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NMR Determination of the Diffusion Mechanisms in Triethylamine-Based Protic Ionic Liquids

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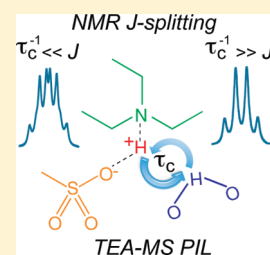
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 Supporting Information

ABSTRACT: Protic ionic liquids (PILs) are highly conductive fluids that have emerged as alternative solvents for electrochemical applications including fuel cells. In the present contribution, the transport properties for a set of triethylamine (TEA)-based PILs were explored with pulsed field gradient stimulated echo (PFG-STE) NMR spectroscopy to obtain the self-diffusion coefficient (D) of the individual molecular species that comprise each system. We report self-diffusion coefficients from measurements conducted in two different laboratories for PILs that were produced by two distinct synthetic routes, a conventional route and a strictly anhydrous route. The PILs of interest are comprised of TEA cations and different anions, methane sulfonate (MS), bis(trifluoromethylsulfonyl)imide (TFSI), tetrachloroaluminate (AlCl_4^-), and bis(perfluoroethylsulfonyl)imide (BETI). In contrast with previous reports, the PFG-STE diffusion measurements presented here show no proton decoupled (Grotthuss mechanism) mobility in these PILs. Additionally, it is shown that the presence of moderate amounts of water (~ 1000 ppm) can have a marked influence on D of the acidic proton.

SECTION: Kinetics, Spectroscopy



Ionic liquids (ILs) have garnered considerable attention as electrolytes, as novel solvents, and as model systems for the study of mass transport.^{1–3} Protic ionic liquids (PILs) are a subset of this group and consist of salts formed by proton transfer between a Brønsted acid and a Brønsted base and are particularly well suited for applications involving the availability of the acidic proton.^{4–11} Much of the utility of these compounds stems from their thermal, chemical, and electrochemical stability, as well as their negligible vapor pressure and high ionic conductivity.^{4,8–12} Additionally, PILs have been shown to be very tunable where viscosity, conductivity, and other physicochemical properties can be adjusted by varying anionic and cationic species.^{2,7,10}

Recently, PILs have emerged as a promising class of nonaqueous proton conductors for proton exchange membrane fuel cells (PEMFCs).^{5,6,11,13–15} Because traditional electrolyte fuel cells rely on hydrated membranes as proton conductors, they only perform well at temperatures below 100 °C, whereas temperatures greater than 120–150 °C are desirable for increased efficiency and reduced catalyst poisoning.¹⁶ PILs, due to their stability and nonvolatility, are capable of operating well in this temperature regime, and some are more conductive than aqueous electrolytes even at room temperature.^{4,15} The origin of the high proton conductivity in PILs is not completely understood however; some pulsed field gradient (PFG) NMR self-diffusion measurements yielded accelerated self-diffusion coefficients (D)

for the acidic proton in comparison to the cation and anion species in some systems.^{6,13,17,18} These results have provided evidence for the presence of decoupled proton mobility (i.e., the Grotthuss mechanism) in these systems analogous to that of water¹⁹ and the current benchmark fuel cell electrolyte, phosphoric acid.²⁰

In this Letter, we examine a set of PILs all based on the triethylammonium (TEA) cation with varying anions. PFG-stimulated echo (STE) NMR techniques are used to determine D of the cation, anion, and acidic proton species. These systems were selected because some PILs in this series were previously shown to exhibit decoupled protonic transport and, thus, evidence for a Grotthuss contribution to proton mobility.^{13,17,18} The PILs were synthesized with two different synthetic routes, a conventional route¹⁰ and an anhydrous route²¹ with predried reagents. The latter synthetic procedure has been shown to produce PILs that are at least an order of magnitude drier than comparative methods and component stoichiometry in excess of 0.1 mol % (see Supporting Information for experimental details).²¹

The self-diffusion coefficients measured with PFG-STE NMR spectroscopy for TEA-based PILs with different anions are reported

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Table 1. Self-Diffusion Coefficients (D) for Neat PILs Measured at 100 °C with PFG-STE NMR^a

