

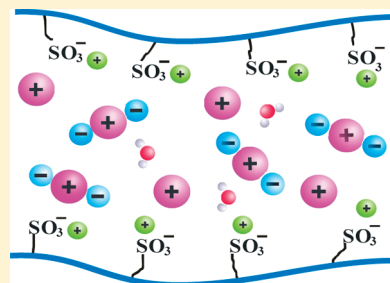
Cation/Anion Associations in Ionic Liquids Modulated by Hydration and Ionic Medium

Jianbo Hou, Zhiyang Zhang, and Louis A. Madsen*

Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia 24061, United States

Supporting Information

ABSTRACT: In order to understand the unique solvation and conduction properties of ionic liquids (ILs), we explore their interionic associations modulated by hydration level and ionic medium. Pulsed-field-gradient NMR allows sensitive measurement of separate cation and anion diffusion coefficients, which combine to reflect ionic aggregation. With increasing hydration of ILs, the anomalous ratio of cation to anion diffusion coefficients reverses, then plateaus to values consistent with expected hydrodynamic radii ratios ($r_{\text{cation}}/r_{\text{anion}} = 1.4$ for $[\text{C}_2\text{mim}][\text{BF}_4]$). When ILs diffuse inside an ionic polymer, ion associations are modulated by ionic interactions between mobile cations and anions, and drag from fixed $-\text{SO}_3^-$ lining the polymer's hydrophilic channels. Surprisingly, cations diffuse substantially faster ($\leq 3\times$) at low hydration inside membranes, revealing prevalent anionic aggregates. At high hydration, isolated anions diffuse faster ($\leq 4\times$) than cations. Probing ionic interactions provides pivotal insight into these subtle fluids, with quantitative implications for electrolyte applications such as batteries and "artificial muscle" mechanical actuators.



1. INTRODUCTION

Ionic liquids (ILs) are salts consisting of bulky cations and/or anions possessing much lower charge density than simple ionic species (e.g., Cl^- , Na^+ , SO_4^{2-}), thus enabling their fluidity at or near room temperature. The delicate combination of noncovalent interactions among these ions imbue ILs with a curious and useful set of behaviors, highly tunable by cation and anion choice. ILs find expanding applications in catalysis and bioscience, and as electrolytes in batteries and polymer-based mechanical actuators due to their high ionic conductivity, thermal and electrochemical stability, and low volatility.^{1,2} When combined with ionic polymers, ILs become potential candidates for the design of ion-based batteries and ionic transducers since they provide mobile charged species while maintaining the performance of these devices after many operation cycles due to their negligible vapor pressure.^{3,4} In particular, transport behaviors of both cations and anions in ILs strongly impact the performance of these materials and devices.^{5,6} Exploring the interplay among ionic species in ILs will improve our fundamental understanding of ion transport,^{7–11} thus enabling targeted design of new ILs as well as novel applications.

A viable strategy for probing interactions between cations and anions is pulsed-field-gradient (PFG) NMR diffusometry.^{12,13} Ion pairing or aggregation in ILs^{14,15} will reduce ion self-diffusion since the diffusion coefficient D is inversely proportional to the size of a diffusing particle as described by the Stokes–Einstein relation:

$$D = \frac{kT}{c\eta r_H} \quad (1)$$

where k is the Boltzmann constant, T is absolute temperature, c is a constant factor depending on the shape and relative size of the

diffusing particle to its surrounding fluid,¹⁶ η is fluid viscosity, and r_H is the diffusing particle's hydrodynamic radius. Empirical observations^{16,17} and theoretical studies¹⁷ on the inverse proportionality between the diffusion coefficient and viscosity agree with the prediction of the Stokes–Einstein equation, even for molecular-scale diffusants where the factor c is less than the 6π obtained for a hard sphere diffusing particle that is large compared with the surrounding fluid molecules (no-slip boundary condition). Thus, we propose that for a given equilibrium ionic fluid, c is fixed for all diffusing ionic species and we may use eq 1 to assess relative hydrodynamic radii of ionic aggregates. Great effort has been devoted to understand ion associations in ILs,^{18–22} which strongly impact ion transport. Ion conductivity measurements on ILs deviate by 20–70% from the values calculated using the Nernst–Einstein equation and diffusion coefficients,^{22,23} suggesting a moderate degree of ion associations. However, using the Nernst–Einstein equation to estimate ion associations strongly rests on the assumption of a single ion conduction mechanism, which is inappropriate for ILs considering the strong interionic interactions. Further studies are necessary for understanding ion aggregation, and for quantifying aggregate populations and dynamics.

