the signals for all three carbon atoms is approximately the same. Because the carbon atoms on the [OAc]⁻ ion are farther away from the interaction site, their ¹³C chemical shifts are less sensitive to cation–anion interactions and thus have been omitted from the discussion.

Taken together the NMR spectroscopy data, the preferential interaction of [OAc]⁻ around the C-2 position of the imidazolium ring is suggested, with the in-plane hydrogen-bonding interactions of secondary importance, yet still guite strong. This is based on the observation of high- and low-sensitivity regimes for the chemical shift of the C-2 proton as a function of $[C_2 \text{mim}]^+/[OAc]^-$ ratio with a transition from high to low sensitivity at about x=0.5, at which point there is one $[OAc]^{-1}$ oxygen atom available for every cation. At x = 0.5, each cation could conceivably have one strong Coulombic interaction with an [OAc]⁻ anion, for example, in a sandwich structure with two cations interacting with the oxygen atoms of a single [OAc]⁻ anion. Interestingly, in the crystal structures previously discussed, only one strong Coulombic interaction is observed per cation. This is probably because the first interaction polarizes the positive charge in one direction, which weakens any others on the other side of the ring. The [OAc]⁻ ion in crystalline [C₂C₂im][OAc] is only observed to interact Coulombically with one cation because the 1:1 ratio of $[OAc]^-$ to $[C_2C_2im]^+$ requires the neighboring cations to participate in Coulombic interactions with other [OAc]⁻ ions. In [C₂mim][OAc]_{0.50}[NTf₂]_{0.50}, the [OAc]⁻ ion appears to "steal" cations from the weakly coordinating [NTf₂]⁻ ion, leading to ion clusters that are probably absent in the neat IL.

2.2. Infrared Spectroscopy

The DSILs of $[C_2 \text{mim}][OAc]_x[NTf_2]_{(1-x)}$ were further analyzed by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to better understand the effects of composition changes on the anions. While the ¹H NMR signal of $[OAc]^-$ is only weakly affected by intermolecular contacts, the frequencies of the symmetric and asymmetric stretching modes of acetate ions are quite sensitive to their environment. For metal acetate salts, the asymmetric and symmetric stretching modes of $[OAc]^-$ are reported to occur between $\tilde{\nu} = 1500$ – 1550 and 1340–1360 cm⁻¹.^[34] When protonated, these bands split further into the C=O and C–O stretching modes of acetic acid at $\tilde{\nu} = 1712$ and 1280 cm⁻¹, respectively.^[35]

Because the negatively charged oxygen atoms of $[OAc]^-$ accept hydrogen bonds from the $[C_2mim]^+$ cation, the carbon–oxygen bonds become unequal compared with the symmetric bonds of "free" $[OAc]^-$ ion, and instead approach the inequivalent C–OH and C=O bonds found in acetic acid.

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Therefore, the IR bands most affected by hydrogen bonding will be the C-O and C=O stretches of [OAc]⁻.

The bond inequivalency and associated effects are consequences of the interactions between the [OAc]⁻ oxygen and imidazolium hydrogen atoms, in which the negative oxygen atom pulls the positive hydrogen atom closer to it, causing polarization of the imidazolium C-H bond (and increasing the intensity of C-H stretching) and respective polarization of the acetate C–O bond. The vacant σ^* molecular orbital of the imidazolium C-H bond overlaps with





Figure 5. FTIR spectra of [C₂mim][OAc]_x[NTf₂](1-x) as a function of the [OAc]⁻/[C₂mim]⁺ molar ratio: A) [OAc]⁻ C–O symmetric stretch (from top to bottom: x = 0.0 to 1.0) and B) S=O stretch (from top to bottom: x = 1.0 to 0.0) (zero corresponds to [C₂mim][NTf₂] and 1.0 to [C₂mim][OAc]).

the filled molecular orbital of oxygen (the lone pair). Electron density from the [OAc]⁻ oxygen atom is transferred to the C-H antibonding orbital, which makes the C-H bond weaker and longer, whereas the [OAc]⁻ C–O bond is weakened and lengthened as well (relative to "free" [OAc]-).

