NMR Characterization of Ionicity and Transport Properties for a Series of Diethylmethylamine Based Protic Ionic Liquids

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Supporting Information

ABSTRACT: The ionicity and transport properties of a series of diethylmethylamine (DEMA) based protic ionic liquids (PILs) were characterized, principally utilizing nuclear magnetic resonance (NMR) spectroscopy. PILs were formed via the protonation of DEMA by an array of acids spanning a large range of acidities. A correlation between the $^1$H chemical shift of the exchangeable proton and the acidity of the acid used for the synthesis of the PIL was observed. The gas phase proton affinity of the acid was found to be a better predictor of the extent of proton transfer than the commonly used aqueous $\Delta pK_a$. Pulsed field gradient (PFG) NMR was used to determine the diffusivity of the exchangeable proton in a subset of the PILs. The exchangeable proton diffuses with the acid if the PIL is synthesized with a weak acid, and with the base if a strong acid is used. The ionicity of the PILs was characterized using the Walden analysis and by comparing to the ideal Nernst–Einstein conductivity predicted from the $^1$H PFG-NMR results.

INTRODUCTION

Ionic liquids (ILs) have been the subject of considerable interest due to their diverse applications, particularly as solvents and electrolytes for fuel cell and battery materials. These compounds exhibit unique combinations of properties such as thermal stability well beyond 100 °C, low vapor pressures, high ionic conductivity, and nonflammability, making them ideal for use in fuel cell and battery applications where chemical stability and safety are necessary.

Ionic liquids are typically grouped into two classes: protic and aprotic. Protic ionic liquids (PILs) are the subset that functions through proton transfer from Bronsted acid–base chemistry while inheriting many of the properties of the aprotic class. The proton transfer reaction creates an equilibrium between molecular species, ion pairs, and dissociated ions where incomplete proton transfer leads to neutral species and ion pair aggregates, making it difficult to quantify and define the ionicity of a PIL. The degree of proton transfer has been estimated using aqueous $pK_a$ values of acids and bases and provides an adequate prediction in systems with large $\Delta pK_a$. However, solvents can play a significant role in proton exchange, as shown by the large differences in $pK_a$ values of acids in various media, thus raising concerns about the validity of using aqueous $pK_a$ values for pure PIL systems. In this paper, we discuss the concept of using proton affinities in place of $pK_a$ to estimate the proton transfer behavior of a PIL based on its constituents.

Although a standard method for determining ionicity is not established, the performance of most PILs has been assessed using a Walden plot when conductivity and viscosity are known. Vibrational spectroscopy and thermal techniques offer qualitative insight into the formation of ionic species, intermolecular interactions, and transport characteristics of PIL and its constituents, which can be used to gauge the degree of proton transfer. In contrast, NMR spectroscopy has proven to be particularly useful for its quantitative ability to probe proton environments, providing measurements of chemical shifts and J-coupling to determine the degree of proton transfer. Perhaps more useful is the ability to directly measure the transport behavior of individual ionic species by NMR, where diffusion coefficients can be obtained from various experiments utilizing magnetic field gradients and spin echo pulse sequences. Recent studies on PIL have taken advantage of these experiments to measure the diffusion coefficients of ionic species in PILs and calculate conductivities via the Nernst–Einstein equation, providing another quantitative method for determining ionicity.

In the present work, $^1$H NMR and $^{15}$N NMR are used to probe the behavior and ionicity of several DEMA based PILs and to compare the results to conductivity based measurements. DEMA based PILs have been studied extensively with various acids (anions) for their ability to form low melting point compounds while showing promise as anhydrous proton conducting materials above 100 °C. Acids of varying strength have been chosen to illustrate a range of proton transfer conditions that can be probed experimentally with...
NMR. These measurements correlate well with calculated proton affinities, providing a useful technique for predicting the proton transfer characteristics of PILs.

