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Investigation of dynamics in BMIM TFSA ionic liquid through variable temperature and pressure NMR relaxometry and diffusometry

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Abstract

A comprehensive variable temperature, pressure and frequency multinuclear (^1H , ^2H , and ^{19}F) magnetic resonance study was undertaken on selectively deuterated 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (BMIM TFSA) ionic liquid isotopologues. This study builds on our earlier investigation of the effects of increasing alkyl chain length on diffusion and dynamics in imidazolium-based TFSA ionic liquids. Fast field cycling ^1H T_1 data revealed multiple modes of motion. Through calculation of diffusion coefficient (D) values and activation energies, the low- and high-field regimes were assigned to the translational and reorientation dynamics respectively. Variable-pressure ^2H T_1 measurements reveal site-dependent interactions in the cation with strengths in the order $\text{MD}_3 > \text{CD}_3 > \text{CD}_2$, indicating dissimilarities in the electric field gradients along the alkyl chain, with the CD_2 sites having the largest gradient. Additionally, the α saturation effect in T_1 vs. P was observed for all three sites, suggesting significant reduction of the short-range rapid reorientational dynamics. This reduction was also deduced from the variable pressure ^1H T_1 data, which showed an approach to saturation for both the methyl and butyl group terminal methyl sites. Pressure-dependent D measurements show independent motions for both cations and anions, with the cations having greater D values over the entire pressure range.

Keywords

BMIM TFSA; FFC NMR; PGSE; NMR; variable pressure; ionic liquid

Introduction

Ionic liquids (ILs) have found numerous applications as replacements for volatile organic solvents due to their characteristically low vapor pressures, large liquid temperature ranges, good thermal and chemical stabilities, and tunable properties. As a result, these materials

have been applied to many technologies including nuclear waste recycling,^{1–3} textile dyeing,^{4,5} alkylation catalyst reactions,⁶ and as electrolytes in electrochemical devices,^{7–16} such as secondary lithium ion batteries,^{7,17–21} supercapacitors,^{8,9,22,23} and solar cells.^{10,11,24,25} One drawback to the use of ILs as electrolytes is their generally higher viscosity and consequent lower ionic conductivity. Understanding the effects of cation and anion structure on IL viscosity is a major focus of IL physical chemists. For example, it has been shown that using small asymmetrical cations with larger, fluorinated anions can produce low-viscosity ILs^{13,14} and adjusting the length and structure of the functional groups can affect the melting and glass transition temperatures.¹² As a cation, the 1-alkyl-3-methylimidazolium ($C_n\text{MIM}^+$) offers significant charge delocalization over its polar head group, as well as molecular asymmetry in its non-polar alkyl side chains. This prevents crystallization, thereby expanding its liquid phase range.¹⁵ As an anion, bis(trifluoromethylsulfonyl)amide (TFSA, $[\text{CF}_3\text{SO}_2\text{-N-SO}_2\text{CF}_3]^-$) has a low barrier for rotation about the N-S bonds, which results in conformational flexibility that produces ILs with lower viscosity and higher ionic conductivity.^{26,27} When combined with $C_n\text{MIM}^+$ cations, TFSA can yield room temperature ILs with high ionic conductivities.¹⁶

Various techniques have been applied to understanding the structural and transport characteristics of ILs, including molecular dynamics simulations,^{26,28,29} Raman spectroscopy,^{30–32} nuclear magnetic resonance,^{26,27,33–39} AC impedance spectroscopy,^{33,40,41} viscosity,^{33,40,41} and small angle X-ray scattering.⁴² While temperature dependence is a commonly used tool to understand the energetic profiles of physical processes in ILs, pressure dependence can provide unique information on mechanistic and mechanical factors underlying IL physical properties, such as conformational changes in cations and anions, and hydrogen bonding interactions.^{27,30–32,43–48} This is the second in a series of studies aimed at elucidating the characteristic dynamics of $C_n\text{MIM}$ TFSA ILs using NMR techniques. The first study examined dynamical processes in 1-ethyl-3-methylimidazolium (EMIM) TFSA, and pressure-dependent diffusion measurements revealed that conformational exchange of the TFSA anion is important for the TFSA self-diffusion process.²⁷