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Crystallographic evidence supports that hydrogen bonding affects the [OAc]⁻ C–O bond more than the out-of-plane Coulombic interactions. In the crystal structure of [C₂C₂im][OAc]^[22] (Figure 3), the [OAc]⁻ oxygen atoms that interact with C-2 through hydrogen bonding in-plane and through Coulombic interactions out-of-plane are symmetry inequivalent. The hydrogen-bonded C-2--O distance of 3.025(2) Å is shorter than the out-of-plane C-2-O distance of 3.115(2) Å, which is a possible indicator of the greater degree of covalency in the hydrogen-bonding interaction (C-2-H-O). The [OAc]- C-O bonds are asymmetric-the hydrogen-bonded oxygen has a longer C–O bond (1.258(1) Å) than the other oxygen atom (1.245(2) Å)-which indicates that the hydrogen-bonded oxygen atom has more sp³ character.^[22] Changes in these bonds are most easily detected by IR spectroscopy.

At low [OAc]⁻ concentrations, the [OAc]⁻ ion is less acetic acid-like because there are so many competing cations that the cation-anion interactions are essentially isotropic and do not break the symmetry of the carboxylate. When the [OAc]concentration is higher, [OAc]⁻ has a slightly greater negative charge because it interacts with fewer cations, but it is more dissymmetric. With fewer competing cations, the anion is able to form more directional and more covalent interactions that have the greatest effect on the structure of the [OAc]⁻ ion. This is consistent with the NMR spectroscopy data, which show that cation-anion interactions get stronger as the [OAc]concentration increases, but is also consistent with IR spectroscopy, which says that the acetic acid like character of the [OAc]⁻ ion increases with increasing acetate concentration (again, as a result of the decreasing number of cations per acetate anion).

In $[C_2 mim][OAc]_x[NTf_2]_{(1-x)}$ systems with an increasing $[OAc]^-/$ $[C_2 \text{mim}]^+$ molar ratio, a redshift from $\tilde{\nu} = 1390$ (x=0.1) to 1373 cm⁻¹ (x = 1.0; Figure 5 A) is observed for the C–O symmetric stretch. Unfortunately, the asymmetric stretch of [OAc]- $(\tilde{\nu} \approx 1558 \text{ cm}^{-1} \text{ in } [C_2 \text{mim}][OAc])$ overlaps with imidazolium CH₃(N) and CH₂(N) stretches^[36] at $\tilde{\nu} \approx 1575 \text{ cm}^{-1}$ (Figure S4b in the Supporting Information). Because of interference from the cation (the same interaction that causes a blueshift in the anion band would cause a redshift in the cation band due to increased carbene character^[37]), we do not discuss this stretch in detail.

The S=O stretching mode of the [NTf₂]⁻ anion occurs in a part of the spectrum where the background from [C₂mim][OAc] is relatively flat and can be easily identified at $\tilde{v} = 1131 \text{ cm}^{-1}$, which is in agreement with the published value.^[38] Because the cations should interact preferentially with the [OAc]⁻ anions as the [OAc]⁻ ion concentration increases, the [NTf₂]⁻ ions should interact less and less with the cations as the [OAc]- concentration increases. This is reflected in the IR spectroscopy data shown in Figure 5B for which a blueshift is observed for the symmetric S=O vibration of [NTf₂]⁻ from $\tilde{v} = 1131$ (x = 0.0) to 1136 cm⁻¹ (x = 0.9); this indicates greater double-bond character and less hydrogen bonding as [OAc]⁻ concentration increases. Because the [NTf₂]⁻ anion is charge diffuse and interacts weakly with the cations, even in the absence of competition, the shift observed in the S=O vibration is much smaller than the shift observed for the [OAc]- C-O symmetric stretch.

Overall, the FTIR data supports the conclusions reached from examining the NMR spectroscopy data, which is that the [OAc]⁻ anion outcompetes [NTf₂]⁻ for close contacts with [C₂mim]⁺. The IR spectroscopy data also indicates that, as the number of and strength of interactions changes, the electronic environment of the [OAc]⁻ anion also changes (from less to more acetic acid character as the [OAc]⁻/[C₂mim]⁺ ratio increases). This shows that each $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ represents not only a unique combination of ions, but also one in which the properties are based on the combined, though competitive, Coulombic interactions and hydrogen bonding between each of the two anions with the cation.