**EXPERIMENTAL METHODS**

**Materials.** N,N-Diethylmethylaniline (DEMA, 97%), acetic anhydride (Ac₂O, ≥99%), trifluoroacetic acid (TFA, 99%), trifluoroacetic anhydride (TFAA, ≥99%), tetrafluoroboric acid (HBF₄, 48%), and perchloric acid (HClO₄, 70%) were obtained from Fisher Scientific (USA). Calcium hydride (CaH₂, 95%), methanesulfonic acid (MS, ≥99.5%), acetic acid (HAc, 97%), nitric acid (HNO₃, 70%), and sulfuric acid (H₂SO₄, 99%) were obtained from Sigma-Aldrich (USA). Calcium hydride (CaH₂, 95%), methanesulfonic acid (MS, ≥99.5%), acetic acid (HAc, 97%), nitric acid (HNO₃, 70%), and sulfuric acid (H₂SO₄, 99%) were obtained from Sigma-Aldrich (USA). Triflic acid (HOTf, ≥98%) was obtained from Alfa Aesar (USA). Bis(trifluoromethane)sulfonimide (HTFSI, ≥95%) was obtained from Synquest Laboratories (USA). Diethylmethylamine (DEMA) was dried via distillation from CaH₂ prior to use. The resulting dried amine was determined to have less than 40 ppm of water, measured by Karl Fischer titration. The acetic acid was dried by mixing with the appropriate amount of acetic anhydride to render it anhydrous. The same method was used to dry the trifluoroacetic acid using trifluoroacetic anhydride. All other materials were used as received.

**Ionic Liquid Synthesis.** Ionic liquids were synthesized by dropwise addition of each acid to form a 1:1 molar ratio mixture with the base. To limit exposure to water, the reactions were carried out under a nitrogen atmosphere. In an effort to prevent decomposition of any of the materials during the course of the exothermic proton transfer reactions, each synthesis was placed in a dry ice in acetone bath. A typical synthesis was carried out using the following procedure: approximately 5 g of dried DEMA (57.4 mmol) was added to a round-bottom flask under a nitrogen atmosphere. A pressure equalizing addition funnel was filled with 57.4 mmol of the appropriate acid and fitted to the round-bottomed flask containing the base. The flask was submerged in a bath of dry ice and acetone and a magnetic stir plate. The acid was then added dropwise to the base, typically resulting in a white/amber solid, which melted upon reheating to room temperature. Ionic liquids synthesized with weaker acids (acetic acid and trifluoroacetic acid) were transferred directly to a nitrogen atmosphere glovebox. Ionic liquids synthesized with stronger acids were dried in a vacuum oven at 80°C for approximately 2 days with a container of P₂O₅. Upon completion of the drying process, the ionic liquids were transferred to a nitrogen atmosphere glovebox. DEMA-TFSI was synthesized with the same procedure except that the solid HTFSI was placed in the round-bottom flask and DEMA was added dropwise to the acid.

**NMR Spectroscopy.** All NMR studies were carried out on samples that were flame-sealed in 5 mm NMR tubes to prevent air exposure. ¹H NMR spectra were collected using a 400 MHz Varian VNMRs spectrometer equipped with a Varian 5 mm double resonance ¹H−X broadband probe. Data were collected using a recycle delay of 5−10 s, eight scans, and a 45° ¹H pulse with a duration of 5.30 μs. The frequency of the spectrometer was not locked during data acquisition due to the lack of a deuterated solvent. The magnetic field was shimmed manually for each sample to minimize magnetic field inhomogeneities. ¹H spectra were collected at 25 °C for all PILs except DEMA-NO₃, and DEMA-BF₄, which are solids at room temperature. ¹H NMR spectra for these PILs were collected at 50 °C; ¹H chemical shifts for all PILs were found to have a negligible dependence on temperature in this range. All ¹H chemical shifts were externally referenced to the TMS peak of a mixture of 1% TMS in CDCl₃ shortly before the spectra were collected. ¹⁵N NMR spectra of the ionic liquids were collected using a 400 MHz Varian VNMRS spectrometer equipped with a Varian 5 mm double resonance ¹H−X broad band probe operating at a 40.49 MHz resonant frequency. ¹⁵N spectra were collected without ¹H decoupling to allow observation of J₉N coupling when present. Data were collected using a recycle delay of 2 s and averaging 256−1024 transients. All ¹⁵N chemical shifts were indirectly referenced to methyl nitrite by setting the resonance for benzamide to −277.8 ppm shortly before the spectra were collected.