We aim to understand specific intermolecular interactions among charged species as reflected by their transport properties via PFG NMR diffusometry. Here we have explored the use of an ionic polymer (Nafion) as a medium to study ion associations in ILs. This ionic polymer consists of hydrophilic and hydrophobic polymer moieties that microphase separate into a nanoscale

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network of interconnected hydrophilic channels, facilitating transport of mobile species such as water molecules and ions.^{24,25} Our strategy allows for investigation of the effects of acidity (Nafion is a polyacid in the H^+ form), specific molecular interactions between different ions, and the effect of a matrix-fixed ion ($-\text{SO}_3^-$ on the polymer) on the motion of IL ions. In our previous study, we examined the effects of IL uptake, temperature, and water content on the IL–water–ionomer system, where dramatic acceleration of ion transport was observed with increased hydration.²⁶

Here we report striking transport phenomena in four types of ILs based on systematic sample variations, either as “free liquids” (neat liquids or solutions with water), or absorbed into ionomer membranes. We scan through a much wider range of water content as compared to our previous study²⁶ and measure diffusion of mobile species. To accurately study ion hydration, we carefully adjust and maintain water content in all cases using a sealed Teflon cell.²⁷ Using spectroscopic resolution, we separately measure D for water, cations, and anions via PFG NMR.²⁶ For free liquids, cations diffuse faster than anions by 30–50% at low water content (χ_{water} , mole ratio of water to ILs), while this reverses at high water content. Inside ionomer membranes this effect is greatly enhanced, exhibiting up to 4× faster (slower) cation diffusion at low (high) water content. Furthermore, at high χ_{water} the cation/anion D ratio in the free liquid state agrees with expected hydrodynamic radii (r_{H} , eq 1), in contrast to free dry ILs, where in all cases studied to date ion aggregation inflates this ratio.^{9,22,23} These results provide new insights into ion associations in ILs, both as free liquids and inside ionomers.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation and Liquid Uptake Determination. Transport behaviors of ions and water in the following four ILs were studied: 1-ethyl-3-methyl imidazolium trifluoromethanesulfonate ($[\text{C}_2\text{mim}][\text{TfO}]$), 1-butyl-3-methyl imidazolium trifluoromethanesulfonate ($[\text{C}_4\text{mim}][\text{TfO}]$), 1-ethyl-3-methyl imidazolium tetrafluoroborate ($[\text{C}_2\text{mim}][\text{BF}_4]$), and 1-butyl-3-methyl imidazolium tetrafluoroborate ($[\text{C}_4\text{mim}][\text{BF}_4]$). All these ILs were purchased from Solvent Innovation GMBH (Cologne, Germany) with purity >99%. Due to their hygroscopic nature, these pure ILs were further dried in vacuum at 70 °C for 48 h to remove residual water prior to diffusion measurements, and diffusion coefficients and NMR spectra were checked for stability over time to verify that water absorption was insignificant. Extruded Nafion 117 (N117) membranes with equivalent weight of 1100 (grams of dry membrane per mole of sulfonate group) were purchased from E.I. DuPont in the acid form with a thickness of 175 μm . Membranes were cut into pieces 5 mm × 5 mm in size, stacked together to a total mass of ~60 mg and dried in a vacuum oven for 12 h at room temperature to determine the dry membrane mass (mass_{dry}). The samples were then soaked with IL– D_2O mixtures (D_2O , 99.9%, Cambridge Isotope Laboratories) at different temperatures to achieve different uptakes. The wet membranes were blotted to remove any free surface liquid (ILs and water) and transferred to a sealed Teflon cell to equilibrate for later diffusion measurement as reported earlier.²⁷ All diffusion measurements were performed at 25 °C after sample equilibration. To vary water content, we allowed the samples to dry in open air while the mass of IL plus the mass of the membranes (mass_{IL}) remained constant due to the negligible vapor pressure. Masses of wet membranes

(mass_{wet}) including water and IL were determined gravimetrically after the NMR experiments. IL uptake and water mole ratio (χ_{water}) were calculated respectively using eqs 2 and 3:

$$\text{IL uptake} = \frac{\text{mass}_{\text{IL}} - \text{mass}_{\text{dry}}}{\text{mass}_{\text{dry}}} \times 100\% \quad (2)$$

$$\chi_{\text{water}} = \frac{\text{mass}_{\text{wet}} - \text{mass}_{\text{IL}}}{\text{mass}_{\text{IL}} - \text{mass}_{\text{dry}}} \times \frac{M_{\text{IL}}}{M_{\text{D}_2\text{O}}} \quad (3)$$