2.3. Solubility of Small Molecules as a Probe for Chemical Properties

The spectroscopic data given above confirms that hydrogen bonding plays an important, although not necessarily predominant, role in DSILs with the composition $[C_2 mim][OAc]_x[NTf_2]_{(1-x)}$. Hydrogen bonding should, however, have an even greater role in the solvent properties of these systems. For example, it has been suggested that the differences in the β parameter, which represents hydrogen-bond basicity, are the main reason for differing solubilities in ILs, and that the anion plays the largest role in most cases of solvation.^[16] In the $[C_2 mim][OAc]_x[NTf_2]_{(1-x)}$ systems, the α parameter, which quantifies the hydrogen-bond-donating ability, and the π^* value (based upon changes in aromaticity and various π interactions) will be approximately constant due to the presence of a common cation. The β values of the parent ILs (Table 1), however, are guite different because of the different hydrogen-bond basicities of the anions. It should therefore be possible to finely tune the hydrogen-bond basicity in $[C_2 mim][OAc]_x[NTf_2]_{(1-x)}$ by controlling the $[OAc]^-/[C_2 mim]^+$ molar ratio. Furthermore, if solvation is controlled by aggregates of competing ions rather than fully dissociated ions, the abrupt changes in speciation implied by the spectroscopic study may be manifested as abrupt changes in solubility.



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Figure 6. Solubility of EtOAc (**■**: left axis) and H_2O (**▲**: right axis) in $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ (zero corresponds to $[C_2mim][NTf_2]$ and 1.0 to $[C_2mim][OAc]$).

that of water (Figure 6, \blacktriangle) increased with increasing $[OAc]^{-}/[C_2mim]^+$ molar ratio. The solubility of water increases slowly up to a $[OAc]^{-}/[C_2mim]^+$ ratio of approximately 0.33, after which the solubility increases more quickly, and the EtOAc solubility decreases rapidly until approximately x=0.67 after which the rate of decrease slows.

The solubility of EtOAc in [C₂mim][NTf₂] appears to be controlled by hydrogen-bonding interactions with the cation; EtOAc is a better hydrogen-bond acceptor than [NTf₂]^{-.[41]} As the abundance of the much stronger hydrogen-bond acceptor [OAc]⁻ anion increases, the cation interacts more strongly with this more basic anion and the solubility of EtOAc decreases. The same rationale can be used to understand the increasing solubility of water in [C₂mim][OAc]_x[NTf₂]_(1-x) as the abundance of [OAc]⁻ increases. Water readily solvates

Table 1. Water content and solubility data for [C ₂ mim][OAc], [C ₂ mim][NTf ₂], and [C ₂ mim][OAc] _x [NTf ₂] _(1-x) .							
$[C_2 mim][OAc]_x[NTf_2]_{(1-x)}$	Water content [ppm]	Solubility [mol solute per mol IL or DSIL] EtOAc H ₂ O Ibuprofen Diphenhydramine					
[C ₂ mim][NTf ₂]	651.2	M ^[a]	0.45 ± 0	0.03 ± 0.01	2.07 ± 0.07		
$(\alpha = 0.63, \beta = 0.23, \pi^* = 1.00^{(16)})$							
[C ₂ mim][OAc] _{0.10} [NTf ₂] _{0.90}	791.0	M ^[a]	0.50 ± 0.03	0.31 ± 0.02	1.75 ± 0.10		
[C ₂ mim][OAc] _{0.20} [NTf ₂] _{0.80}	820.8	10.62 ± 0.05	0.58 ± 0.03	0.55 ± 0.03	1.38 ± 0.06		
[C ₂ mim][OAc] _{0.33} [NTf ₂] _{0.67}	778.4	8.30 ± 0.17	0.82 ± 0.02	0.93 ± 0.02	0.85 ± 0.07		
[C ₂ mim][OAc] _{0.50} [NTf ₂] _{0.50}	829.2	5.44 ± 0.22	1.29 ± 0.04	1.42 ± 0.09	0.42 ± 0.04		
[C ₂ mim][OAc] _{0.67} [NTf ₂] _{0.33}	1246.3	2.52 ± 0.07	1.81 ± 0.02	2.14 ± 0.14	0.21 ± 0.03		
[C ₂ mim][OAc] _{0.80} [NTf ₂] _{0.20}	992.1	1.09 ± 0.09	2.34 ± 0.05	2.42 ± 0.20	0.11 ± 0.02		
[C ₂ mim][OAc] _{0.90} [NTf ₂] _{0.10}	1584.7	0.53 ± 0.11	2.92 ± 0.10	2.99 ± 0.09	0.08 ± 0.02		
[C ₂ mim][OAc]	1604.1	0.25 ± 0.07	M ^[a]	3.86 ± 0.11	0.06 ± 0.02		
$(\alpha = 0.57, \beta = 1.06, \pi^* = 0.97^{[16]})$							
[a] M: Miscible in all proportions.							

