## **Relating Geometric Nanoconfinement and Local Molecular Environment to**

# **Diffusion in Ionic Polymer Membranes**

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## Abstract

Understanding structure-diffusion relationships in ionic polymer membranes not only illuminates fundamental mechanisms for membrane transport, but also informs further membrane development. In this study, we employ NMR diffusometry and molecular dynamics (MD) simulations to investigate diffusion coefficients and activation energies of diffusion  $(E_a)$  for both a lithium-form perfluorosulfonic acid membrane and aqueous solutions of lithium triflate. NMR shows that, at high water/ion molar ratio ( $\lambda$ ),  $E_a$  for water diffusion is slightly lower in the membrane than in solution. Conversely, membrane transport exhibits much higher  $E_a$  at low hydration as compared to solutions. MD simulations of a model system consisting of carbon nanotubes with varying diameter reveal that  $E_a$  of diffusion clearly relates to both the geometric nanoconfinement of the hydrophilic pathways in the membrane as well as the local molecular environment. These results demonstrate that  $E_a$  of diffusion can serve as a revelatory tool for the study of molecular transport processes and the coupling of morphology with transport at the nanoscale. This study thus provides new insights and new experimental and computational models for understanding transport in a wide range of polymer membranes, such as those used in molecular separations applications.

Keywords: PFSA membrane, Activation energy of diffusion, NMR, MD simulations

## Introduction

A key function of ionomer membranes is their permselectivity, due to which ionomer membranes find applications in fields ranging from fuel cells to water purification.<sup>1-2</sup> While ionomer membranes have been developed and used for more than half a century, thorough fundamental understanding is still lacking regarding how transport in these membranes relates to their structure. A major challenge in our understanding emerges from the nanostructure of the ionomer membranes.<sup>2-3</sup> While some debates still persist, there is substantial consensus on key structural features of ionomer membranes such as perfluorosulfonic acid (PFSA) membranes. PFSA membranes consist of hydrophobic polymer backbones and ionic sidechains, which phase separate on the nanometer scale into hydrophobic and ionic domains.<sup>4-12</sup> Researchers have intensively studied PFSA membranes due to their superior transport properties as well as chemical and mechanical stabilities. Upon hydration, the membrane's ionic domains conduct water and ions, highlighting the importance of the hydrophilic channels on molecular transport.

Knowledge of how ionic domains regulate transport in ionomer membranes is not only valuable as fundamental science, but is also crucial for enhancing membrane performance. Water transporting through ionic domains experiences the tortuous network of these domains,<sup>13-14</sup> geometric confinement of the hydrophilic channels,<sup>15</sup> and intermolecular interactions with the confinement medium.<sup>15</sup> Optimizing ionomer morphology and understanding morphology-transport relationships have attracted great efforts in the past few decades.<sup>14, 16-25</sup> Meanwhile, understanding the relation between nano-scale structure and membrane transport remains challenging due to the difficulty in probing nanoscale dynamics. Berrod et al. studied nanoscale motions of water and protons in PFSA membranes with Quasielastic Neutron Scattering.<sup>26-27</sup> Habenicht et al.,<sup>28-29</sup> Clark et al.,<sup>30-31</sup> and Zelovich et al.<sup>32</sup> studied transport of proton and small

molecules under nanoconfinement with ab-initio molecular dynamics simulations. Previous studies outside the field of polymer membranes demonstrated that nanoconfinement can affect the dynamics and states of water molecules. Klameth et al.<sup>33</sup> and Geske et al.<sup>34</sup> observed retarded water dynamics near neutral confinement structures. Youssef et al.<sup>35</sup> and Gallo et al.<sup>36</sup> observed glassy behavior of water molecules under sub-nanometer hydrophilic confinement. Floquet et al.<sup>37</sup> reported crystallization of water at room temperature in the nanopores of AIPO<sub>4</sub>-5 zeolite. Experimental<sup>38-40</sup> and computational<sup>39, 41-42</sup> work has also revealed the formation of ordered water in carbon nanotubes and graphene nanocapillaries.