2.2. Diffusion Measurement by Pulsed-Field-Gradient NMR. We applied the robust and simple pulsed-gradient stimulated echo (PGSTE) sequence for all diffusion measurements. We measured ^1H and ^{19}F diffusion for ILs using a Bruker Avance III WB 400 MHz (9.4 T) NMR equipped with a Micro5 triple-axis-gradient microimaging probe and 8 mm double resonance ($^1\text{H}/^2\text{H}$) RF coil. The triple axis gradients each having a maximum value of 300 G/cm allowed for measurement of diffusion along three orthogonal directions relative to membranes, denoted as X , Y (in plane), and Z (through plane).²⁷ Verification of orientations of the membrane stacks in the magnetic field was via using an Y – Z image slice collected with a RARE pulse sequence (Rapid Acquisition with Relaxation Enhancement).²⁸ The PGSTE sequence used a $\pi/2$ pulse time of 32 μs , gradient pulse durations δ ranging from 2 to 5 ms, and diffusion times Δ ranging from 30 to 600 ms, depending on the uptake of IL and water in the membranes and suited to the corresponding relaxation times. Sixteen gradient steps with appropriate selection of maximum gradient strength resulted in 50–90% of NMR signal attenuation. Due to differences in signal intensity, the number of scans varied from 4 to 512 to produce sufficient signal-to-noise ratio for each data point. All parameters for the gradient have been calibrated and optimized as reported earlier.^{27,29}

We have performed diffusion measurements on both free ILs and ILs inside Nafion membranes at room temperature (25 °C). For free IL experiments (aqueous solutions), a water mixture ($n_{\text{D}_2\text{O}}:n_{\text{H}_2\text{O}} = 9:1$) forms a homogeneous phase with ILs as they are mixed. ^1H NMR allowed determination of the mole ratio of water to IL. For ILs inside membranes, depending on the type of ILs and content of liquid (ILs and water) in Nafion membranes, the longitudinal relaxation time (T_1) varied in the range of 580 ms–1.3 s for cations and 300 ms–2 s for anions. The spin–spin relaxation time (T_2) fell in the range 5–40 ms for cations and 10–900 ms for anions. Measurement of cation and anion diffusion coefficient D vs diffusion time Δ allowed probing of any possible heterogeneous structures that may exist over the 0.5–3.3 μm range. Due to limiting factors within the experiment (gradient strength, relaxation time), Δ could vary over a relatively wide range at higher liquid uptake but Δ was limited (>250 ms) at low uptake to produce sufficient signal attenuation. All measurements resulted in clean single component fits to determine diffusion coefficients. Consistent with our previous studies,^{29,30} diffusion in Nafion 117 membranes was slightly anisotropic (slightly faster diffusion along extruded direction) and we uniformly measured diffusion along the extrusion direction in this study.

3. RESULTS AND DISCUSSION

3.1. Hydration Effects on Ion Transport in Free ILs. For free IL, we examine a broad range of water content in order to understand how variation in hydration level (water content) affects ion diffusion and thus the intermolecular associations of

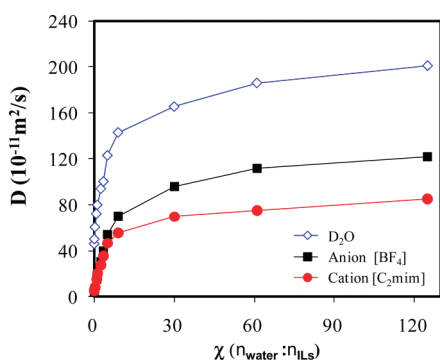


Figure 1. Water and ion diffusion of “free” $[\text{C}_2\text{mim}][\text{BF}_4]$ vs water content (χ_{water}) at 25 °C. D_{cation} is faster than D_{anion} at low χ_{water} but becomes slower than D_{anion} at high χ_{water} . Both D_{cation} and D_{anion} increase with water content, with anion diffusion increasing slightly faster. Error bars are within the size of each data point.

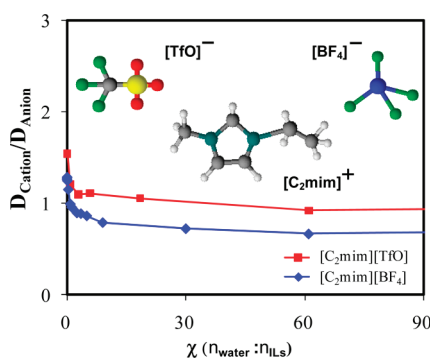


Figure 2. $D_{\text{cation}}/D_{\text{anion}}$ vs water content χ_{water} in free $[\text{C}_2\text{mim}][\text{BF}_4]$ and $[\text{C}_2\text{mim}][\text{TfO}]$ ILs. Cations diffuse faster than anions by 30–50% in the absence of water whereas the trend reverses at high χ_{water} , where the diffusion ratios match those expected from the Stokes–Einstein equation. Errors in D ratios are $\pm 5\%$.