2.3.1. Solubility of Ethyl Acetate and Water

To test this hypothesis, the solubilities of both a polar protic solvent (water, polarity index: 9)^[39] and a polar aprotic solvent (EtOAc, polarity index: 4.4)^[39] were measured at 25 °C in $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ as a function of acetate concentration. Each solute was added dropwise to 1.0 g of each sample until a saturation point was reached (observed visually as a turbid solution). Compositional analysis was performed by means of ¹H NMR spectroscopy, with which the solute/[C₂mim]⁺ molar ratios were calculated through direct integration of appropriate signals.^[40]

Water is completely miscible with $[C_2mim][OAc]$, and EtOAc is completely miscible with $[C_2mim][NTf_2]$. As expected, the solubility of EtOAc in $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ (Figure 6, \blacksquare) decreased with increasing $[OAc]^-/[C_2mim]^+$ molar ratio, whereas

whereas the hydrophobic nature of the weak hydrogen-bond acceptor $[\rm NTf_2]^-$ reduces water solubility. $^{[42]}$

both $[C_2 mim]^+$

and [OAc]⁻,

Although more study is needed, the solubility data is suggestive of a break in the solubility trends at about x=0.33 for increasing water solubility (at which point there is 1 [OAc]⁻ anion for every 3 [C₂mim]⁺ cations) and about x=0.67 for decreasing EtOAc solubility (at which point there are 2 [OAc]⁻ anions for every 3 [C₂mim]⁺ cations). Preferential interactions of the ions could affect the solubilities of water and EtOAc because water would prefer to interact through hydrogen bonding to the [OAc]⁻ anion^[43] and EtOAc would prefer to interact by accepting hydrogen-bond interactions from the [C₂mim]⁺ cations.

In a recent study, García et al. reported the liquid-liquid extraction of toluene from heptane by using mixtures of



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1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4-C₁C₄py][NTf₂]) and 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate $([C_2mim][CH_2F_2CF_2SO_3]),$ namely, $[C_2 mim]_x [4-C_1 C_4 py]_{(1-x)} [CH_2 F_2 CF_2 SO_3]_x [NTf_2]_{(1-x)}$ at 40 °C pressure.^[44] and atmospheric Although chemical no provided explanation was in this study, [C₂mim]_{0.70}[4-C₁C₄py]_{0.30}[CH₂F₂CF₂SO₃]_{0.70}[NTf₂]_{0.30} provided efficient extraction of toluene from heptane with a higher separation factor relative to those of sulfalone or $[4-C_1C_4py][NTf_2]$. This example and our current study indicate the possibility that DSILs can provide systems with unique and tunable solubilities that might find use in many new separation techniques.

2.3.2. Solubility of APIs

To apply the tunability of solvation in $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ towards a problem with industrial relevance, the solubilities of two APIs, ibuprofen free acid, which is a good hydrogen-bond donor, and diphenhydramine free base, which is a good hydrogen-bond acceptor, were determined. Each of the prepared $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ liquids were saturated with the desired API at 25 °C through weight addition and constant stirring. Concentrations of each API in $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ (Figure 7)



Figure 7. Solubility of ibuprofen (\bullet : right axis) and diphenhydramine (\blacktriangle : left axis) in $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ (zero corresponds to $[C_2mim][NTf_2]$ and 1.0 to $[C_2mim][OAc]$). Linear trend lines with boundaries at 0.67 (for ibuprofen) and 0.50 (for diphenhydramine) have been added for visual emphasis.

were then evaluated by UV/Vis spectroscopy based on predetermined calibration curves (Figure S5 in the Supporting Information).

The APIs exhibited similar solubility behavior to that of the molecular solvents (EtOAc and H₂O), with the hydrogen-bond-donating API (ibuprofen) becoming more soluble as the $[OAc]^{-}/[C_2mim]^+$ molar ratio increased and the hydrogen-bond-accepting API (diphenhydramine) becoming more soluble as the $[OAc]^{-}/[C_2mim]^+$ ratio decreased. Again, the solubility changes were not linear as a function of $[OAc]^{-}$ concentration. Breaks in the solubility changes were not as pronounced

as those with H₂O and EtOAc, but did appear to occur near specific molar ratios (3 [C₂mim]⁺ cations per 2 [OAc]⁻ anions for ibuprofen and 2 [C₂mim]⁺ cations per [OAc]⁻ anion for diphenhydramine). The solubilities of both molecular solvents and APIs in [C₂mim][OAc]_x[NTf₂]_(1-x) complement the spectroscopic data; this suggests that the solvent properties of [C₂mim][OAc]_x[NTf₂]_(1-x) can be finely tuned by controlling the abundance of unique interactions (i.e. Coulombic interactions and hydrogen bonding) between the ions in this system.