In the present paper we present a multinuclear (^1H , ^2H , ^{19}F) variable temperature, frequency and pressure study of the spin-lattice relaxation time (T_1) and self-diffusion coefficient (D) of selectively deuterated 1-butyl-3-methylimidazolium (BMIM) TFSA. NMR is one of the most useful tools in the study of ion dynamics because it is non-destructive, nucleus specific, and allows access to motions spanning a range of $\sim 10\text{--}10^{10}$ Hz through determination of spin-lattice relaxation times and self-diffusion coefficients. Whereas the T_1 provides information about motions near the inverse of the resonant frequency, self-diffusion provides access to motions in the 1–100 ms and μm length range. Therefore by measuring both T_1 and D , we are probing short- and long-range dynamics, respectively. Additionally, by determining T_1 as a function of frequency through fast field cycling (FFC) NMR, we can expand the capability of T_1 measurements by determining motions over an expanded frequency range. By using selective deuteration, we can isolate specific dynamics of the cation through ^1H ($I = 1/2$) and ^2H ($I = 1$) probe nuclei. As a probe, ^1H offers dynamics dominated by dipole-dipole interactions (intra- and inter-molecular), a far less indiscriminate interaction. However, the ^2H nucleus is extremely sensitive to rotational dynamics and gives

details about the nuclear quadrupole moment's interaction with its surrounding electric field gradient.

Previous studies have probed ionic liquids at high pressure, including BMIM-TFSA.^{33, 42, 47, 49} However, previous high pressure studies of BMIM-TFSA have only gone as high as 40 MPa at room temperature. Here we observe these ILs at pressures up to 250 MPa. Additionally, we present FFC ¹H T₁ measurements over the frequency range of 100 kHz and 35 MHz. By combining variations of temperature, pressure, frequency and selective deuteration, our goal is to provide a more detailed view of the role of the longer alkyl chain on the BMIM⁺ cation on the IL's ion dynamics. Because of the importance of the hydrogen bonding network in ILs and the effects of increasing temperature and pressure on its strength, we will use it to explain our results where applicable.

Experimental

Sample Preparation

Detailed descriptions of the synthetic procedures for three isotopologues of BMIM TFSA are included in the Supporting Information. The samples were dried in a vacuum to remove water content to levels below 200 ppm. Samples were then stored in an argon glovebox to avoid contact with atmospheric moisture.

Nuclear Magnetic Resonance

Spin-lattice relaxation and self-diffusion NMR measurements were conducted on a Chemagnetics CMX-300 spectrometer with a 7.3 T superconducting magnet. Measurements were made as a function of temperature between 296 and 373 K, and pressure from ambient to 250 MPa. Measurements were made by observing the ¹H, ²H, and ¹⁹F nuclei, for which resonances occurred at 309, 47, and 283 MHz respectively. For variable-temperature measurements, samples were placed in 5 mm NMR tubes and a 5 mm Nalorac gradient probe was used with a Magnetic Resonance Instruments current amplifier. For variable pressure measurements, samples were hermetically sealed in polyethylene bags and then placed in a custom copper-beryllium high-pressure NMR probe. The probe was attached to an Enerpac manual hydraulic pump to control the pressure using a pressure transmitting fluid. For ¹H and ¹⁹F measurements, Fluorinert FC-3283 (3M Company) and vacuum oil were used, respectively, as the pressurizing fluids.

Multinuclear T₁ measurements were made using an inversion recovery pulse sequence ($\pi - \tau - \pi/2 - Acq$) for 15 values of τ . Data were fit to Equation 1:

$$I(\tau) = I_0 \left(1 - 2e^{-\tau/T_1} \right) \quad [1]$$

Here I represents the integral of the NMR signal, τ is the delay used between pulses, and T₁ is the characteristic spin-lattice relaxation time. A minimum of 5 T₁s were used as a delay between repetitions and uncertainties were ~5% for each value of T₁. An additional high-

resolution ^1H NMR spectrum was acquired using a Bruker Avance 400 MHz spectrometer utilizing a one-pulse sequence at 298 K. As high-pressure T_1 measurements in the low-resolution probe result in a very broad signal, the high-resolution spectrum was used as a reference to make peak assignments.