cations and anions. “Free” is defined as IL or IL + water solution in the liquid state, not inside the ionic polymer. Figure 1 shows the plot of cation, anion, and water (D_2O) diffusion in free $[\text{C}_2\text{mim}][\text{BF}_4]$ vs water content χ_{water} , which is defined as the mole ratio of water to IL ($n_{\text{water}}:n_{\text{IL}}$). Here, 1 mol IL includes 1 mol cations and 1 mol anions. In general, both cation and anion diffusion increase with water content; however, anion diffusion increases faster than cation diffusion to result in faster moving anions at high water content. To quantify the difference between cation and anion diffusion. Figure 2 shows $D_{\text{cation}}/D_{\text{anion}}$ vs water content χ_{water} for free $[\text{C}_2\text{mim}][\text{BF}_4]$ and $[\text{C}_2\text{mim}][\text{TfO}]$. We use eq 1 to quantify the difference between cation and anion diffusion in free ILs. Molecular dynamics simulations^{31,32} suggest the formation of structured ionic domains in pure ILs due to ion associations (specific molecular packing) the presence of which obscures the picture of isolated ions with uniformly well-defined sizes. Thus, at the moment, we cannot directly quantify individual ion size using diffusion coefficients and eq 1. Nevertheless, eq 1 should provide relative information on transport of different diffusing particles with effective radii r_{H} if ions are aggregated.

The average hydrodynamic radii of cation and anion are estimated from the volume of ions mentioned above ($r_{\text{H}} \sim V^{1/3}$).⁶ Since these two ions exist in the same thermodynamic phase, $D_{\text{cation}}/D_{\text{anion}}$ equals the reciprocal of their hydrodynamic radius ratio, or

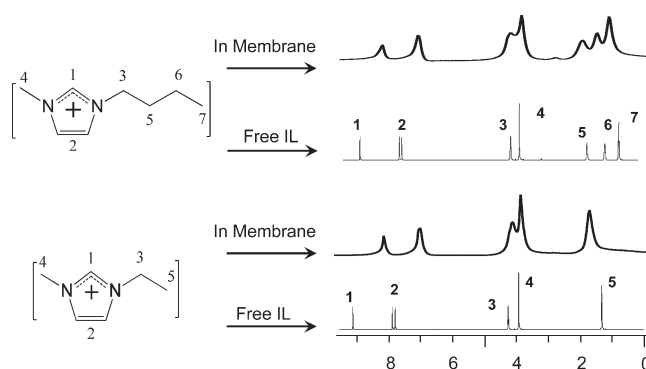


Figure 3. Chemical structures of $[\text{C}_2\text{mim}]^+$ and $[\text{C}_4\text{mim}]^+$ cations (both with $[\text{BF}_4]^-$ counterions, $[\text{TfO}]^-$ spectra in SI) with corresponding ^1H spectra for free state dry ILs, and for IL– D_2O mixtures soaked into Nafion (N117) membranes. We assign proton peaks using numbers, as shown. For ILs inside membranes, peak 3 includes a small residual $^1\text{H}_2\text{O}$ signal due to slightly impure D_2O .

$r_{\text{H(anion)}}/r_{\text{H(cation)}}$. Under low χ_{water} , cation diffusion is faster than that of the anion by 30–50%, regardless of its relatively much larger size. However, at high χ_{water} , where ions are fully hydrated and interion interactions are screened, the pattern is reversed and one experimentally obtains $D_{[\text{C}_2\text{mim}]}^+/D_{[\text{BF}_4]}^- = 0.70$ and $D_{[\text{C}_2\text{mim}]}^+/D_{[\text{TfO}]}^- = 0.93$, which agree with the results of density-based ion radius calculations (0.74 for $[\text{C}_2\text{mim}][\text{BF}_4]$ and 0.92 for $[\text{C}_2\text{mim}][\text{TfO}]$).⁶ The agreement of diffusion ratio with r_{H} ratio, as predicted by the Stokes–Einstein equation, supports the picture of totally isolated ions under dilute conditions. This sheds light on the puzzle of the anomalous cation/anion diffusion ratio in dry ILs, which is at odds with expected (isolated) ionic radii. In addition, the ratio of water to cation diffusion at low and high water content further supports these arguments, where $D_{\text{water}}/D_{[\text{C}_2\text{mim}]}^+$ approximates to 8.0 and 2.3 respectively under low ($\chi_{\text{water}} = 0.035$) and high ($\chi_{\text{water}} = 125$) water content. If one estimates the volume occupied by a water molecule from water density ($v = M/N_A\rho$) and uses eq 1 to calculate the diffusion ratio, one would expect to have $D_{\text{water}}/D_{[\text{C}_2\text{mim}]}^+$ equal to 1.8, which is similar to the experimental value of 2.3 at high water content and implies that the ion’s hydration sphere slightly enlarges its effective radius. Again, consistent with cation/anion diffusion at low water content, the unexpected high value of $D_{[\text{water}]}^+/D_{[\text{C}_2\text{mim}]}^+ (= 8)$ implies specific interactions exist among ions within ILs, which will be further discussed in the next section. Differences in aggregates involving cations and anions must arise from specific molecular interactions (e.g., excluded volume, shape anisotropy, charge distribution, polarizability, hydrogen bonding), among groups of cations and anions in neat ILs.