2.4. Separation of [C₂mim][OAc] and [C₂mim][NTf₂] from [C₂mim][OAc]_x[NTf₂]_(1-x)

Separation of the ILs would be useful in chemical processes as a way to recycle them. Above their saturation limits in a given $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$, water and EtOAc will form separate (lighter) phases. Given the different solubilities of $[C_2mim][OAc]$ and $[C_2mim][NTf_2]$ in these solvents, we hypothesized that $[C_2mim][OAc]$ and $[C_2mim][NTf_2]$ could be separated from $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ through solvent extraction. To test this, equal masses of $[C_2mim][OAc]_{0.50}[NTf_2]_{0.50}$ and water were mixed together, and the separation procedure outlined in the Experimental Section was followed. The recovered ILs from the top and bottom phases were analyzed by NMR spectroscopy to identify the compositions.

¹H NMR spectroscopy analysis of the bottom phase (Figure S6 in the Supporting Information) indicated that this phase was [C₂mim][NTf₂], and no [OAc]⁻ protons were detected (the small signal at $\delta = 1.56$ ppm was attributed to the presence of water in CDCl₃). After removal of water, the upper phase was identified as [C₂mim][OAc] with no detectable [C₂mim][NTf₂] present, as indicated by signal integrations of the imidazolium ring protons and [OAc]⁻ methyl protons (Figure S7 in the Supporting Information). To increase our detection limits, the concentration of [NTf₂]⁻ in recovered [C₂mim][OAc] was determined by ¹⁹F NMR spectroscopy (Figure S8 in the Supporting Information) by using trifluoroacetic acid (TFA) as an internal standard. Based on signal integrations, the concentration of [NTf₂]⁻ anion in recovered [C₂mim][OAc] was 0.5 mol%.

We also tried to separate $[C_2mim][OAc]$ and $[C_2mim][NTf_2]$ from $[C_2mim][OAc]_{0.50}[NTf_2]_{0.50}$ by extraction with EtOAc through a similar procedure, as described in the Experimental Section. The results (Figure S9 in the Supporting Information) showed that the molar ratio of $[C_2mim][OAc]$ to $[C_2mim][NTf_2]$ in the ILs recovered from the top EtOAc phase was 0.47:0.53, which made this a rather inefficient way to separate the two-ion ILs from $[C_2mim][OAc]_{1-x}$.

3. Conclusions

The physical properties of multi-ion fluids (e.g. IL mixtures, high ionicity ILs, DSILs, etc.) have been the focus of most recent studies of such systems, whereas their chemical properties, which are important in the applications of these systems, have received much less attention. Herein, DSILs containing three ions, one common $[C_2mim]^+$ cation and two anions $([OAc]^-$ and $[NTf_2]^-$), with different properties, particularly hy-



drogen-bond basicity, were used as an example to investigate the specific interactions between the ions and the solvent properties accompanying these interactions. Spectroscopic data revealed that the interionic interactions varied based on the abundance of charge-localized $[OAc]^-$ anions and $[C_2mim]^+$ cations. Spectroscopy also gave evidence for single acetate ions forming strong interactions with multiple imidazolium cations, a situation that arose from the presence of both Coulombic interactions and hydrogen bonding, and which could not be achieved in the 1:1 salt. Unique interactions between the ions led to nonlinear, tunable solubilities of ethyl acetate, water, and two pharmaceuticals as a function of ionic composition. Thus, the chemical properties of DSILs could be finely tuned by changing the ion composition in the system.

This study suggested that unique and tunable solvent property sets were available that were derived and controlled by the properties and concentrations of the ions present. Not only were the properties of the DSIL tunable, but evidence was found for nanoscale structuring that would have been impossible in the parent ILs. Although further studies are necessary to fully understand ion-ion specific interactions and favorable solvation behavior, this work shows that the ion interactions with solutes in specific DSILs can be controlled by careful choice of the chemical nature and abundance of each ion. The fine- and coarse-scale tunability of the chemical properties of multi-ion liquids thus offer opportunities for expanding the range of IL solvents, particularly in the area of separations, and an appreciation of the differences between DSILs and their parent salts may yet lead to the development of DSILs with truly divergent properties.