While studying confinement effects on diffusion of mobile species in PFSA membranes, most previous work has focused on the diffusion coefficients. Here we leverage a novel probe quantity, the activation energy ( $E_a$ ) of diffusion, to study the effects of nanoconfinement on mobile species. Lingwood et al.<sup>15</sup> and Kidd et al.<sup>43</sup> reported that the  $E_a$  of diffusion was similar between bulk liquid and liquid confined within structures larger than a few nanometers. The authors asserted that the  $E_a$  of diffusion arises from molecular-scale interactions, which are on the lengthscale of nanometers and timescale of picoseconds.  $E_a$  relates to the energetic costs for a molecule to diffuse through a medium, and is therefore naturally sensitive to the strength of interactions between the diffusing species and the medium. Moreover,  $E_a$  of diffusion is sensitive to the size of nanoconfinement,<sup>15</sup> making it a quantitative tool to study the confinement effect in ionic domains of ionomer membranes. We extract  $E_a$  of diffusion from the Arrhenius equation

$$D = D_0 e^{-\frac{E_a}{RT}} \tag{1}$$

where *D* is the diffusion coefficient,  $D_0$  is the preexponential factor, *R* is the gas constant, and *T* is absolute temperature. While Kreuer et al.,<sup>44</sup> Hammer et al.,<sup>45</sup> and Galitskaya et al.<sup>46</sup> reported

 $E_a$  of water in PFSA membranes as a function of membrane hydration, a deep understanding of the connection between  $E_a$  and the nano-scale environment inside ionomer membranes is currently lacking.

In this work, we aim to contribute to the description by adding to the understanding of the relationship between ionomer nanostructure and the dynamics of water moving through it, via use of the  $E_a$  of diffusion. In order to move beyond previous work,<sup>15</sup> we have combined NMR diffusometry and molecular dynamics (MD) simulations to investigate the Ea of water diffusion in a model PFSA membrane (Nafion®). This system serves as a benchmark to understand transport in nanostructured conducting polymer membranes. Using NMR, we measure  $E_a$  of water diffusion in aqueous lithium triflate solutions and lithium-form PFSA. We chose lithiumform PFSA in order to minimize contributions from the Grotthuss diffusion mechanism on proton transport, as well as to separately investigate diffusion of the lithium ion. In order to focus on nanoconfinement effects in this manuscript, here we report only results of water diffusion. Using MD simulations, we separately model the effects of nanoscale geometric confinement and molecular environment in the hydrophilic domains of ionomers by incorporating models including confined water in carbon nanotubes and mixtures of water and Nafion sidechains. We report the correlation between the  $E_a$  of diffusion and nanoscale confinement/environment. These results reveal the richness our novel probe,  $E_a$  of diffusion, and shed light on how nanostructure and local molecular interactions regulate transport of small molecules and ions inside ionic polymer membranes.

## Experimental

*Materials.* Lithium triflate (LiOTf) was purchased from Strem Chemicals (USA) with 99% purity and used as received to make aqueous solutions. Solution concentrations were determined

by mass ratios. Solutions with  $\lambda$  values (molar ratio of water molecules to lithium ions) of 3.0. 4.0, 5.0, 6.1, 9.0, 12, 17, and 20 were prepared. The solutions were flame-sealed into NMR tubes to maintain concentration. Ammonium-form Nafion 117 (PFSA) obtained from GasHub (Singapore) was pretreated using the following procedures. The membrane was washed in 3%  $H_2O_2$  at 80°C for 1 hour followed by another hour in lightly boiling HPLC  $H_2O$ . The yellowish membrane turned colorless during this process. Then, the membrane was treated with 0.5 M H<sub>2</sub>SO<sub>4</sub> at 80°C for 1 hour followed by three rinses in lightly boiling HPLC H<sub>2</sub>O. To fully transform the ammonium-form membrane into lithium-form membrane, the membrane was placed in 1 M LiOH aqueous solution at 80°C for 2 hours followed by rinsing in lightly boiling HPLC H<sub>2</sub>O for another 2 hours. This process was repeated twice to ensure exchange of ammonium ions with lithium ions. The membrane was cut into small slices (2.5 mm x 10 mm) and 6-8 layers were stacked together to enable rapid NMR measurements with high signal-tonoise ratio (SNR). The membrane stack was placed in HPLC water for at least 48 hours to achieve full hydration. To attain variable hydration ( $\lambda$ ), the fully hydrated membrane was dried in air for varying times, followed by mass determination. For NMR measurements, the membrane stack was tightly wrapped in plastic film and Teflon tape before placing it into a plastic cell manufactured in house from Delrin.<sup>18</sup> The Delrin cell was machined to fit the size of the stacked PFSA sample so that the dead volume was minimal. The Delrin cell was sealed by silicone grease after loading the membrane, which was subsequently equilibrated in the sealed cell for 2-6 hours before measurements. The membrane was weighed again after measurements. At the end of all measurements, a dehydrated membrane was obtained by heating the membrane at 105 °C under vacuum for two days. The mass of membrane after measurements  $(m_{hydrated membrane})$  and the mass of dehydrated membrane  $(m_{dehydrated membrane})$  were used