Diffusion coefficients were measured using a pulsed field gradient stimulated echo (PFG-STE) pulse sequence with bipolar gradient pulses. Data were collected on an 800 MHz Varian VNMRs spectrometer equipped with a 5 mm Doty PFG probe operating at proton resonant frequency of 799.85 MHz and a ¹⁹F resonant frequency of 752.5 MHz. Proton spectra were collected with a recycle delay of 5 s, 16 transients, a 90° pulse with a duration of 16.5−18.0 μs, 20−40 ms diffusion delay (Δ), 0.5 ms gradient length (δ), and a maximum gradient strength (g) of approximately 1200 G/cm depending on the diffusivity of the ionic liquid. For the PILs synthesized with fluorinated acids (TFA and OtF³), ¹³C PFG-NMR was used to measure the diffusivity of the anions. The ¹³C spectra were collected with a recycle delay of 3 s, 16 transients, a 90° pulse with a duration of 19.5 μs, 25 ms diffusion delay (Δ), 0.5 ms gradient length (δ), and a maximum gradient strength (g) of approximately 1000 G/cm depending on the diffusivity of the ionic liquid. During each measurement the temperature was regulated at 25 °C.

**Electronic Structure Calculations.** In an attempt to quantify the strength of the acids used in this study, gas phase electronic structure calculations were used to obtain proton affinities. Proton affinity for each acid was calculated using the density functional theory (DFT) B3LYP functional with the 6-31G (d) basis set in Gaussian 09. The structures of the acid, its conjugate base, and a bare proton were geometry optimized prior to executing thermochemistry calculations. A comparison of the proton affinities obtained from ab initio calculations to available literature values is shown in Figure S1 in Supporting Information. The results obtained via electronic structure calculations are all within ±6 kcal/mol of literature values.

**Conductivity Measurements.** Ionic conductivities were determined from complex impedance data from a PAR VMP2 potentiostat (Princeton Applied Research) with a frequency range of 10 Hz to1 MHz. The dip-type conductivity cells for liquid electrolytes were constructed with platinum electrodes sealed in soft glass. Cell constants of about 1 cm⁻² were determined using a standard 0.01 M KCl solution. Approximately 1 mL of solution was used to perform each measurement. Conductivities were measured from 25 to 105 °C with 10 °C steps. Temperatures were controlled using a Yamato Scientific DKN-402 programmable oven. Viscosity for each PIL was determined using a Brookfield DV-E viscometer. Densities were measured using a 1.5 mL volumetric flask and a scale.

**RESULTS AND DISCUSSION**

¹H NMR is a valuable tool in the study of PILs due to its ability to investigate the properties of the transferred proton. A subset of the ¹H NMR spectra collected for the DEMA PILs is shown in Figure 1. The resonances below 4 ppm labeled with “B₁−B₄”
are associated with the diethylmethylamine base (cation). The peaks denoted with "A" are resonances associated with the acid (anion). The peaks labeled with "E" are resonances associated with the exchangeable proton for each ionic liquid and have chemical shifts ranging from approximately 6 to 14 ppm. The exchangeable proton is the hydrogen atom, which has been transferred from the Brønsted acid to the base. The general trend observed in this series of spectra is that as the strength of the acid increases, the chemical shift of the exchangeable proton is shifted upfield (to lower ppm values). The shift of the exchangeable proton has information about how strongly the proton is associated with the base. There is a large difference in chemical shift between the proton associated with an acid (∼10–12 ppm) and associated with the DEMA-H⁺ (3–4 ppm).

Due to the fast exchange of the proton between the acid and the base relative to the time scale of the NMR measurement, a single peak is observed for the exchangeable protons. Furthermore, as the strength of the acid increases, the chemical shift of the exchangeable proton approaches that of the protonated base without any weak base interaction from the shift of the exchangeable proton approaches that of the pure PIL state. However, this does not appear to be the case. In the weakest acid case studied here, an exchangeable proton chemical shift of 14.35 ppm is observed, which is downfield from pure acetic acid (12.2 ppm). This indicates that the hydrogen bond formed between the anion and the protonated base is causing a deshielding of the exchangeable proton.28 The trend of chemical shift of exchangeable proton with acid strength is consistent with a previous study on a smaller set of TEA based PILs.20 A similar trend has been observed by Denisov et al. when recording the ¹H chemical shifts of a series of 1:1 mixtures of acids and pyridine dissolved in CD₃Cl₂.29 A chemical shift maximum was observed at 20.5 ppm for the exchangeable proton of dichloroacetic acid and pyridine (ΔpKₐ = 3.9). This chemical shift indicates the presence of a strong hydrogen bond between the acid and the base. We predict that if weaker acids were included in this set of ionic liquids, a similar result would be observed. A chemical shift maximum was not observed in our system due to DEMA being a stronger base (pKₐ = 10.6) than pyridine (pKₐ = 5.2). This difference in strength of conjugate acids leads to a more complete proton transfer for DEMA than for pyridine, with acids of comparable strength.