PIL	D_{H^+} ($\text{m}^2 \text{s}^{-1}$)	D_{TEA} ($\text{m}^2 \text{s}^{-1}$)	D_{A^-} ($\text{m}^2 \text{s}^{-1}$)	$D_{\text{H}^+}/D_{\text{TEA}}$
TEA-MS ^b (<100 ppm H ₂ O)	1.59×10^{-10}	1.55×10^{-10}	1.60×10^{-10}	1.02
TEA-MS ^c (~1000 ppm H ₂ O)	1.49×10^{-10}	1.24×10^{-10}	1.29×10^{-10}	1.20
TEA-TFSI	2.18×10^{-10}	2.14×10^{-10}	1.71×10^{-10}	1.02
TEA-BETI	1.16×10^{-10}	1.16×10^{-10}	7.97×10^{-11}	1.00
TEA-AlCl ₃	2.3×10^{-10}	2.3×10^{-10}	not measured	1.00

^a The error in the self-diffusion coefficients is <5%. ^b Produced with conventional routes. ^c Produced with anhydrous synthetic routes.

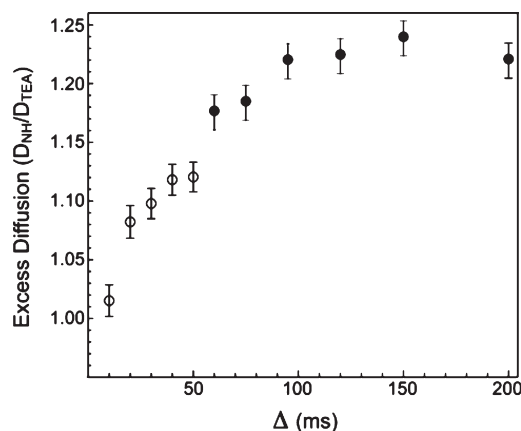


Figure 1. The apparent excess proton diffusion measured for the NH proton compared to that of the TEA cation ($D_{\text{NH}}/D_{\text{TEA}}$) for conventional TEA-MS as a function of the diffusion time (Δ). Measurements conducted with (●) a standard single-axis gradient BBFO double-resonance 5 mm liquid-state NMR probe at 100 °C and (○) a 5 mm DIFF30 water-cooled diffusion NMR probe at 90 °C are shown. The maximum gradient strength was 55 and 1200 G/cm for the standard and high-power gradient NMR probe, respectively. The high-power gradient probe permits D measurements with short Δ .

in Table 1. Because resonances can be resolved for the cation, anion, and acidic proton species in the ^1H and ^{19}F NMR spectrum, the unique D for each component is obtained with this approach. A distinct difference is observed for the diffusion behavior of TEA-MS when comparing the samples produced by the two different synthetic routes. For the other PILs, similar behavior was observed for both synthetic protocols. For TEA-TFSI, TEA-BETI, and TEA-AlCl₃, the D of the acidic proton and TEA cation are equivalent, consistent with proton transfer to the triethylamine and formation of a triethylammonium cation. Further, the anionic species in both TEA-TFSI and TEA-BETI diffuse at slower rates compared to the cation and acidic proton, indicating that the cation and anion do not diffuse as strongly bound ion pairs. A similar difference between cation and anion diffusion rates has been observed for a related set of TEA-based PILs.¹⁸

To further explore the origin of the difference between the TEA-MS samples produced by the two different synthetic procedures, the Δ dependence for the acidic proton compared to the TEA cation ($D_{\text{NH}}/D_{\text{TEA}}$) was measured. Figure 1 shows the Δ dependence of the excess diffusion observed for the acidic proton compared to the TEA cation from PFG-STE NMR measurements for the conventionally synthesized TEA-MS. These measurements were conducted in two different laboratories. In the first set of measurements (●), a standard liquid-state NMR probe was used with typical gradient strengths (0–55 G/cm). The

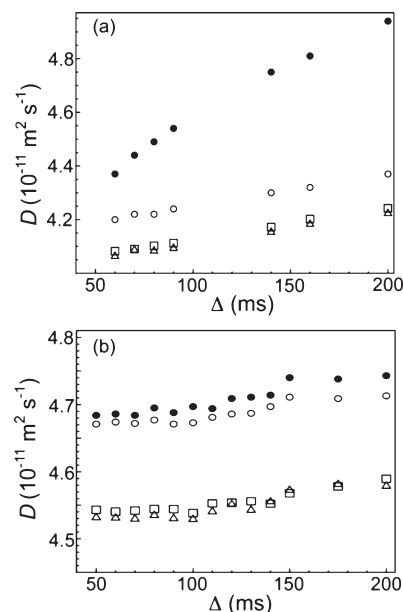


Figure 2. The self-diffusion coefficient D measured with PFG-STE NMR at 60 °C as a function of Δ for TEA-MS produced by the (a) conventional (~1000 ppm water) and (b) anhydrous (<100 ppm water) synthetic routes. The D is reported for the (●) NH proton, (○) CH₃ of the MS anion, (Δ) CH₃, and (□) CH₂ of the TEA cation.