Experimental Section

Chemicals

The ILs [C₂mim][NTf₂] and [C₂mim][OAc] were purchased from lonic Liquids Technologies Inc. (Tuscaloosa, AL). CDCl₃ was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Sodium ibuprofen, diphenhydramine hydrochloride, and TFA (with a purity of 99%) were obtained from Sigma–Aldrich (Milwaukee, WI). Concentrated hydrochloric acid (36–38%) and sodium hydroxide were supplied by VWR International, LLC (San Dimas, CA). Deionized (DI) water was obtained from a commercial deionizer (Culligan, Northbrook, IL) with a specific resistivity of 16.82 M Ω cm at 25 °C. All other solvents and reagents, such as EtOAc and ethanol, were obtained from Sigma–Aldrich (St. Louis, MO) and used as received.

Preparation of [C₂mim][OAc]_x[NTf₂]_(1-x)

Before mixing, the ILs were individually dried to minimize the water content. Water was easily removed from $[C_2mim][NTf_2]$ by placing it under high vacuum for 48 h at 60 °C with magnetic stirring. To dry $[C_2mim][OAc]$, additional measures were needed, and this IL was dried through a series of toluene-based azeotropic distillations under high vacuum at 60 °C with magnetic stirring in a modified Schlenk flask. Any trace solvent was finally removed by placing $[C_2mim][OAc]$ under high vacuum for 48 h. The water content was measured by the Karl-Fischer method, and found to be 1604.1 ppm for $[C_2mim][OAc]$ and 651.2 ppm for $[C_2mim][NTf_2]$

after drying. Water content measurements were made once per sample and were found to be in reasonable agreement with those of $[C_2mim][NTf_2]$ and $[C_2mim][OAc]$ used in analytical studies.^[45]

 $[C_2mim][OAC]_x[NTf_2]_{(1-x)}$ (in which x is the $[OAC]^-/[C_2mim]^+$ molar ratio) were prepared as about 6 g samples through mass addition of the corresponding amount of each IL with x=0.10, 0.20, 0.33, 0.50, 0.67, 0.80, and 0.90. Each system was stirred thoroughly for 1 h, then dried under high vacuum at 60 °C for 24 h, and stored under argon. All samples were found to be homogeneous.

Synthesis of Ibuprofen and Diphenhydramine

Sodium ibuprofen (15 mmol) was dissolved in DI water (15 mL), then a 2 m solution of HCI (7.5 mL, 15 mmol HCI) was added dropwise to the solution. The mixture was stirred at room temperature for 2 h. The precipitated solid ibuprofen was isolated by filtration, washed with DI water twice, and dried in an oven (Precision Econotherm Laboratory Oven, Natick, MA) at 65 °C for 48 h. ¹H NMR (500 MHz, CDCl₃): δ =7.25 (d, 2H), 7.13 (d, 2H), 3.73 (q, 1H), 2.46 (d, 2H), 1.87 (m, 1H), 1.52 (d, 3H), 0.91 ppm (d, 6H).

Diphenhydramine hydrochloride ([DPH][Cl], 20 mmol) was dissolved in DI water (20 mL) and sodium hydroxide (20 mmol) was dissolved in DI water (10 mL). The solution of NaOH was added dropwise to the solution of diphenhydramine hydrochloride. The mixture was stirred at room temperature for 2 h. Water in the solution was then evaporated by using a rotary evaporator, and acetonitrile (20 mL) was added to precipitate NaCl and any starting materials that might have remained. Acetonitrile was then removed by using a rotary evaporator, and the solution was washed with more acetonitrile (20 mL), following by removal of the organic solvent. The product was a light yellow liquid that was dried under high vacuum at 50 °C for 24 h. ¹H NMR (500 MHz, CDCl₃ external): δ =7.16 (d, 4H), 6.96 (t, 4H), 6.85 (t, 2H), 5.11 (s, 1H), 3.31 (t, 2H), 2.31 (t, 2H), 1.92 ppm (s, 6H).