Self-diffusion measurements were made using either static or pulsed field gradients while utilizing a Hahn spin-echo pulse sequence (PGSE) ($\pi/2 - \tau - \pi - \tau - \text{Acq}$). Variable temperature diffusion measurements were obtained by the PGSE technique using square-shaped gradient pulses. The duration of the gradient pulses and the mixing time were chosen to allow adequate attenuation of the echo intensity. The gradient strength g was varied over 15 values, up to 3 T/m. The attenuation curves could be fit to Equation 2:

$$I(g) = I_0 e^{-2\tau/T_2} e^{-D(\gamma\delta g)^2(\Delta - \delta/3)} \quad [2]$$

For variable pressure diffusion measurements, the static field gradient technique was utilized. Gradient pulses generated in the Cu-Be high-pressure probe would lead to prohibitively large eddy currents that would interfere with the NMR signal. For this, the probe was moved below the homogenous field of the magnet to utilize the naturally occurring static magnetic field gradient of the superconducting magnet. These measurements were conducted at 80 MHz, which corresponds to a static field gradient of 35 T/m. For static field measurements, the length of the delay τ was varied between pulses for 15 values to obtain adequate attenuation of the echo intensity. The attenuation curves could then be fit to Equation 3:

$$I(\tau) = I_0 e^{-2\tau/T_2} e^{-2D\tau(\gamma\tau g)^2/3} \quad [3]$$

All variable assignments are consistent with Equation 2. From the fit, D could be obtained with uncertainties of ~5%.

^1H and ^{19}F fast field cycling NMR measurements were conducted on undeuterated BMIM TFSA between field strengths corresponding to 100 kHz and 35 MHz for ^1H spins (~0.002–0.822 T) over the temperature range of 263–333 K using a Stelar Spinmaster spectrometer. FFC NMR allows for the measurement of T_1 times at various magnetic field strengths and temperatures. For measurements of field strengths greater than 12 MHz, a non-polarized pulse sequence was used, and for field strengths below 12 MHz a polarizing pulse sequence was utilized.⁵⁰

Results and Discussion

1. Ambient Pressure Experiments

1.1. Variable Temperature T_1 Relaxation and Diffusion Studies—Figure 2 depicts Arrhenius plots of ^1H and ^{19}F T_1 relaxation times for the all-proton BMIM TFSA measured

from 296–373 K. All inversion recovery attenuation curves observed in this study were exponential in nature, allowing us to compute T_1 times as previously described. Analogous graphs for the two partially deuterated isotopologues are included in the Supporting Information. The general trend was an increase in T_1 with increasing temperature for both ^1H and ^{19}F nuclei. While the H4 and H5 ring protons exhibit the longest T_1 s, the 2A and 2B alkyl chain protons had the shortest. This is expected considering that greater flexibility is realized with increasing distance from the ring. This is similar to what we observed for the EMIM TFSA system where the ring protons and alkyl chain methylene groups had the longest and shortest ^1H T_1 s respectively.²⁷

Nuclear relaxations are caused by dynamical fluctuations in local magnetic fields that can result from dipolar interactions, chemical shift anisotropy (CSA), scalar couplings, and spin rotations. Spin $I = \frac{1}{2}$ nuclei such as ^1H and ^{19}F relax mainly through the dipole-dipole interaction, which depends on inversely on the cube of the atomic internuclear distance and as a result is stronger for intramolecular interactions than intermolecular ones. When long-range translational motions are likely the intermolecular dipole-dipole interactions are further reduced, making them even less likely as the dominating relaxation mechanism. Therefore, T_1 times are sensitive to the nature of molecular motion. All variable temperature ^1H and ^{19}F T_1 measurements show T_1 increasing with temperature. This is indicative of being on the high temperature side of the T_1 minimum as per the Bloembergen Purcell Pound (BPP) theory, although the minimum was not directly observed.

Variable temperature ^2H T_1 results measured over the range of 235–370 K are depicted in Figure 3 for the two deuterated isotopologues. The deuteron (^2H) is a spin $I = 1$ nucleus and has a quadrupole moment. While dynamical fluctuations also occur at the site of the deuterons, the result is an interaction between its quadrupole moment and the surrounding electric field gradient. The trend observed for the ^2H T_1 was $\text{MD}_3 > \text{CD}_3 > \text{CD}_2$ at all temperatures, suggesting somewhat different interactions between each group and its environment, which in the first solvation shell is comprised mainly of anions. Additionally, the quadrupole relaxation mechanism is most efficient at the site of the CD_2 group, which suggests it is interacting with the largest electric field gradient of the three. A similar behavior was observed for the EMIM TFSA system²⁷ where dissimilar ^2H T_1 s were also observed for the isotopologues with the order observed as $\text{MD}_3 > \text{CD}_3 > \text{CD}_2$.