in the determination of  $\lambda$ . The water/ion molar ratio, denoted by  $\lambda$ , was determined by the following equation:

$$\lambda = \frac{m_{hydrated\ membrane} - m_{dehydrated\ membrane}}{m_{dehydrated\ membrane}} \times \frac{EW_{Nafion}}{M_{w,H_2O}}$$
(2)

where  $EW_{Nafion}$  is the equivalent weight of PFSA (Nafion 117 - 1100 grams dry polymer/mole sulfonate groups), and  $M_{w,H_2O}$  is the molecular weight of water.  $\lambda$  values ranging from 3.0 to 20 were prepared for the membrane measurements.

*NMR measurements.* NMR measurements for both aqueous lithium triflate solutions and lithium-form PFSA were performed on a 400 MHz Bruker Avance III (9.4 T) spectrometer, and the Diff60 diffusion probe (Bruker Biospin, Billerica, MA) using a maximum gradient strength of 2400 G/cm. *D* of water was measured with a 5 mm <sup>1</sup>H coil and the pulsed-gradient stimulated echo (PGSTE) sequence. The PGSTE pulse sequence measures NMR signal intensity as a function of magnetic field gradient parameters. In these experiments, the normalized signal intensity  $I/I_0$  as a function of varying field gradient strength *g*, was fitted with the Stejskal-Tanner equation<sup>47-48</sup>

$$I/I_0 = e^{-\gamma^2 D g^2 \delta^2 (\Delta - \frac{\delta}{3})}$$
<sup>(3)</sup>

where  $\gamma$  is the gyromagnetic ratio of the probe nucleus, *D* is the self-diffusion coefficient (diffusion will be used interchangeably with self-diffusion throughout this article),  $\delta$  is the duration of the gradient pulse, and  $\Delta$  is the time between gradient pulses, also called the diffusion time. For lithium triflate solutions, gradient pulse durations  $\delta$  of 1.5 - 2 ms, diffusion times  $\Delta$  of 20 - 40 ms, PGSTE experiment repetition times of 1 - 4 s, and maximum gradient strengths *g* of 40 - 100 G/cm were applied to achieve over 80% attenuation in signal intensity, and with 8 - 32scans per gradient step to obtain sufficient SNR . For diffusion measurements of lithium form PFSA,  $\delta = 1.5$  ms,  $\Delta = 20$  ms, repetition times of 0.3 - 0.5 s, and maximum *g* of 200 - 1800 G/cm were used. Temperature calibration was done with neat ethylene glycol. Pure ethylene glycol exhibits two peaks in proton NMR, and the chemical shift difference ( $\Delta\delta$ ) between the two peaks is related to the absolute temperature by<sup>49</sup>

$$T = -99.00 \times \Delta\delta + 463.00 \tag{4}$$

 $E_a$  of diffusion is determined by measuring *D* as a function of temperature. Five temperatures were used for each membrane measurement. The temperature range for the measurements of lithium-form PFSA was 300 K to 310 K. The temperature range was chosen to minimize any effect of the dependence of  $E_a$  on temperature. Measurements for lithium triflate solutions were performed over a slightly expanded temperature range (300 – 330 K, five temperatures within 300 – 310 K, and another five temperatures between 310 K and 330 K) to facilitate comparison with both experimental and computational results.