Solubilities of EtOAc and H₂O

The solubilities of EtOAc and H₂O in [C₂mim][OAc]_x[NTf₂]_(1-x) were determined by adding EtOAc or H₂O dropwise to each sample (1.0 g) until the solution just became turbid. These saturated solutions were analyzed by ¹H NMR spectroscopy, and the solute/ [C₂mim]⁺ molar ratios were calculated through direct integration of appropriate signals.^[40] Solubilities of the solutes in each DSIL were measured twice, and results were reported as the average values with error bars.

Solubility of Ibuprofen

A calibration curve for ibuprofen was obtained by analyzing five different solutions of known concentrations of ibuprofen. For that, ibuprofen was weighed, transferred to a 25 mL volumetric flask, dissolved in ethanol, and diluted to the correct volume with ethanol to obtain stock solutions. Then various dilutions were made by the addition of fresh ethanol. Selected dilutions, with concentrations from 0.1×10^{-3} to 3.0×10^{-3} mol L⁻¹, were scanned by UV/Vis spectroscopy and the absorbance at $\lambda = 263$ nm was selected for analysis. The data for absorbance versus ibuprofen concentration were treated by linear least-squares regression to obtain a coefficient of correlation (R^2) of 0.99918, with the resultant equation Abs = 0.00355 + 0.30603[C] (Figure S5, left, in the Supporting Information).



The solubility of ibuprofen was tested by loading ibuprofen (0.05 g) into a vial loaded with $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ (0.5 g) and stirring. If all added ibuprofen was dissolved, an additional amount was added until no more could dissolve and the solvent was saturated. The solution was then separated from the particulate matter by using a polytetrafluoroethylene (PTFE) syringe filter with pore size of 0.45 µm, and the concentration of ibuprofen was analyzed by UV/Vis spectroscopy [Cary 3C UV/Vis spectrophotometer (Varian Instruments, Palo Alto, CA) by using fused quartz cuvettes with a 1 cm path length] based on the absorbance at $\lambda = 263$ nm and the predetermined calibration curve.

To prepare samples for UV analysis, each of the saturated solutions (0.01–0.02 g) were loaded into a 25 mL volumetric flask and diluted with ethanol to the correct volume. To eliminate the effect of the presence of ions on the absorbance, UV/Vis spectra of solutions of $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ in ethanol were recorded for baseline correction. An amount of $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$ corresponding to the amount present in the saturated solutions of ibuprofen was dissolved in ethanol to a total volume of 25 mL, and the baseline absorbance at $\lambda = 263$ nm was subtracted from the absorbance of the unknown.

Solubility of Diphenhydramine

A calibration curve for diphenhydramine was obtained by analyzing five different solutions of known concentrations of diphenhydramine. Diphenhydramine was weighed in a 25 mL volumetric flask, dissolved in ethanol, and diluted to the correct volume with ethanol to obtain a stock solution. Then various dilutions were made by the addition of fresh ethanol. Selected dilutions, with concentrations from 0.1×10^{-3} to 2.5×10^{-3} mol L⁻¹, were scanned by UV/Vis spectroscopy and the absorbance at $\lambda = 258$ nm was selected for analysis. The data for absorbance versus diphenhydramine concentration were treated by linear least-squares regression to obtain a coefficient of correlation (R^2) of 0.99981, with the resultant equation Abs = 0.00151 + 0.43233[C] (Figure S5, right, in the Supporting Information).

The solubility of diphenhydramine was tested by adding neat diphenhydramine dropwise into a vial loaded with $[C_2mim][OAC]_x[NTf_2]_{(1-x)}$ (0.5 g) until the solution became turbid. The concentration of diphenhydramine in the saturated solution was analyzed by UV/Vis spectroscopy based on the absorbance at $\lambda = 258$ nm and the predetermined calibration curve. The same method as that described above for ibuprofen was used to eliminate the influence of the presence of ions on the UV absorbance.

Separation of $[C_2mim][OAc]$ and $[C_2mim][NTf_2]$ from $[C_2mim][OAc]_x[NTf_2]_{(1-x)}$