Unlike the ^1H and ^{19}F measurements, ^2H T_1 measurements include the T_1 -temperature minimum. T_1 minima occur at 275 K, 267 K, and 250 K for CD_2 , MD_3 , and CD_3 ^2H spins, respectively. Using the T_1 minimum, the correlation time (τ_c) was calculated as 3.353 ns. It should be noted that BMIM-TFSA freezes at temperatures below 270 K.¹² Imidazolium cations are known to have asymmetric charge distributions as shown by Molecular Dynamics simulations data, with majority of the charge centered on and closer to the ring.^{51–53} Additionally, the interaction between the imidazolium cation and the TFSA anion was shown to occur at sites on the anion in order of favorability $\text{N} > \text{O} > \text{F}$.^{52–53} The CD_2 having the shortest T_1 suggests its electric field gradient is largest, but it may also point to it being a more favorable interactions site.^{51–53}

Activation energies were computed from all ^1H , ^2H and ^{19}F T_1 data and the results are presented in Table 1. Values ranged around ~11–15 kJ/mol for the all-proteo BMIM TFSA. ^1H relaxation activation energies for the deuterated isotopologues were slightly different compared to the all-proteo sample, which is similar to what was observed for the EMIM TFSA samples, with the exception that while the all-proteo EMIM cation had the lowest T_1 s, the same cannot be said for the BMIM.²⁷ All ^{19}F values were identical as expected. The ^2H activation energies ranged from ~24–28 kJ/mol in the order $\text{MD}_3 < \text{CD}_3 < \text{CD}_2$. These values are significantly larger than previously found for EMIM-TFSA (12–16 kJ/mol) and shows the reduction in short-range mobility that results from an increase in the alkyl chain length.²⁷

Variable-temperature self-diffusion coefficients were determined by the PGSE NMR technique for the cations (^1H) and anions (^{19}F) of all three isotopologues of BMIM TFSA. The results are shown in Figure 4 and tabulated in Supporting Information Table SI6. These measurements agree with previous studies.^{12,49,54} As expected, D increases with increasing temperature, and the dependence is stronger for BMIM than for TFSA. On average, D^+ for a given BMIM isotopologue is 17% lower than D^- for TFSA at 298 K and 32% higher at 357 K. Taking all isotopologues together, the calculated activation energies for D^+ and D^- are 31.7 ± 0.6 and 26.7 ± 0.7 kJ/mol respectively.

Because of the correlation between the temperature dependences of the EMIM TFSA^{33,35} diffusion coefficient and viscosity through the Stokes Einstein relationship: $D = kT/c\pi r\eta$, where r is the effective hydrodynamic radius, c is a constant (4–6), k is the Boltzmann constant, T is the temperature and η is the viscosity, we were prompted to determine if such a relationship exists for BMIM. The result of this is shown in Figures 5(a) and (b) for ^1H (left) and ^{19}F (right) respectively for all three BMIM TFSA isotopologues with the viscosity data taken from literature values.⁴⁹ The results show a greater average hydrodynamic radius for the TFSA anion by 28% compared to the BMIM cation. An even larger result was observed for the EMIM TFSA system, where the TFSA anion's average hydrodynamic radius was 35% greater than the EMIM cation.²⁷

1.2. Fast Field Cycling T_1 Relaxation Measurements— ^1H fast field cycling (FFC) relaxation $T_1(\omega)$ measurements were performed on the all-proteo BMIM TFSA isotopologue between field strengths corresponding to 100 kHz and 35 MHz (~0.002–0.822 T) over the temperature range of 263–333 K. FFC NMR relaxometry provides frequency-dependent relaxation measurements, thereby allowing information on dynamical processes on different time scales. Whereby PGSE measurements are on the order of milliseconds and conventional T_1 measurements occur at the inverse Larmor frequency, $T_1(\omega)$ can cover milliseconds to tens of nanoseconds. For measurements of field strengths greater than 12 MHz, a non-polarized pulse sequence was used, and for field strengths below 12 MHz, a polarizing pulse sequence was employed.⁵⁰