*MD simulations.* All MD simulations were performed using the GROMACS 5.0.5 package.<sup>50-52</sup> Various simulation models were used to cleanly separate contributions from geometric confinement and molecular environment to the  $E_a$  of diffusion (**Figure 1**). The model designed to probe nanoconfinement consists of a 20 nm single wall carbon nanotube (CNT) (**Figure 1(a)**). The CNT is hydrated by 4 nm cubic water reservoirs containing a total of 4096 rigid three-site SPC/E<sup>53</sup> water molecules. A graphene sheet prevents hydration of the CNT outer wall. The diameter of the CNT was varied from 1.2 to 2.5 nm to explore confinement dimension. Aqueous lithium triflate solutions (**Figure 1(b**)) were modeled with the TIP4P/2005 rigid four-site water model.<sup>54</sup> The level of hydration was adjusted by fixing the number of ions and varying the number of water molecules to obtain  $\lambda$  values of 3, 4, 5, 6, 9, 12, and 17. The diffusion coefficients calculated with this model were directly compared to experimental NMR

measurements to validate the force field. The effect of intermolecular effects on water diffusion through PFSA membranes was investigated with an aqueous solution of PFSA sidechains and lithium counterions (**Figure 1(c)**). The number of TIP4P water molecules was varied while maintaining a fixed number of ions to obtain  $\lambda$  values of 3, 4, 5, 6, 9, 12, and 15. This model was instrumental in revealing effects from both of the sidechain dynamics and the nanoscale phase separation in PFSA membranes. The effect of sidechain dynamics was probed by either fixing the anchor sidechain atoms to random points in the simulation box or by allowing full freedom of motion. To study the influence of nanoscale phase separation, solutions were created in which the sidechains were aggregated into domains or uniformly dispersed in water.

Diffusion coefficients for all systems were computed from 300 K to 340 K at 10 K intervals. Fits of the diffusion coefficients to an Arrhenius equation provided  $E_a$  of diffusion. All models were equilibrated at constant temperature and pressure (1 bar) for 1 – 5 ns before production NVT calculations were run for 1 – 20 ns. Diffusion coefficients were extracted from the linear region of mean square displacement (MSD) plot vs. time<sup>55</sup>

$$D = \frac{MSD}{2nt} \tag{5}$$

where D is the diffusion coefficient, t is the diffusion time, and n is the dimension factor (2 for one-dimensional diffusion, 4 for two-dimensional diffusion, and 6 for three-dimensional diffusion).



**Figure 1.** Simulation models involved in this work. The model shown in (a) consists of a hydrated carbon nanotube with diameter varying from 1.2 - 2.5 nm, designed to probe the effects of nanoconfinement. Model (a) was used to explore nanoconfinement effects. Model in (b) represents an aqueous lithium triflate solution, which was used in force field optimization and to probe intermolecular effects. An aqueous solution of PFSA sidechains and Li counterions ( $\lambda = 4$ ) is displayed in (c), which was designed to additionally investigate the effect of molecular environment.

*Force field optimization.* Sample calculations that used standard force-field parameters for lithium triflate solutions showed large deviations between calculated and measured diffusion coefficients. In order to improve the accuracy of the force-field parameters, NMR diffusometry measurements on the lithium triflate solutions were used to benchmark and optimize the simulations. A number of force fields exist for water molecule, and some of them, such as TIP4P/2005 and OPC models,<sup>54, 56</sup> are well tailored for predicting diffusion properties at ambient conditions. Taking directly the OPLS-AA force field for the bonding interactions in triflate,<sup>57</sup> comparison with NMR diffusometry measurements in lithium triflate aqueous solutions were

used to optimize the non-bonding terms. Starting with literature values,<sup>58-59</sup> a set of partial charges for triflate were developed that nicely reproduced NMR experiments using a trial-anderror approach. The force field of the membrane sidechains was developed based on the literature<sup>59</sup> and the modified force field for lithium triflate. Detailed force field parameters can be found in the SI.

## **Results and discussion**

#### Water diffusion measurements in bulk and under nanoconfinement.

We measured the diffusion coefficient of water ( $D_{water}$ ) in both lithium-form PFSA and in lithium triflate solutions over the same range of water-ion mole ratio ( $\lambda$ ).  $D_{water}$  in the bulk salt solutions serves as a hydration-dependent chemical sibling of the PFSA hydrophilic channels, but without the geometric confinement imposed by the nm-scale channels in the membrane. The measured  $D_{water}$  values in the membrane are 3 – 20 times smaller than those in the aqueous solutions over the hydration-level range probed (**Figure 2(a)**). Based on the diffusion time of the NMR experiment, the diffusion length (root-mean-square displacement) of water molecules in the membrane is 1 – 10 µm. Thus,  $D_{water}$  in the membrane is sensitive to not only the local molecular environment but also the long-range membrane morphology.<sup>14-15</sup> We note that we have previously shown that the PFSA membrane shows no variation of  $D_{water}$  as a function of the accessible diffusion times and lengths,<sup>15</sup> and that we verified this diffusion-time independence for the present membrane.