3.2. Hydration Effects on Ion Transport Inside an Ionic Polymer. In order to obtain a fundamental understanding of hydration effects on ion transport in ionic polymer membranes and to compare ion behaviors with the case of free ILs, we soaked various D_2O –IL mixtures into Nafion membranes to achieve certain uptakes using our procedures reported earlier.²⁶ In our previous study, we noticed that the $^1\text{H}_2\text{O}$ proton NMR peak shifted as a function of water content and sometimes overlapped with other IL cation peaks. Using D_2O rather than H_2O to prepare the liquid mixture allows accurate measurement of water diffusion (eliminating multicomponent fitting due to overlap of proton peaks) and simplifies proton spectra as well. Figure 3 lists chemical structures of the $[\text{C}_2\text{mim}]^+$ and $[\text{C}_4\text{mim}]^+$ cations used in this study, along with the relevant proton spectra for

free state ILs (dry) and IL–D₂O mixtures soaked into Nafion membranes (spectra for [BF₄][−] counterions shown, spectra with [TfO][−] anions similar but not shown; See the Supporting Information (SI)). For IL–D₂O mixtures in Nafion, spectral resolution varies from case to case, depending on the uptake of IL and water in the system (see the SI for representative spectra). We observe minimal ¹H₂O peaks in these spectra due to the high purity of D₂O. In ²H spectra (not shown), we observe only a doublet of ²H₂O peaks (≤ 50 Hz splitting) due to the partially averaged quadrupolar interactions of water O–D bonds in the weakly aligned hydrophilic channels. ²⁹ For ¹⁹F spectra (see the SI), one peak appears for [TfO][−] and two peaks for [BF₄][−] (not observable for ILs inside ionomers due to broad line) due to the two boron isotopes present (¹⁰B and ¹¹B).

Figure 4 shows ion diffusion vs diffusion time of [C₄mim][BF₄] inside the ionic polymer membrane over a range of χ_{water} . The root-mean-square displacement based on the measured diffusion coefficient $\langle r^2 \rangle^{1/2} = (2D\Delta)^{1/2}$ is plotted vs $\Delta^{1/2}$, resulting in linear regression for both cation and anion diffusion. Diffusion is independent of diffusion time Δ , characterizing an absence of restricted diffusion effects in these membranes. At relatively high χ_{water} where ion diffusion is fast and the T_2 relaxation time is long, diffusion is measured over a relatively wide range of Δ (30–600 ms). Note that this diffusion measurement length scale ranges from 0.5 to 3.3 μm (low and high water content, large and small Δ), in agreement with our previous study of ion diffusion in Nafion 212. ²⁶ In addition, one also notes that the corresponding slopes associated with cation and

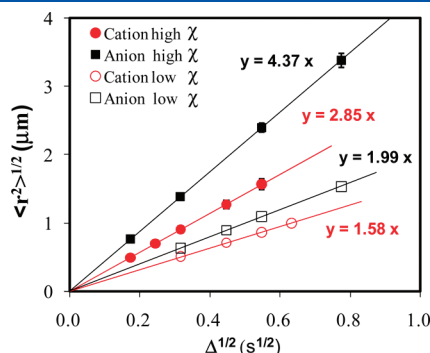


Figure 4. Root-mean-square displacement ($\langle r^2 \rangle^{1/2}$) of cation and anion vs $\Delta^{1/2}$ for [C₄mim][BF₄] IL inside the ionic polymer membrane at low and high χ_{water} . These linear regressions indicate nonrestricted diffusion behavior in the experimental diffusion length range 0.5–3.3 μm . Each individual line slope equals $(2D)^{1/2}$.

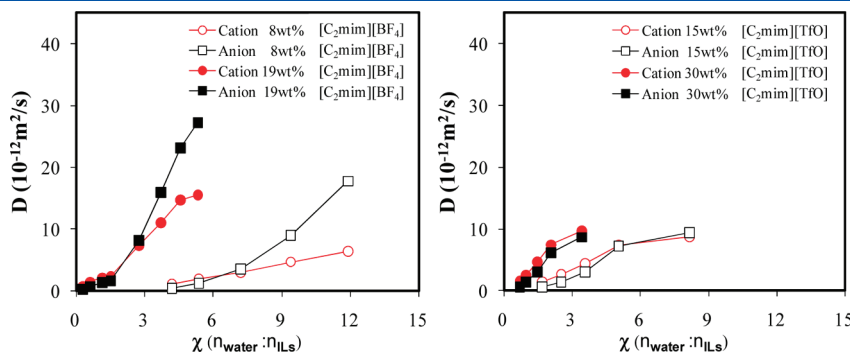


Figure 5. Cation and anion diffusion inside Nafion membrane vs water content χ_{water} with different uptakes of [C₂mim][BF₄] and [C₂mim][TfO]. Higher IL uptake results in substantially faster ion (cation and anion) transport under the same χ_{water} value. Water accelerates the transport of both cation and anion whereas the anion is more highly accelerated than the cation for [C₂mim][BF₄].