NMR relaxation mechanisms for spin $I = 1/2$ nuclei are caused by fluctuating magnetic fields at the site of the observed species and are affected by both translational and rotational motions. For ^1H nuclei T_1 measurements are dominated by intra- and inter-molecular dipole-dipole interactions. The intramolecular component is due to the reorientational dynamics

within the molecule containing the observed species, while the intermolecular component is dominated by translational motion of the whole molecule. How fast these fluctuations occur is related to the correlation and spectral density functions. The relaxation rate which is related to the spectral density function were calculated from the $T_1(\omega)$ through by equation 4. Results for the ^1H species are shown in Figure 6 and appears to be the sum of two Cole-Davidson (CD) functions. The general trends are a decrease in R_1 with both increasing temperature and relaxation field strength. Using methods described in the literature, this dispersion data were used to calculate ^1H and ^{19}F time-dependent D data as shown in Figure 7.⁵⁵⁻⁵⁸

$$R_1 = 1/T_1 \quad [4]$$

At low fields the relaxation rate can be described by Equation 5:

$$R_1(\omega) = R_1(0) - N_H \left(\frac{\mu_0 \gamma_H^2 \hbar}{4\pi} \right)^2 \left(\frac{\sqrt{2} + 8}{30} \right) \left(\frac{\pi}{D} \right)^{3/2} \sqrt{\omega} \quad [5]$$

Here $R_1(0)$ is a constant at low frequencies representing the relaxation contribution from rotational dynamics, N_H is the number density of ^1H nuclei, μ_0 is the permeability of free space, γ_H is the gyromagnetic ratio of ^1H , and D is the time-dependent self-diffusion coefficient. The low field regime was taken to be the region in which the R_1 vs $(\omega_L)^{1/2}$ could be represented with a linear fit. At 263 K, this was taken to be equivalent to a Larmor frequency of 1.5 MHz. Although with increasing temperatures the linear region seems to expand to higher Larmor frequencies, the 1.5 MHz threshold was still used to fit the data to Equation 5.

The determination of the time-dependent D data from the low field FFC T_1 data is reasonable for the following reason. In general, intramolecular dipolar interactions fluctuate more rapidly compared to the intermolecular ones and would therefore show up in the high field regime. Because intermolecular interactions are also dependent on the Brownian translational motion of the whole molecule, which is slower, the corresponding data would therefore appear in the low field regime. Figure 7 shows a comparison of PFG and FFC NMR diffusion calculations. Data show good agreement within the temperature range inspected.

Reasonable agreement between FFC and PGSE diffusion values support the assignment of intermolecular motions to the low field region and suggests that the other FFC frequency ranges may be used to extract additional dynamics.

Activation energies were calculated as a function of frequency for ^1H T_1 and the results are shown in Figure 8. Values decreased with increasing field and those in the low field regime range from 25.1 ± 0.6 to 24.2 ± 0.5 kJ/mol. Because translational motion tends to be associated with higher activation energies compared to reorientational motion, the larger

values obtained in the low field regime further support its assignment to translational mediated motion.

A comparison of the low field FFC ^1H activation energies (24.2–25.1 kJ/mol) with those obtained from the single frequency variable temperature ^1H D measurements (31.7 ± 0.6 kJ/mol) do not agree within the experimental errors. The FFC D values are generally greater than the PGSE values. Although the PFG data obtained by us was limited to room temperature and above, lower temperature diffusion data from Hayamizu, et al.¹² also show significant departure from the values obtained by FFC. This is due to higher order terms being ignored in Equation 5, through the assumption that $\omega\tau_c \ll 1$. Therefore, the FFC evaluation of diffusion coefficients is only valid over a limited range due to the presence of the other relaxation modes in the different dynamic regions. Despite this, the FFC method does provide insight into these other molecular motions, which will be described in later work.

The activation energies in the high field regime of the FFC data seem to be approaching those calculated from the variable temperature ^1H T_1 data, supporting the argument that more localized rapid motions are being detected at higher fields. A more substantial description and interpretation of the FFC data, including ^{19}F results will be presented elsewhere.

2. Variable Pressure T_1 Relaxation and Diffusion Measurements

Variable pressure ^2H T_1 , and ^1H and ^{19}F D measurements were made at 47 MHz, and 80 MHz respectively. As shown in Figure 9, the ^2H T_1 for the two deuterated isotopologues decrease to a plateau with increasing pressure. It should be noted that for the BMIM-D9 isotopologue, both the CD_3 and CD_2 peaks were easily resolved. The order of T_1 s is: $\text{MD}_3 > \text{CD}_3 > \text{CD}_2$, the same as observed for the variable temperature ^2H T_1 data. Whereas no saturation in the variable pressure ^2H T_1 data was observed for EMIM TFSA, clear saturation is shown for all BMIM TFSA isotopologues. As mentioned previously, deuterons relax through interactions between their quadrupole moment and fluctuations in the surrounding electric field gradient. The order of the T_1 data implies the CD_2 group experiences the largest electric field gradient. To determine if this behavior was completely quadrupolar and not dipole-dipole, we performed variable pressure ^1H T_1 and these results are shown in Figure 10. As shown, while different ^1H T_1 s were observed for the three isotopologues, no saturation was observed for any, therefore confirming the dominant quadrupolar nature of the interaction.