The extent of protonation in protic ionic liquids has previously been correlated to the value of ΔpKₐ, which is defined as the difference between the aqueous pKₐ of the protonated base (pKₐ(BH⁺)) and the protonated acid (pKₐ(AH)) as shown in eq 1.11,16

$$\Delta pK_a = pK_a(BH^+) - pK_a(AH) \quad (1)$$

The larger the ΔpKₐ for a PIL, the stronger is the driving force for the proton transfer. The aqueous pKₐ values for superacids are typically obtained by measuring the relative acidity of the molecule of interest with respect to a standard in a nonaqueous solvent and then approximating the solvation effect of water.30 The assumption associated with using ΔpKₐ in this context is that the free energy of solvation by water, from the pure PIL state to the aqueous standard state, is the same for cation and anion components, which is not unreasonable when both anion and cation are large.30 However, this approximation cannot be expected to hold in all cases. Furthermore, there is evidence of solvation energies playing an important role in the relative acidities of a set of superacids.31

A plot correlating the ¹H chemical shift of the exchangeable proton of each ionic liquid with its ΔpKₐ is shown in Figure 2. The overall trend observed is that as the strength of the acid increases, the resonance of the exchangeable proton is shifted upfield (lower ppm values). In general, the ionic liquids with smaller ΔpKₐ values fit the trend more closely, while the ionic

Figure 1. ¹H NMR spectra for DEMA based ionic liquids generated with various acids. The structure and abbreviation for each acid are shown to the right of the corresponding spectrum. The symbols A, B, and E correspond to protons associated with the acid, base, and exchangeable protons, respectively.

Figure 2. Chemical shift of the exchangeable proton for each DEMA based ionic liquid extracted from the ¹H spectra as a function of acid strength. The solid line on this plot is a guide for the eye.
liquids synthesized with superacids seem to have larger deviations from the trend. Furthermore, in the case of the acid HBF₄, the aqueous ΔpKₐ leads to chemical shift that does not match the trend, likely due to the role water plays in its acidity. Most of these issues appear to arise from aqueous superacid pKₐ values having less bearing on the true acidity of these molecules in the context of ionic liquid synthesis.

A way to classify the strengths of acids, which does not rely on their activity in a solvent, is by determining their gas phase proton affinity using electronic structure calculations. Proton affinities were calculated by obtaining the ΔH of the protonation of the anions; this reaction scheme is shown in eq 2:

$$A^- (g) + H^+ (g) \rightarrow AH (g)$$  

(2)

The lower the proton affinity of an anion, the stronger is the associated acid. Similar gas phase ab initio calculation studies have been a focus of recent publications estimating the acidity of superacids. A plot correlating the gas phase proton affinity for each anion and the chemical shift of the exchangeable proton upon reaction with the base DEMA is shown in Figure 3. The stronger acids will have lower proton affinities, resulting in the exchangeable proton forming a stronger bond to the amine of the base. This increased interaction with the lone pair of the nitrogen on the base results in the chemical shift of the exchangeable proton shifting upfield (to lower ppm). The good correlation between the gas phase proton affinity and the chemical shift of the exchangeable proton has also been observed in a set of PILs generated with a base of considerably different basicity, 1,3-dimethyl-2-imidazolidinone (DMI) (see Figure S2). This set of PILs will be the focus of a separate publication from our group; however this observation demonstrates that this correlation is not unique to PILs generated using simple amines as bases.