Two regions are evident in the  $E_a$  of water plots as a function of hydration for the two materials (**Figure 2(b)**). At high  $\lambda$  (7 – 20),  $E_a$  of water is very similar for the membrane and the solutions. This similarity indicates that water within the membrane is behaving locally as it does in the bulk at high hydration. Note that, in the high- $\lambda$  region,  $E_a$  measured in the membrane is

slightly lower than that of salt solutions and approaches that of liquid water, which is consistent with previous work on acid-form PFSA.<sup>15</sup> Another behavior appears at low  $\lambda$  (3 – 7), where  $E_a$  of diffusion in the membrane becomes substantially larger than in the bulk salt solutions.



**Figure 2.**  $D_{water}$  at 30 °C (a) and  $E_a$  of water (b) in LiOTf solution and in Li<sup>+</sup>-form PFSA as a function of water/ion ratio  $\lambda$ .  $D_{water}$  in the membrane is always lower than that in LiOTf solution.  $E_a$  in the membrane is substantially higher than that in the salt solution at low  $\lambda$ , and slightly lower at high  $\lambda$ . Errors in  $D_{water}$  are  $ca. \pm 3\%$ , and errors in  $E_a$  are  $ca. \pm 5\%$ .

Examining the environmental details in the LiOTf solutions and the hydrophilic domains of lithium form PFSA, we identify a few major differences. First, transport of water and ions is nanoconfined in the membrane but free in aqueous solutions. Second, the polymer's ionic sidechains in the ionomer membrane are phase-separated on the nanometer scale, while in bulk solutions the ionic groups are fully mixed. The difference in the  $E_a$  variation with hydration behaviors likely result from these structural differences. As previously mentioned, nanoconfinement in a liquid will lead to unique properties as compared to the bulk state. To delve deeper into the influence of nanoconfinement on  $E_a$  of diffusion, and to try to separate this effect from the molecular environment that diffusing molecules encounter, we turn to molecular simulations.

## Simulation of water diffusion under nanoconfinement.

We simulate the effect of geometric restriction on the  $D_{water}$  and  $E_a$  by confining water molecules in the nanometer-scale environment of the carbon nanotube (CNT) shown in **Figure 1(a)**. We vary the CNT diameter in order to mimic the changing ionic domain size with water content in the PFSA.<sup>12</sup> In Figure 3, the  $D_{water}$  and  $E_a$  plots show two distinctive regions, similar to the trend seen in the membrane experiments. The first region appears when the tube diameter is above 1.3 nm. In this region, simulations of the CNT model and bulk water show nearly identical  $E_a$  of diffusion while the diffusion coefficient of the confined water is slightly lower than in bulk liquid. The minor difference in  $D_{water}$  and similar  $E_a$  indicates that the confined water can behave *locally* like bulk water even when the confinement dimension is a few nanometers. Nevertheless, the behavior of water in the CNT becomes distinctively different from that of liquid water as the tube diameter drops below 1.3 nm. In this region,  $D_{water}$  in the CNT sharply decreases while  $E_a$  of the confined water sharply increases with respect to liquid water.



**Figure 3**.  $D_{water}$  (a) and  $E_a$  of water (b) from MD simulation of the CNT model in **Figure 1(a)**. Water diffusion in the CNT mimics that of free liquid when the CNT diameter is above 1.3 nm. We observe ordering of water molecules in the CNT when the tube diameter reaches 1.3 nm, below which both the  $D_{water}$  and  $E_a$  change drastically.