Activation volumes (ΔV) were calculated from the variable pressure data using Equation 6, where R is the universal gas constant, T is the temperature, P is the pressure, and α can either be self-diffusion, D , or $1/T_1$ depending upon the measurement being analyzed.

$$\Delta V = -RT \left[\frac{\partial \ln \alpha}{\partial P} \right]_T \quad [6]$$

Here, the activation volume can be a good indicator of the ease of mobility, where larger activation volumes correspond to greater restrictions on motion, that is, motion that requires cooperative rearrangement of many atoms. Activation volumes for ^2H T_1 measurements are shown in Table 2. While all three isotopologues showed two regions, which can be characterized as the low and high-pressure regime, for both the CD_3 and CD_2 sites the point of intersection occurred at about 60 MPa, but at 100 MPa for the MD_3 site. The saturation that is observed suggests that pressure induces packing-optimization between the ions and involves their respective conformations. While there are two conformations possible for the fluid TFSA anion about the C-S...S-C dihedral angles - described as *trans* or *anti* (C_2 symmetry) and *cis* or *gauche* (C_1 symmetry) there are at least four low-energy optimized states for the BMIM cation involving the C7-C8 and C9-C10 carbons.²⁶ Because of the motion possible about the C7-C8 and C9-C10 groups, we can have *trans-trans*, *trans-cis*, *cis-cis*, and *cis-trans* conformations of the alkyl chain. This is different from the EMIM TFSA system where the conformations are *trans* and *cis*, with the proportion of the *trans* conformation increasing with decreasing temperature. Additionally, since the BMIM TFSA system has four low-energy conformations, the saturation that is observed could be viewed as being due to the lack of available 'free volume' to accommodate the mobility associated with the conformations. In the high-pressure regime, activation volumes at all sites approached $0 \text{ cm}^3/\text{mol}$, i.e. a region of incompressibility.

Variable pressure ^1H T_1 data was also collected for the all-proteo isotopologue. To accurately assign the three broadened low-resolution peaks obtained in the high-pressure probe, we obtained a high-resolution ^1H NMR spectrum at 400 MHz and 298 K using a single pulse sequence, then the respective chemical shift ranges were used for peaks assignment. Activation volumes determined from ^1H T_1 data as shown in Figure 10 do not show the bi-component activation volume. This indicates the effect is more likely the result of changes in the quadrupolar relaxation, which is much more sensitive to local reorientational dynamics than dipolar relaxation. It is also seen that all ^1H activation volumes, reported in Table 3, are smaller than their corresponding ^2H activation volumes, and although no bi-component feature was obtained. The data for both the CH_3 and MH_3 groups appear to flatten with increasing pressure, suggesting that they too are approaching a point of incompressibility. It is expected that as the pressure increases the interactions (both intra and inter) should increase in strength due to the reduction in bond lengths. Although the proton relaxation depends more on intra- than inter- molecular dynamics, it suggests that a reduction in the reorientational dynamics that may be mediated by translational ones. Considering this, the decrease that is observed for the deuterons may also be attributed to a reduction in the reorientational dynamics. However, because the deuteron relaxation mechanism is quadrupolar and depends almost entirely on intramolecular reorientation dynamics, the saturation that is observed is a strong suggestion that large amplitude motions previously detected have ceased, and that what remains may be of smaller amplitudes and possibly greater frequencies. Additionally, the effect is greatest for the alkyl chain than for the ring terminated methyl group as evident from their saturation-initiated pressures (60 MPa for both the CD_3 and CD_2 sites, and 100 MPa for the MD_3 site).