Details about the extent of proton transfer as a function of acid strength can be elucidated using ¹⁵N NMR. Natural abundance ¹⁵N NMR is possible on neat ionic liquids due to the high concentration of the DEMA cation. A series of ¹⁵N NMR spectra were collected for the set of DEMA based ionic liquids without ¹H decoupling to observe the J₅H coupling, and these spectra are shown in Figure 4. As the acid strength increases, the exchangeable proton is more associated with the nitrogen of the base, resulting in a shift of the ¹⁵N resonance downfield (higher ppm). This shift is consistent with previous studies that measured the ¹⁵N chemical shift of amines as a function of the extent of protonation. Furthermore, when the acid used to generate the PIL is stronger than nitric acid, the J₅H coupling (76 Hz) is clearly observed. In the weak acid case, the exchangeable proton is exchanging faster than the time scale of the ¹⁵N NMR measurement, resulting in the observation of a singlet. In the intermediate case (DEMA-
a peak broadened by exchange is observed, reminiscent of temperature-induced coalescence.\(^3\) The observation of the \(J_{\text{NH}}\) splitting in ionic liquids made with acids stronger than nitric acid implies that the proton exchange in these PILs is slower than the time scale associated with the observed \(J_{\text{NH}}\). Additionally, the observation of a singlet for the ionic liquids synthesized with acids weaker than nitric acid implies that the rate of exchange is faster than the time scale associated with the \(J_{\text{NH}}\). PILs formed with weak proton transfers seem to have properties more similar to molecular liquids, such as an appreciable vapor pressure.\(^8\) The observation of these properties is consistent with the claim that these latter ionic liquids have a low ionicity.

Pulsed field gradient stimulated echo (PFG-STE) NMR can be used to measure the transport properties of ionic liquids and thereby provide information about the extent of proton transfer.\(^9\) This pulse sequence was used instead of the spin echo (SE) pulse sequence\(^10\) because the magnetization during the diffusion delay relaxes according to \(T_1\) instead of \(T_2\), \(T_1\) relaxation is typically slower than \(T_2\) relaxation in liquids, resulting in the PFG-STE sequence having better sensitivity than the PFG-SE version. Furthermore, bipolar gradient pulses were implemented to limit eddy-current effects. Using this technique, it is possible to determine the diffusion coefficient of the cation, anion, and exchangeable proton simultaneously if each is NMR active. To determine the diffusion coefficients, the decrease in area of each peak as a function of gradient strength was fit with the Stejskal–Tanner\(^1,42\) equation:

\[
\ln \left( \frac{S(2\tau)}{S_0} \right) = -Dg^2\gamma^2\delta^2 \left( \Delta - \frac{\delta}{3} \right)
\]

where \(S(2\tau)\) is the attenuated signal, \(S_0\) is the signal with zero gradient strength, \(g\) is the gradient strength, \(\gamma\) is the gyromagnetic ratio, \(\delta\) is the gradient length, and \(\Delta\) is the diffusion delay. An example of a diffusion NMR analysis result is shown in the Stejskal–Tanner plot of Figure 5. The resonances that have a larger diffusion coefficient will have a steeper slope in the plot. On the basis of the similarity of the diffusion coefficients of the anion and the exchangeable proton, they can be considered to be diffusing together. Observation of the exchangeable proton diffusing at a similar rate to the Ac anion indicates that there is a weak proton transfer from the acid to the base in DEMA-Ac and that this ionic liquid has a low ionicity. A summary of the diffusion \(^1\)H NMR results is shown below in Table 1. For the PIL with the strongest acid (DEMA-OTf), the diffusion coefficient of the exchangeable proton closely matches the cation, indicating that this PIL has a high ionicity. For the two moderately ionic PILs, the anion, cation, and exchangeable proton appeared to be diffusing at the same rate. This similarity in diffusion coefficient could indicate that the cation and anion are diffusing as hydrogen bonded ion pairs.

Quantifying the ionicity of protic ionic liquids and establishing trends are important for the prediction of the properties of ionic liquids. To quantify ionicity, results of the diffusion NMR experiments can be used to calculate the ideal Nernst–Einstein conductivity using the following equation:

\[
\Lambda_{\text{NE}} = \frac{N_Ae^2}{kT}(D^+ + D^-)
\]

where \(\Lambda_{\text{NE}}\) is the ionic conductivity predicted via PFG-NMR, \(N_A\) is the Avogadro number, \(e\) is the electronic charge, \(k\) is Boltzmann’s constant, \(T\) is temperature, and \(D^+\) and \(D^-\) are the measured diffusion coefficients of the cation and anion, respectively. The ratio of this ionic conductivity and the experimentally measured ionic conductivity from an impedance experiment is related to the ionicity of the ionic liquid.

Additionally, the deviation from the ideal viscosity limited Walden conductivity (\(\Delta W\)) can be used as a measure of ionicity.\(^\text{8,11,12,15}\) The \(\Delta W\) is calculated by correlating the log of equivalent conductivity with the log of fluidity for an ionic liquid and comparing it to the ideal case for conductivity of 1 M KCl.\(^\text{8,11}\) A plot summarizing the characterization of the ionicity of a subset of the ionic liquids using these two methods is shown in Figure 6. The two different measures of ionicity are in good agreement, as was also found by Miran et al. for the case of a series of acids protonating the superbase 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU). However, the data point for the most ionic IL analyzed (DEMA-OTf) deviates from linearity.