second set of measurements (○) was conducted with a NMR diffusion probe equipped with high-field gradients (0–1200 G/cm). The latter permits the use of very short Δ , down to 10 ms in this case, while retaining a high degree (>95%) of signal attenuation. The apparent excess diffusion for the acidic proton measured with $\Delta \geq 50$ ms is similar to other PFG-STE measurements for this system.¹³ However, a clear Δ dependence is observed here, and $D_{\text{NH}}/D_{\text{TEA}}$ approaches unity when short Δ times are applied. This indicates that the diffusion of the acidic proton is not faster than the TEA cation, and some other mechanism must be contributing to the decay in the diffusion measurement when longer Δ are used. Note, varying Δ on a standard liquid-state NMR probe in a regime where reliable decay is still observed in the diffusion curve ($\Delta \geq 50$ ms) would result in a similar D within reasonable error.

When the acidic proton is probed as a function of temperature, a noticeable difference between D for the acidic proton and the TEA cation occurs at 60 °C. A comparison of the Δ dependence of the various species in the two TEA-MS preparations at 60 °C is shown in Figure 2. For the conventionally synthesized TEA-MS, a strong Δ dependence is observed for the acidic proton with a D that decreases with decreasing Δ similar to the results at 100 °C (Figure 1). The D for the cation (TEA) and anion species (MS) is constant as a function of Δ within error for the conventional

TEA-MS. The Δ dependence differs for the TEA-MS produced by the anhydrous route, where a constant D is observed as a function of Δ for all three species and $D_{\text{NH}}/D_{\text{TEA}}$ is near unity (1.03).

The fundamental difference between the TEA-MS samples synthesized with the two synthetic procedures is the water content. For the conventional route, the water content is ~ 1000 ppm, while

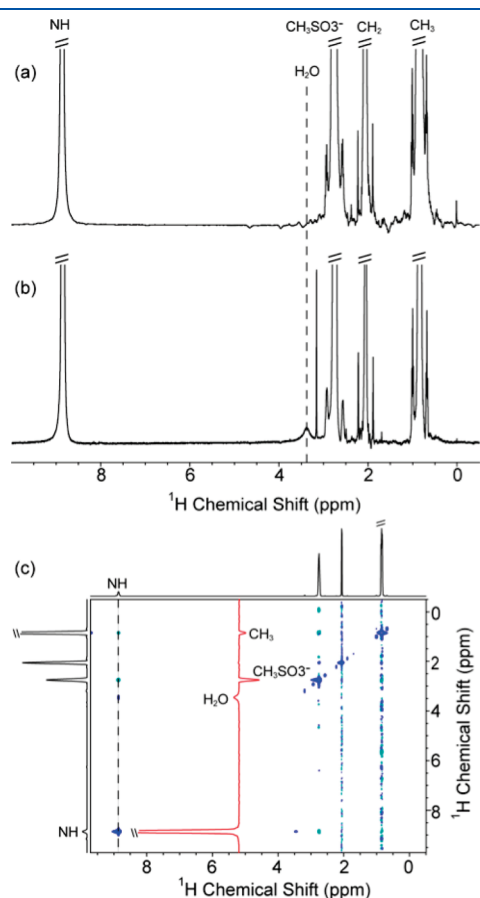


Figure 3. The ^1H NMR spectrum collected at 100°C of TEA-MS produced by the (a) anhydrous (<100 ppm water), (b) conventional synthetic routes (~ 1000 ppm water), and (c) 2D ^1H NOESY spectrum of conventional TEA-MS at 100°C with a mixing time of 200 ms. A slice taken at the NH chemical shift (dotted line) is shown in red.

the anhydrous route has a very low water content, <100 ppm (Table S2, Supporting Information). The presence of water in the conventionally produced sample can be detected in the ^1H NMR spectrum (Figure 3b) compared to the TEA-MS synthesized with the anhydrous approach (Figure 3a). When the ^1H spectra of the two TEA-MS samples are blown up, there is a broad resonance at 3.4 ppm observed in the conventionally produced TEA-MS sample that is not present in the sample synthesized with the anhydrous route. This resonance sharpens and shifts toward the typical shift observed for H_2O (4.8 ppm) when H_2O is added dropwise to this TEA-MS sample, confirming the assignment (data not shown). Further, the integrated ratio of this resonance with respect to the PIL resonances is consistent with the ~ 1000 ppm water content obtained with Karl Fischer titration.