Variable pressure ^1H and ^{19}F self-diffusion coefficients were determined for the all-proteo BMIM TFSA at room temperature and the results are shown in Figure 11. Previous studies

have made ambient temperature, self-diffusion measurements of BMIM TFSA up to 40 MPa, and our data are in good agreement.⁴⁹ At all pressures, the cation diffuses faster than the anion and no saturation was observed for either over the pressure range studied. The calculated activation volumes, using Equation 3, were 19 ± 1 and 23 ± 3 cm³/mol for the cation (¹H) and anion (¹⁹F), respectively. For comparison in the EMIM TFSA system the respective activation volumes are 14.6 and 28.8 cm³/mol.²⁷ Compared to EMIM TFSA, in BMIM TFSA the cation diffusion activation volume is significantly larger and the anion $V^\ddagger$ is smaller. The longer alkyl chain in BMIM introduces additional conformational exchange processes, mentioned above in the context of relaxation, which are potentially sensitive to the reduction in free volume with increasing pressure. Conversely, the longer alkyl group changes the structure of the IL polar region⁵⁹ enough to relax the barrier to anion conformational exchange, reducing $V^\ddagger_{\text{TFSA}}$ in comparison to the EMIM case. In the BMIM case, the difference between the BMIM and TFSA diffusion activation volumes is at the edge of statistical significance; for longer chains the cation and anion $V^\ddagger$ values are essentially the same, and both increase with chain length.²⁷ The trend of increasing self-diffusion activation volume with increasing alkyl chain has also been observed for the C_nMIM BF₄ family^{27,60} from the comparison of EMIM BF₄, BMIM BF₄ and OMIM BF₄.

Discussion and Conclusions

A comprehensive analysis of the effect of the longer alkyl chain on the selectively deuterated BMIM TFSA ionic liquid isotopologues was undertaken using multi-nuclear (¹H, ²H and ¹⁹F) magnetic resonance T₁ and D measurements as functions of temperature, frequency and pressure. Data spans the temperature range of $-38 - 100$ °C and the pressure range of $0.1 - 250$ MPa. Single-frequency, variable-temperature T₁ (¹H, ²H and ¹⁹F) and D (¹H, and ¹⁹F) data show increasing short- and long-range dynamics resulting from increasing temperature. This is expected since increasing temperature increases the available free volume, which increases mobility. Variable frequency ¹H T₁ measurements through FFC NMR reveal frequency-dependent dynamics, with the low frequency regime assigned to long-range translational dynamics and the high frequency regime to the more rapidly oscillating reorientational ones. Comparison of the low field FFC calculated D data with the variable temperature ¹H D values gave very good agreement, lending further support to its assignment as belonging to long range intermolecular Brownian dynamics. Calculated activation energies from the FFC ¹H T₁ data also provided support for these regime assignments, with values of 25.1–24.2 kJ/mol and 24.2–18 kJ/mol obtained for the low and high field regimes respectively. Translational motions require greater free volume than reorientational ones. Because of this, translational motions are often associated with larger activation energies, thus the values obtained from the FFC data are in line with what is expected.

Selective deuteration of the BMIM cation at various sites (MD₃, CD₃ and CD₂) allowed access to the short-range motions through determination of the ²H T₁s. Results show site-dependent interactions on the cation with ²H T₁s in the order MD₃ > CD₃ > CD₂. Since deuterons relax through the quadrupolar interaction which describes the effect of the surrounding electric field gradient on the deuteron's quadrupole moment, the order in the T₁s suggest the electric field gradient is strongest at the CD₂ site and makes it the most

likely interaction site - outside of the ring C2, C4 and C5 protons - for the anions in the first solvation shell of the cation. Variable pressure D data showed that increasing pressure slowed both the cation and anion, however the effect on the anion was slightly greater. When the results are compared with those for EMIM TFSA, we see a smaller activation volume for anion diffusion in BMIM TFSA. This suggests that the longer alkyl chain may be reducing the strength of the interactions between the cation and the anion, ergo allowing the anions more mobility.