Further analysis of the simulations reveals that water molecules become ordered at low tube diameters (Figure S3). As previously mentioned, formation of ordered water under nanoconfinement has been recognized both experimentally<sup>38-40</sup> and computationally,<sup>39, 41-42</sup> not only in the cylindrical geometry<sup>41</sup> imposed by the CNT but also in a planar geometry.<sup>39</sup> Thus, nanoconfinement may in general lead to the formation of slow-diffusing, solid-like water. Even though the ordering of water in the CNT is apparently similar to that in a solid, the ordered water still exhibits relatively fast diffusion:  $D_{water}$  is less than a factor of 10 smaller than that of liquid water. We hypothesize that as the water molecules experience increasing confinement in the CNT or in the membrane, the potential energy governing water molecule motion becomes more *orientationally dependent*. That is, the potential energy minima vary as a function of the water molecule orientation. This localizes the water molecules in energy minima flanked by steep potential energy surfaces, which have the effect of restricting their random diffusion. A similar potential-energy argument was presented by Horstmann et al.<sup>60</sup> for water under neutral confinement. We include an initial discussion of this effect below, and we are working toward a more comprehensive view of such energetic effects in a future manuscript.

To validate this hypothesis regarding an anisotropic potential energy surface, we calculated the potential energy of water molecules in the CNT model (**Figure S4**) as a function of the z-axis coordinate of molecules. We compute potential energy based on short-range intermolecular interactions with a 2.4 nm cut-off distance while we ignore long-range electrostatic interactions. The water in a 1.248 nm-diameter CNT model, which shows the highest  $E_a$  in **Figure 3(b)**, shows the lowest potential energy. Thus, the ordered water is in a low-energy configuration. Although we cannot directly compare potential energies to  $E_a$  values, we note that the difference in potential energy between ordered water and disordered liquid-like

water is much smaller in magnitude than the difference in  $E_a$  values, reinforcing that  $E_a$  of diffusion probes the energetics of water dynamics through the surrounding molecular medium. We believe the  $E_a$  of diffusion relates to the energy required to disrupt the local interactions and move beyond the instantaneous hydration shell of a given diffusing molecule. For liquid water, the hydration shell of a water molecule is fleeting, signifying a relatively isotropic interaction potential and low  $E_a$  of diffusion. For a water molecule ordered inside a narrow CNT or a slightly hydrated ionomer membrane, the hydration shell is more permanent, suggesting a more stable configuration and a larger  $E_a$  of diffusion.

We now discuss these results in the context of diffusion in real ionic polymer membranes. The hydrophilic domains in hydrated PFSA are around 1 - 3 nm in size, and this diameter varies strongly with  $\lambda$ . We expect that confinement will affect the experimental  $E_a$  of diffusion in membranes at low  $\lambda$ . The sharper and steeper upturn in the  $E_a$  of diffusion for the CNT simulations compared to the trend seen in the membrane most likely is a consequence of the geometric homogeneity of the CNT model. This uniformity of diameter is surely not present in the more tortuous and irregular hydrophilic channels of PFSA membranes (**Figure 4(a)**). We propose that this geometric inhomogeneity of hydrophilic domains gives rise to a *distribution of water configurations on the lengthscale of nanometers*, including some that are analogous to the ordered configurations present in the CNT model, as well as liquid-like configurations (**Figure 4(b**)). Note the lengthscale probed by NMR diffusometry is around 1 µm. Thus, the measured diffusion coefficient becomes the average of all configurations and local geometries, which makes the variation in the  $E_a$  of diffusion with  $\lambda$  (and nanochannel size) more gradual than in the CNT model, which probes a uniform tube at a significantly smaller lengthscale.



**Figure 4.** (a) Tortuous hydrophilic domains in PFSA membranes on the lengthscale of nanometers. Blue represents the hydrophilic domains while yellow represents polymer matrix. The size of hydrophilic domains varies from region to region. Part (b) highlights the oval region in panel (a), showing that ordered (solid-like) water and disordered (liquid-like) water can coexist in the hydrophilic domains. At high hydration, solid-like water becomes less abundant due to the expansion of all hydrophilic domains.

## Effects of molecular environment on diffusion.

We now turn our attention to probing the effects of local molecular environment on  $D_{water}$ . Two characteristic features of the hydrophilic domains in ionomer membranes are their nanoscale phase separation and the fact that the sidechains with pendant ions are anchored to the backbones. To understand the effect of both of these features on water transport, we employ the salt solution simulation model shown in **Figure 1(c)**. This model consists of a solution of lithium ions and sidechains of PFSA ((C)O-CF<sub>2</sub>-CF(CF<sub>3</sub>)-O-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>3</sub><sup>-</sup>). To gain further insight using this model, we conduct a range of simulations in which we control both the level of phase separation and the physical anchoring of the sidechain.