![Figure 5. Example Stejskal–Tanner plot obtained from \(^1\)H PFG-NMR experiments for DEMA-Ac protic ionic liquid using the stimulated echo sequence with bipolar gradients.](image1)

![Figure 6. Summary of the characterization of the ionicity of a subset of the DEMA based ionic liquids studied via the deviation from Walden conductivity (\(\Delta W\)) and the ratio of the measured conductivity through impedance measurements and the predicted conductivity from NMR (\(\Lambda_{\text{exp}}/\Lambda_{\text{NE}}\)).](image2)

<table>
<thead>
<tr>
<th>PIL</th>
<th>(D^+)</th>
<th>(D^-)</th>
<th>(\Lambda_{\text{NE}})</th>
<th>(\Lambda_{\text{exp}})</th>
<th>(\Lambda_{\text{exp}}/\Lambda_{\text{NE}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEMA-Ac</td>
<td>8.46</td>
<td>9.03</td>
<td>13.1</td>
<td>49.5</td>
<td>2.72</td>
</tr>
<tr>
<td>DEMA-TFA</td>
<td>3.90</td>
<td>3.93</td>
<td>3.97</td>
<td>16.0</td>
<td>3.69</td>
</tr>
<tr>
<td>DEMA-MS</td>
<td>2.48</td>
<td>2.46</td>
<td>2.45</td>
<td>10.7</td>
<td>3.55</td>
</tr>
<tr>
<td>DEMA-OTf</td>
<td>1.91</td>
<td>4.40</td>
<td>4.35</td>
<td>12.5</td>
<td>7.69</td>
</tr>
</tbody>
</table>

\(^*\)Diffusion coefficients are shown as \(D \times 10^3\) (m\(^2\)/s), and conductivities are reported in mS/cm.
which indicates a difference between these two methods for determining ionicity as the ionic liquid approaches higher ionicities. The inability of an ionic liquid’s conductivity to approach the ideal Nernst–Einstein conductivity has previously been attributed to the effects from ion-pair diffusion.\(^1^2,\!^43\) PFG-NMR results for the PILs with intermediate proton transfer strengths showed the cation and anion diffusing at approximately the same rate, which supports the presence of ion-pairing (see Table 1). However, for the strong proton transfer case (DEMA-Otf), different diffusion rates were observed for the anion and cation, suggesting that ion pairing is not prominent for this PIL. In cases where ion-pairing is not expected, the deviation from the Nernst–Einstein conductivity can be attributed to interionic friction as described previously for molten salts by Berne and Rice.\(^44\) The effect should be a function of the magnitude of opposing ion fluxes and thus should diminish with decreasing conductivity, as seen in both aqueous solutions and molten salts where it approaches zero in the glassy state.\(^45\)

## CONCLUSIONS
The ionicities of several liquids in a set of DEMA based PILs were characterized using \(^1\)H NMR spectroscopy, electronic structure calculations, and conductivity measurements. The chemical shift of the exchangeable proton for each PIL was observed to have a linear relationship with the gas phase proton affinity of the acid. Consequently, our results show that proton affinity is a better predictor of ionicity than aqueous ΔpK\(_a\) values. Furthermore, diffusion results indicated that the exchangeable proton diffuses primarily with the anion in weakly ionic PILs (DEMA-Ac), while in strongly ionic PILs (DEMA-Otf) it diffuses with the cation. To predict the ionicity of a more general set of ionic liquids, the difference in the proton affinity of the acid and the proton affinity of the base (ΔPA) can be used. Some data collected by our group for a set of DMI based ionic liquids indicate that this is a general trend (see Figure S2).

## ASSOCIATED CONTENT
### Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.6b01203.

Details of the electronic structure calculations (density functional theory level calculations) performed and comparisons to literature values for the proton affinities; the \(^1\)H and \(^15\)N chemical shifts of PILs containing the base 1,3-dimethyl-2-imidazolidinone (DMI), presented as further verification that our trends of proton affinity hold for other PILs (PDF)

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### Notes
The authors declare no competing financial interest.

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