A number of processes can influence the accurate measurement of D with PFG-STE NMR spectroscopy. Contributions from chemical exchange,^{22,23} cross-relaxation effects,^{24–26} and restricted diffusion²⁷ have been shown to impact the diffusion decay curve and, thus, the measured D with these experiments. The latter case of restricted diffusion can be discounted here because restricted diffusion (confinement effects) causes D to decrease with increasing Δ .²⁷ This is the opposite of what is observed in Figures 1 and 2 for the conventionally prepared TEA-MS, where D increases with increasing Δ , indicating that restricted diffusion is not occurring. The PFG-STE NMR radio frequency pulse sequence is analogous to the sequence used to probe cross-relaxation and chemical exchange, nuclear Overhauser enhancement spectroscopy (NOESY), and exchange spectroscopy (EXSY). Therefore, contributions to the diffusion decay curve from cross-relaxation and/or chemical exchange need to be considered.

To probe the effect of chemical exchange and/or cross-relaxation, a two-dimensional (2D) ^1H NOESY spectrum was obtained for the conventionally synthesized TEA-MS sample (see Figure 3c). When a slice is taken at the NH proton resonance (8.9 ppm), NOESY correlations with negative phase are observed to the CH_3SO_3^- group (2.7 ppm) and the CH_3 on the TEA cation (0.9 ppm), and a positive correlation is observed to the broad water resonance (3.4 ppm). The observation of NH correlations to the CH_3SO_3 group (2.7 ppm) and the CH_3 on TEA that have negative phase is consistent with NOE cross-relaxation processes in the fast motion limit, while the strong positive phase correlation to the water resonance indicates a chemical exchange process.²⁸ The effect of cross-relaxation on

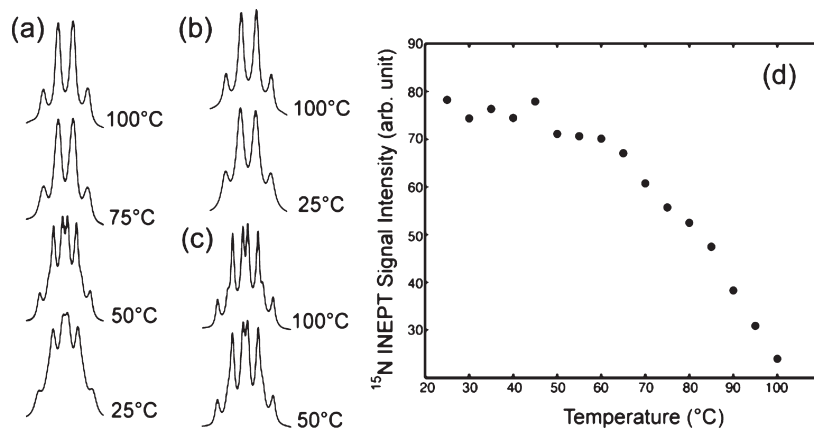


Figure 4. The ^1H NMR J_{HH} -splitting pattern of the TEA CH_2 resonance for (a) conventional TEA-MS, (b) anhydrous TEA-MS, and (c) TEA-BETI. (d) The INEPT ^{15}N NMR signal intensity as a function of temperature for conventional TEA-MS.

the PFG-STE NMR diffusion measurements has been minimized in this study by implementing π pulses sandwiched between the bipolar pulse pairs.^{29,30} The inclusion of these π pulses in the pulse sequence suppresses cross-relaxation effects during the diffusion measurement.^{24,25} This leaves chemical exchange between the acidic proton and water as the process that potentially influences the diffusion measurement.