Figure 5 depicts the various simulation schemes adopted with these models. We first create a simulation box containing randomly dispersed water molecules, Li ions, and PFSA sidechains at a variety of  $\lambda$  values. We subsequently restrict the sidechain motion by immobilizing (at arbitrary locations in the box) the carbon atom that would anchor the sidechain to the polymer backbone in the membrane. In order to achieve a nanoscale phase-separated model, the randomly dispersed system (with free sidechains) is equilibrated (NPT ensemble) for sufficient time (10 – 20 ns) to ensure that the density and energy of the system reaches equilibrium (**Figure S5**). The amphiphilic nature of the sidechains leads to phase-separated systems, which is more thermodynamically favorable than the randomly dispersed system.



**Figure 5.** (a) Simulations of randomly dispersed and phase-separated models of ionomer sidechain solutions. Equilibration of the dispersed system (NPT ensemble) leads to a phase-separated system. The  $E_a$  values shown in panel (a) correspond to  $\lambda = 4$ . Higher  $\lambda$  values yield similar trends, but with smaller differences in  $E_a$ . (b) shows the difference between fixed sidechain and free sidechain. In the fixed-sidechain scenario, we immobilize the anchored carbon (shaded in red) in the sidechain while keeping all other atoms (shaded in green) free. Errors in computed  $E_a$  values are  $ca \pm 2$  kJ/mol.

**Figure 6** shows  $D_{water}$  and  $E_a$  of diffusion for the randomly dispersed and phase-separated models corresponding to **Figure 5(a)** with both free and fixed sidechains. Within the dispersed systems, limiting the dynamics of the sidechain by fixing the sidechain anchor atom increases  $E_a$ compared to the free sidechain scenario. While the effect diminishes as  $\lambda$  increases, we still observe substantial differences in  $E_a$  at  $\lambda = 15$ . In the phase-separated system, the  $E_a$  is consistently lower than that of the randomly dispersed system. The dispersed system has the same composition and nearly identical density as the phase-separated system, yet their  $E_a$  values are distinctly different.



**Figure 6.**  $D_{water}$  (a) and  $E_a$  (b) from MD simulations of aqueous solutions of Li<sup>+</sup> and membrane sidechains (model in **Figure 1(c)**). Solid circles represent results for the randomly dispersed model while open circles are for the phase-separated model. Phase-separation leads to elevation of  $D_{water}$  and decrement of  $E_a$ . Note that the  $E_a$  difference between free and fixed sidechain scenarios, which is distinct in randomly dispersed systems, becomes much weaker in the phase-separated system.

To understand why  $E_a$  in the phase-separated system is significantly lower than in the randomly dispersed model, we analyzed radial distribution functions (RDFs) for both systems. The RDFs in **Figure 7** reveal that the local environment of water varies markedly for the phaseseparated and randomly dispersed systems, with the phase-separated system showing an increased density of neighboring water molecules in the hydrophilic phase compared to water in the dispersed system. Comparing these two systems in terms of both RDFs (local molecular environment) and  $E_a$  (transport energetics), we see that a water-rich neighboring environment correlates with a lower  $E_a$  of water diffusion as compared to a local environment with an increased average presence of membrane sidechains. Based on these results, we see that the  $E_a$  of water diffusion critically depends on the immediate neighbors (molecules or ions). The differences in RDFs between phase-separated and randomly dispersed systems diminish with  $\lambda$ , which is nicely correlated with a reduction in the differences between the  $E_a$  for phase-separated and randomly dispersed models at high  $\lambda$ .



**Figure 7.** Radial distribution functions (RDFs) of the O<sub>water</sub>-O<sub>water</sub> distance (oxygen atoms between water molecules) in the model of **Figure 1(c)**. Panel (a) and (b) correspond to  $\lambda = 4$  while panel (c) and (d) correspond to  $\lambda = 15$ . Panel (a) and (c) correspond to randomly dispersed systems while panel (b) and (d) correspond to fixed-sidechain systems. In the phase-separated system, a water molecule sees more water molecules (higher intensity in RDF) in its immediate neighborhood than in the randomly dispersed system. After 10 - 20 ns simulations of free sidechains in the dispersed system, the system shifts to a phase-separated system.