anion in Figure 4 deviate significantly from each other at high water content, reflecting the fact that the slope ratio is equal to the square root of the diffusion ratio. Interestingly, cation and anion diffusion behaviors substantially differ inside the ~ 2 nm hydrophilic channels of Nafion membranes, as revealed in Figure 5. We note several attributes of these observations as follows. D_{anion} is more sensitive to the presence of water than D_{cation} , especially at low IL uptake. As IL uptake increases, water still preferentially accelerates D_{anion} but less strongly. More generally, for BF₄-based ILs ([C₂mim][BF₄], [C₄mim][BF₄]) we observe striking enhancement in anion diffusion as compared to cations (up to a factor of 4.3) at high water content. However, TfO-based ILs ([C₂mim][TfO], [C₄mim][TfO]) exhibit a smaller effect.

We attribute these observations to the following factors: (1) interactions of polymer-fixed sulfonate groups and cations and (2) difference in basicity and ion pairing between [TfO][−] and [BF₄][−]. ³³ Sulfonate groups on the side chains can attract positively charged species to reduce the average transport of cations inside the hydrophilic channels of Nafion. [BF₄][−] will be more inert than the more Lewis-basic [TfO][−] anion ³³ and thus will travel more freely. On the cation side, [C₂mim]⁺ or [C₄mim]⁺ will tend to equally pair with free [TfO][−] and fixed $-\text{SO}_3^-$ groups on the polymer chain due to the similarity in chemical structures between these two anions. Thus, in TfO-based ILs, cations and anions are more likely to move in pairs (than BF₄-based ILs) and show less enhanced anion diffusion. One may suppose that fast diffusing [F][−] may be generated, which might skew our diffusion measurements in the BF₄-based systems. We emphasize that there is no evidence of hydrolysis for [BF₄][−] inside ionomers at high water content since we obtained a single ¹⁹F spectral peak (no other observed ¹⁹F anion signals) and a single diffusion coefficient over the full range of membrane hydration. It is also worth mentioning that even at high water content, interactions (coulombic, ion packing) between cation and anion are only partially screened by water molecules for ILs inside ionomers, as compared to the case of free ILs. This effect is illustrated by the diffusion ratio of water to anion as shown in Figure 6. Here the Stokes–Einstein equation can aid in understanding ionic interactions in our water–IL–ionomer systems. As mentioned earlier, our measured apparent diffusion coefficients exhibit no dependence on diffusion length scale, which suggests the diffusion results on both water and ions should equally reflect global (averaged over ~ 1 μm) information on structures as sampled by diffusants. On the basis of this consideration, the global viscosity should affect both ions and water

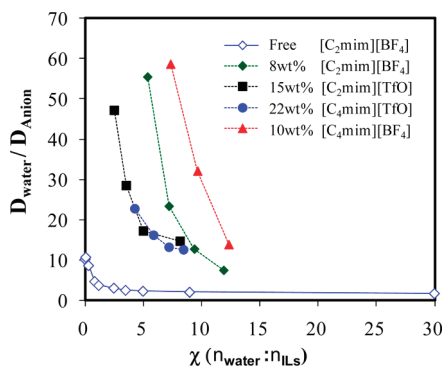


Figure 6. Diffusion ratio of water to anion ($D_{\text{water}}/D_{\text{anion}}$) as a function of water content χ_{water} for free $[\text{C}_2\text{mim}][\text{BF}_4]$ and for ILs inside Nafion membrane. Even at high hydration ($\chi_{\text{water}} \sim 9$), water diffusion in Nafion is $>10\times$ faster than anion diffusion, as compared with free IL, where water is only $2\times$ faster. The difference between D_{water} and D_{anion} drastically increases as χ_{water} decreases, indicating the interactions among ions and ion-charged polymer at low χ_{water} are more dynamically constrained than at high χ_{water} , while water moves relatively freely.

molecules in the same way. Thus, one can rule out the factor η in the Stokes–Einstein equation and compare the diffusion ratio ($D_{\text{water}}/D_{\text{anion}}$ or $D_{\text{water}}/D_{\text{cation}}$) inside ionomers with the values for free ILs to understand the degree of ion association. For example at $\chi_{\text{water}} = 9$, the diffusion ratio of water to anion $D_{\text{water}}/D_{\text{anion}} \approx 12$, in contrast to the corresponding values for free water–IL mixture ($D_{\text{water}}/D_{\text{anion}} \approx 2$) mentioned earlier. Moreover, as shown in Figure 6, in comparison with free ILs, $D_{\text{water}}/D_{\text{anion}}$ inside the ionomer increases drastically as the hydration level decreases, indicating progressively enhanced ionic interactions that strongly impact the translational motion of ions. As a result, these interactions among ions and ion-lined polymer nanochannels critically determine the transport properties of IL-based materials and devices at both high and low water content.