Evidence for a chemical exchange process involving the acidic proton for the conventional TEA-MS sample can be detected in the J_{HH} -splitting pattern for the CH_2 resonance of the TEA cation (Figure 4a). At higher temperature ($>60^\circ\text{C}$), the J_{HH} -splitting of the TEA CH_2 resonance is split into a quartet by the neighboring CH_3 group ($J_{\text{HH}} = 7\text{ Hz}$), but at lower temperatures ($<60^\circ\text{C}$), the observed splitting pattern becomes a quartet of doublets due to the presence of the acidic proton at the nitrogen with an additional $J_{\text{HH}} = 5\text{ Hz}$. The disappearance of the acidic proton contribution to the J_{HH} -splitting pattern at higher temperature can be attributed to the time scale of the chemical exchange process between the acidic proton and water. If the exchange rate greatly exceeds the J -coupling ($k \gg 2\pi|J_{\text{HH}}|$), the splitting will disappear. In order to further confirm that the changes in the TEA CH_2 splitting pattern were due to variation in the exchange dynamics of the acidic proton, ^{15}N refocused insensitive nuclei enhanced by polarization transfer³¹ (INEPT) NMR spectra were collected as a function of temperature. The signal of the ^{15}N INEPT NMR spectrum decreases considerably as the temperature is raised to 100°C (see Figure 4d). This confirms that there is indeed a change in the dynamics of the acidic proton at the nitrogen of TEA on the J_{NH} -coupling time scale. Note that this J_{NH} -coupling is considerably larger ($J_{\text{NH}} = 78\text{ Hz}$; see Supporting Information) than the J_{HH} -coupling (5 Hz) from the acidic proton, but the INEPT experiment has delays on this J_{NH} time scale. This larger J_{NH} -coupling correlates with a faster exchange time scale ($k = 490\text{ s}^{-1}$, $\tau_c \approx 2\text{ ms}$). This is likely the reason why there is still INEPT signal observed at 100°C in contrast with the J_{HH} -splitting pattern from the acidic proton that completely disappears when the temperature exceeds 60°C .

An estimate of the exchange rate of the acidic proton with water can be made of 31 s^{-1} at a temperature of 60°C (the crossover point) from the 5 Hz J_{HH} -splitting of the TEA CH_2 resonance by the acidic proton. This exchange rate for the acidic proton has a corresponding correlation time (τ_c) shorter than 32 ms. This observed τ_c is less than the typical Δ diffusion time ($\geq 50\text{ ms}$) in the PFG-STE NMR measurement conducted on the standard liquid-state NMR probe (Figure 2). Thus, the acidic proton on TEA undergoes exchange with water during the diffusion experiment if Δ is not kept short ($<32\text{ ms}$), increasing the signal loss due to exchange and producing an overestimate of D for the acidic proton. When Δ can be kept short ($\sim 10\text{ ms}$) by using a high-power gradient diffusion NMR probe, the D of the acidic proton approaches the TEA cation (Figure 1). Therefore, the apparent enhanced acidic proton diffusion in conventional TEA-MS is due to a contribution from chemical exchange.

Interestingly, the J_{HH} -splitting pattern is consistently a quartet as a function of temperature for the anhydrous TEA-MS sample, indicating that the acidic proton is either rapidly exchanging on the J_{HH} -coupling time scale or not bound to the nitrogen (Figure 4b). The latter is actually consistent with what is observed for the D of the different species in anhydrous TEA-MS, where the acidic proton actually diffuses with the MS anion species, as evidenced by their nearly identical D (see Figure 2b). Further, the TEA-BETI exhibits the quartet of doublets J_{HH} -splitting pattern consistent with the

acidic proton bound to the TEA cation. This is also consistent with the D NMR measurements where the acidic proton and the TEA cation diffuse at the same rate (see Table 1).

In conclusion, PFG-STE NMR diffusion measurements were reported for a series of TEA-based PILs. In contrast with previous reports, no evidence for decoupled proton mobility (Grotthuss mechanism) was observed in any of the systems. However, it was shown that the presence of even moderate water contents ($\sim 1000\text{ ppm}$) could influence the diffusion measurement because of a chemical exchange process if the measurement was not conducted with sufficiently short Δ diffusion times leading to the observation of accelerated diffusion for the acidic proton. Additionally, it was shown that considerable insight into the structure and dynamics of PILs can be obtained from the J_{HH} -splitting patterns if care is taken to carefully shim each sample.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental section describing materials, synthetic methods, and NMR techniques; table of anionic species structures and water contents determined by Karl Fischer Titration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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