 H_2O (2.0 g) was added to $[C_2mim][OAc]_{0.50}[NTf_2]_{0.50}$ (2.0 g). The mixture was stirred at room temperature for 2 h, and then was allowed to stand for 1 h to equilibrate. A biphasic system was formed, and the top and bottom layers were separated by using a pipette. To extract all $[C_2mim][OAc]$ from $[C_2mim][OAc]_{0.50}[NTf_2]_{0.50}$, the bottom phase was further washed with water twice more, following the procedure described above. The aqueous solutions were combined, and water was evaporated by using a rotary evaporator followed by drying under high vacuum at 60 °C for 8 h. The bottom layer was also dried under high vacuum at 60 °C for 8 h. The ILs recovered from the top and bottom phases were analyzed by ¹H NMR spectroscopy. The concentration of $[NTf_2]^-$ in recovered $[C_2mim][OAc]$ was determined by ¹⁹F NMR spectroscopy by using TFA as an internal standard compound. A stock solution of TFA in [C₂mim][OAc], with a concentration of 0.66×10^{-3} molmol⁻¹ [C₂mim][OAc], was prepared, and equal volumes of the solution of TFA/[C₂mim][OAc] and recovered [C₂mim][OAc] were mixed, and then used for ¹⁹F NMR spectroscopy analysis to determine the [NTf₂]⁻ concentration.

A similar procedure was used to attempt the extraction of $[C_2mim][NTf_2]$ from $[C_2mim][OAc]_{0.50}[NTf_2]_{0.50}$ with EtOAc. Briefly, $[C_2mim][OAc]_{0.50}[NTf_2]_{0.50}$ and EtOAc, with molar ratio of 1:10 (determined by the solubility data), were mixed together and stirred at room temperature for 2 h. The resulting mixture was then allowed to stand for 1 h to equilibrate, after which a biphasic system was observed and the two phases were separated using a pipette. The lower phase was further extracted with EtOAc twice more using the same procedure. The top EtOAc layers were combined and the solvent was evaporated using a rotary evaporator, followed by drying under high vacuum at 60 °C for 8 h. The bottom layer was also dried under high vacuum at 60 °C for 8 h.

Characterization

Density and viscosity: Density measurements of the DSILs were taken by using an Anton-Paar DMA 500 density meter (Ashland, Virginia, USA) at 30 °C (\pm 0.1 °C) with a repeatability of 0.0002 g cm⁻³. The viscosity of the DSILs was measured by using a Cambridge Viscosity viscometer, VISCOlab 3000 (Medford, MA). Approximately 1 mL of sample was placed in the sample chamber. The correct-sized piston corresponding to the expected viscosity range was added and the measurement was taken at 40 °C.

NMR spectroscopy: NMR spectra were taken by utilizing a Bruker Avance NMR spectrometer (Karlsruhe, Germany) at 500 MHz for ¹H NMR spectroscopy and 125 MHz for ¹³C NMR spectroscopy. Each sample, except for ibuprofen, was loaded solventless in a flamesealed capillary, and the spectra were collected at 25 °C by using CDCl₃ as the external lock. Ibuprofen, a solid at 25 °C, was dissolved in CDCl₃ for analysis. The ¹⁹F NMR spectrum of recovered [C₂mim][OAc] was obtained on a Bruker Avance 360 MHz NMR spectrometer (Karlsruhe, Germany) by using TFA as an internal standard and CDCl₃ as the external lock.

IR spectroscopy: IR spectroscopic measurements were taken on neat samples by utilizing a Bruker Alpha ATR-FTIR spectrometer (Billerica, MA), which allowed direct observation of the liquids. Spectra were obtained in the range of $\nu_{\rm max}$ =400-4000 cm⁻¹.

UV/Vis spectroscopy: Solubilities of ibuprofen and diphenhydramine were determined by dissolving certain amounts of solutions of ibuprofen or diphenhydramine/DSIL in ethanol and analyzing them with a Cary 3C UV/Vis spectrophotometer (Varian Instruments, Palo Alto, CA).

Acknowledgements

We thank the Novartis-Massachusetts Institute of Technology (MIT) Center for Continuous Manufacturing (CCM) for financial support.

Keywords: concentration effects · ionic liquids · IR spectroscopy · NMR spectroscopy · solvent effects

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Received: December 18, 2014 Published online on ■■ ■, 2015

ARTICLES

Testing the waters (or salts): lonic environments, and thus chemical properties, of multi-ion fluids can be tuned by changing the ion types and concentrations. NMR and IR spectroscopy are used to determine the electrostatic interactions in a liquid comprised of a single cation, 1-ethyl-3-methylimidazolium ($[C_2mim]^+$), and two anions with different properties, acetate ($[OAc]^-$) and bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$) (see figure).



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Ionic Fluids Containing Both Strongly and Weakly Interacting Ions of the Same Charge Have Unique Ionic and Chemical Environments as a Function of Ion Concentration