We further examine ion transport inside ionic polymer membranes at low water content. In order to further assess specific ionic associations as a function of hydration and IL uptake, Figure 7 summarizes systematic results regarding cation and anion diffusion vs water content for different types and uptakes of ILs. Surprisingly, D_{cation} becomes substantially faster than D_{anion} at low water content for C_2mim -based ILs, where $D_{\text{cation}}/D_{\text{anion}}$ approaches 2.5 for $[\text{C}_2\text{mim}][\text{TfO}]$ and 3.0 for $[\text{C}_2\text{mim}][\text{BF}_4]$. This clearly contradicts the conventional expectation that cations will diffuse slower in an anionic matrix due to drag from the polymer-fixed sulfonate groups. Again, considering that both cations and anions exhibit nonrestricted diffusion behavior in the same phase, differences in viscosity experienced by cations and anions can be ruled out, and specific ionic interactions should account for these phenomena. In addition, as compared to the diffusion ratios for free ILs, these results strongly demonstrate the formation of ionic aggregates with specific features,³⁴ based on which we postulate the prevalence of anion-rich ionic aggregates inside the ionic polymer at low water content. The use of ion aggregation to explain the behavior of concentrated ionic solutions has a long history, both in solutions³⁵ and inside polymers.³⁶ For ion-dense fluids such as these ILs at low hydration, many-body effects will likely be prevalent and thus difficult to conceptualize. With this in mind, we begin by attempting to understand the problem in terms of ionic aggregates.

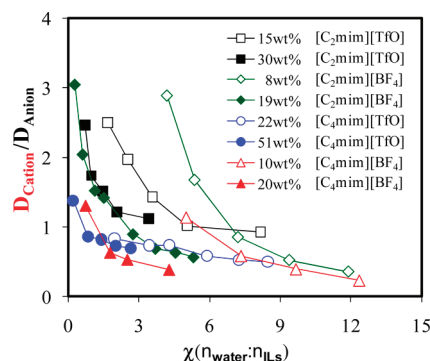


Figure 7. Summary of diffusion ratio $D_{\text{cation}}/D_{\text{anion}}$ as a function of water content χ_{water} for various types and uptakes of ILs inside Nafion membranes. Anion diffusion dramatically accelerates at higher hydration levels for BF_4 -based ILs, and $D_{\text{anion}}/D_{\text{cation}}$ reaches 3 and 4 for $[\text{C}_2\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$, respectively. At low hydration, cation diffusion becomes substantially faster than anion diffusion for $[\text{C}_2\text{mim}][\text{TfO}]$ and $[\text{C}_2\text{mim}][\text{BF}_4]$, where $D_{\text{cation}}/D_{\text{anion}}$ reach 2.5 and 3.1, respectively.

We explain our rationale for aggregation as follows. Considering the NMR experimental time scale (~ 100 ms) during which ionic clusters form and disassociate due to fast dynamic processes (\sim ns to 100 ps), our NMR measurements on ion transport (cation or anion) represent average diffusion behaviors of all the ionic species (single, dipole, triple, etc.) involved, which can be interpreted by the following equations:

$$D_{\text{Average}}^+ = \sum_i x_i^+ D_i^+ \quad (4)$$

$$D_{\text{Average}}^- = \sum_i x_i^- D_i^- \quad (5)$$

where D_{Average}^+ and D_{Average}^- are average cation and anion diffusion coefficients measured by NMR experiments. D_i^+ and D_i^- correspond to the diffusion of individual ionic species that contain cations and/or anions, e.g., single ions, dipoles, triple ions, etc. Similarly, x_i^+ and x_i^- represent the mole fraction of each type of ionic cluster that contains cations and/or anions. We are working toward a quantitative aggregation model using these concepts, but we require more data and most likely molecular dynamics simulations as further inputs. To illustrate these concepts, Figure 8 depicts a simple model in which only four types of ionic species are considered: single, dipole, triple, and quadrupole ions. According to this model, anionic triple ions dominate at low hydration and lead to more isolated (single) cations, resulting in enhanced cation diffusion. Dipoles and quadrupoles do not produce imbalanced average D ratios since cations and anions are symmetrically distributed, and cationic triple ions will be less likely to exist as they contribute negatively to the observed D_{Average}^+ . In other words, we conclude that anionic aggregates with reduced diffusion are prevalent at low hydration, while the presence of more isolated cations results in faster cation diffusion on average.