It is accepted that both charge ordering⁶¹ that creates alternating cation and anion shells extending over large distances, and nanoscale segregation^{59,62} resulting from the mesoscopic organization between the cation and anions into hydrophilic and hydrophobic domains exist in IL structures. Aiding the existence of these is hydrogen bonding. Theoretical studies on the gas-phase interactions for C_nMIM TFSA systems show hydrogen bonding between the cation and the anion at various locations, the strongest of which is through the C2 hydrogen on the imidazolium ring.^{51–53} Local conformations of both the cation and anion can affect these bonds. While for imidazolium-based cations, nine interactions sites are favored by the TFSA anion, not all are occupied simultaneously.^{51,52} This is the result of factors such as anion size and Coulombic repulsions. The fewer interaction sites on the cation occupied the weaker and less ordered the hydrogen bonding network.^{51,52}

The strength of the hydrogen bonding network depends on several factors and some are discussed here. First, the substitution of hydrogen by deuterons have been shown to affect hydrogen bonding due to reduction in the rotational motions and rates of hydrogen bonding breakage and formation – the two processes that are key for an efficient hydrogen bonded network.⁶³ In fact, early single crystal studies have shown that substituting ²H for ¹H can increase the lattice dimensions,^{64,65} due to weakened bonds. The large increase in the ²H activation energy in the BMIM isotopologues could be due to the large number of deuteron substitutions significantly increasing bond lengths and the distances between interacting sites resulting in decreasing intramolecular interactions along the alkyl chain. Secondly, the effect of increasing temperature is known to reduce the strength of the bonds and positively assist proton translational motion through the vehicle mechanism. The reverse effect is expected and observed for increasing pressure, whereby the bond strengths are expected to increase, thereby reducing translational motion. Added to these is the effect of pressure on the ions' conformation. The saturation observed in the ²H T₁ data suggests a significant reduction in the reorientational dynamics of the BMIM cation. This can affect the interactions between it and the interacting anions, resulting in impeded dynamics as observed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Molecular diagrams of partially deuterated BMIM cations (deuterons shown in green) and a TFSA anion.

Figure 2. 1H and ^{19}F T_1 relaxation times for BMIM-TFSA including labelled molecular diagram of the BMIM cation.

Figure 3.
 ^2H T_1 relaxation times for partially deuterated isotopologues of BMIM-TFSA.

Figure 4. ^1H and ^{19}F self-diffusion as a function of inverse temperature for three isotopologues of BMIM-TFSA.

Figures 5(a) and (b).

^1H (left) and ^{19}F (right) self-diffusion coefficients vs T/η for all isotopologues of BMIM-TFSA.

Figure 6.
 ^1H relaxation rate measurements obtained via FFC NMR for BMIM TFSA between 263 and 333 K.

Figure 7.
Time dependent ^1H self-diffusion (D) coefficient data for the BMIM⁺ cation calculated using both PFG and FFC NMR techniques.

Figure 8.
 ^1H T_1 activation energies presented as a function of Larmor frequency, calculated from FFC NMR.

Figure 9. Variable pressure ^2H T_1 for the three BMIM-TFSA isotopologues.

Figure 10.
Variable pressure ^1H T_1 for the all-proteo BMIM TFSA.

Figure 11. Variable pressure ^1H and ^{19}F self-diffusion coefficient measurements of the all-proteo BMIM TFSA system.

Table 1

T_1 relaxation activation energies (in kJ/mol) for BMIM TFSA.

Position	BMIM	BMIM-MD ₃	BMIM-D ₉
H _{4,5}	11.8 ± 0.4	11.4 ± 1.1	10.4 ± 0.5
H ₂	11.3 ± 0.4	10.9 ± 0.4	10.3 ± 0.4
MH ₃	13.6 ± 0.5	-	10.1 ± 0.7
2A	12.7 ± 1.2	14.9 ± 0.4	-
2B	14.6 ± 0.6	15.4 ± 0.5	-
2C	12.8 ± 0.7	11.5 ± 0.6	-
CH ₃	10.9 ± 0.7	12.4 ± 0.3	-
TFSA (¹⁹ F)	12.2 ± 0.2	12.2 ± 0.3	12.2 ± 0.3
² H	-	23.8 ± 0.6	25.8 ± 0.3 (CD ₃) 27.8 ± 0.5 (CD ₂)

Table 2

^2H spin-lattice activation volumes (in cm^3/mol) for partially deuterated isotopologues of BMIM TFSA.

Position	Activation Volume	
MD_3	14.3 ± 0.5 (0–100 MPa)	2.9 ± 0.3 (100–250 MPa)
CD_3	9 ± 1 (0–60 MPa)	~ 0
CD_2	20 ± 3 (0–60 MPa)	~ 0

Table 3

^1H T_1 activation volumes (in cm^3/mol) for all-proteo BMIM TFSA.

Positions	Activation Volume
H2, H4, H5	7 ± 2
MH ₃ , 2A	1.4 ± 0.6
2B, 2C, CH ₃	4.7 ± 0.6