While we have not revealed the fundamental molecular mechanisms driving formation of these anionic aggregates, recent bending tests on $[\text{C}_2\text{mim}][\text{TfO}]$ based ionic polymer actuators support our aggregation model. With applied DC voltage, the actuator bends toward the anode at short times, followed by reversed bending back toward the cathode at longer

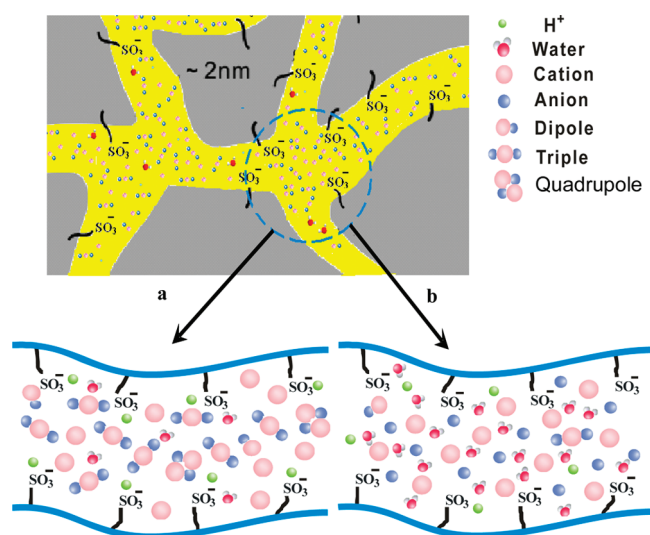


Figure 8. Ion associations of ILs inside the ~ 2 nm hydrophilic channels of Nafion membrane. At low water content (a), negatively charged triple ions are prevalent due to strong electrostatic attractions among charged species, leaving more isolated cations and resulting in enhanced cation diffusion on average. At high water content (b), water dramatically reduces electrostatic interactions among cations and anions and leads to ion disassociation. Anions (especially $[\text{BF}_4]^-$) are released from local electrostatic networks and move relatively freely, while sulfonate groups fixed to polymer side chains attract cations and thus slow their average translational motion.

times and with greatly enhanced bending curvature.^{37,38} This is consistent with (1) cations transporting quickly to accumulate at and swell the cathode and (2) anionic aggregates transporting slowly to accumulate at the anode, and then resulting in increased swelling due to their larger size. Regarding specific intermolecular interactions, we emphasize that we do not observe significantly higher $D_{\text{cation}}/D_{\text{anion}}$ for $[\text{C}_4\text{mim}]^+$ based ILs ($[\text{C}_4\text{mim}][\text{TfO}]$ or $[\text{C}_4\text{mim}][\text{BF}_4]$) at low water content χ_{water} . This further signifies that anionic aggregation caused by specific molecular packing strongly depends on the structural features of the cation. When comparing $[\text{C}_2\text{mim}]^+$ with $[\text{C}_4\text{mim}]^+$, factors such as shape anisotropy (e.g., planar or rodlike structures), charge distribution, and conformational flexibility (short alkyl chain of the $[\text{C}_2\text{mim}]^+$ vs $[\text{C}_4\text{mim}]^+$ chain) should strongly impact and determine molecular packing among cations and anions. Finally, in correlation with practical mechanical actuator studies, these trends qualitatively correlate with empirical observations that $[\text{C}_2\text{mim}][\text{TfO}]$ and $[\text{C}_2\text{mim}][\text{BF}_4]$ appear to form the best performing IL-based polymer actuators.^{6,39} If anions and cations conduct equally well in an ionomer membrane, electrolyte efficiency is greatly diminished, since anion conduction can cancel out cation conduction. This work provides further insight into the mechanism of ion conduction inside an ionic polymer membrane and may facilitate design of new types of ion containing polymers.

4. CONCLUSIONS

We have investigated cation and anion diffusion of four related ILs ($[\text{C}_2\text{mim}][\text{TfO}]$, $[\text{C}_2\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{mim}][\text{TfO}]$, and $[\text{C}_4\text{mim}][\text{BF}_4]$) both outside and inside Nafion membranes, and as a function of water content. With increasing hydration of free ILs, the ratio of cation to anion diffusion coefficients

reverses, then plateaus to values consistent with expected hydrodynamic radii ratios for cations and anions ($r_{\text{cation}}/r_{\text{anion}} = 1.4$ for $[\text{C}_2\text{mim}][\text{BF}_4]$ and 1.1 for $[\text{C}_2\text{mim}][\text{TfO}]$). When ILs are absorbed into an ionic polymer membrane, a drastically different ionic environment, associations are modulated by relative anion basicity (protonation) and drag from the fixed $-\text{SO}_3^-$ anions lining the polymer's hydrophilic channels. Cations are substantially faster (up to $3\times$) at low water content inside membranes and these observations may be explained by a simple aggregation model, indicating an excess of negatively charged triple ions. At high water content, this trend reverses to give faster isolated anions (up to $4\times$), while cation transport is slowed by interactions with immobile SO_3^- anions. Investigating such cation/anion interactions provides insight into these complex fluids and informs design strategies for IL electrolyte applications such as batteries and polymer-based "artificial muscle" mechanical actuators. We are working toward quantitative models to assess relative aggregate populations, as well as chemically specific measurements of E-field-driven ion motion.

■ ASSOCIATED CONTENT

S Supporting Information. ^1H and ^{19}F NMR spectra of ILs inside ionomers and ^{19}F NMR spectra for free ILs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lmadsen@vt.edu.

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