By comparing both  $D_{water}$  and  $E_a$  of diffusion, we notice that  $E_a$  provides very different information as compared to the diffusion coefficient. Taking  $\lambda = 4$  as an example, one can see  $D_{water}$  is almost identical between randomly dispersed and phase-separated systems, either in the free- or fixed-sidechain cases (Figure 6(a)), but the  $E_a$  of diffusion is significantly different (Figure 6(b)). In the phase-separated systems, water molecules do not distribute as uniformly as in the randomly dispersed model (Figure S6). Instead, water-rich and water-poor environments coexist. We anticipate that water molecules in the water-rich region behave more like bulk liquid water, similar to the liquid-like water in the CNT, and water molecules in the water-poor environment diffuse slower and have higher  $E_a$  of diffusion. For this phase-separated system, the average of different environments results in similar  $D_{water}$  as in the dispersed system, but the overall  $E_a$  is much lower than that in the dispersed system. The reasoning here is that the  $E_a$  of diffusion in the phase-separated system is more weighted toward the water-rich regions. For clarity, we present the derivation of average  $E_a$  in a multi-component system here. Component 1 and component 2 (which correspond to the fast- and slow-diffusing water) are diffusing at different D and possess different  $E_a$ . Their Arrhenius equations are

$$D_1 = D_{0,1} e^{-\frac{E_{a,1}}{RT}} \tag{6}$$

$$D_2 = D_{0,2} e^{-\frac{E_{a,2}}{RT}}$$
(7)

Here, D is diffusion coefficient,  $D_0$  is the pre-exponential factor, and  $E_a$  is the activation energy of diffusion. Quantities with subscript 1 correspond to component 1 and quantities with subscript 2 correspond to component 2. Assuming the components have  $n_1$  and  $n_2$  molecules, the average diffusion coefficient is

$$D_{average} = \frac{n_1 D_1 + n_2 D_2}{n_1 + n_2} = (\frac{n_1}{n_1 + n_2}) D_1 + (\frac{n_2}{n_1 + n_2}) D_2 = \frac{n_1 D_{0,1} e^{-\frac{E_{a,1}}{RT}} + n_2 D_{0,2} e^{-\frac{E_{a,2}}{RT}}}{n_1 + n_2}$$
(8)

Based on the Arrhenius equation, the activation energy can be expressed as

$$E_a = -\frac{\partial(lnD)}{\partial(\frac{1}{RT})} \tag{9}$$

Substituting equation (8) into equation (9), the activation energy for the average diffusion coefficient would be

$$E_{a,average} = -\frac{\partial(lnD_{average})}{\partial\left(\frac{1}{RT}\right)} = \frac{n_1D_1E_{a,1} + n_2D_2E_{a,2}}{n_1D_1 + n_2D_2} = \left(\frac{n_1D_1}{n_1D_1 + n_2D_2}\right)E_{a,1} + \left(\frac{n_2D_2}{n_1D_1 + n_2D_2}\right)E_{a,2} \tag{10}$$

Thus, while the average D is only weighted by the population of different components (in a heterogeneous system), the weights for the average  $E_a$  are the product of the population and the diffusion coefficient of each component. This means that the component with faster diffusion coefficient has an increased influence on the average  $E_a$ . This explains the experimental trend observed at high  $\lambda$  in the ionomer membrane (**Figure 2**). Due to the phase-separated nature of PFSA membranes, a bulk-like water region will form in the center of the hydrophilic domains at high hydration. The bulk-like water region, which possesses faster diffusion coefficient, becomes also more populated with increasing hydration, which tilts the overall  $E_a$  in the membrane to nearly that of bulk liquid water.

Another striking result in the phase-separated system is that the difference in  $E_a$  between fixed- and free-sidechain scenarios is notably smaller than in the randomly dispersed model. This phenomenon also likely results from the different molecular environments for water molecules in the two models. As mentioned above, phase segregation leads to water-rich and sidechain-rich regions. Consequently, the number of water molecules with sidechains in their immediate neighborhood is smaller in phase-separated system than in the dispersed system, and therefore sidechain dynamics are less influential. This has important implications for water diffusion in PFSA membranes. With nanoscale phase separation, the fixed sidechains within PFSA membranes should not heavily influence  $E_a$  of diffusion, especially at high hydration.

## *Emerging picture of* $E_a$ *of diffusion in ionomer membranes at varying hydration.*

The results of this work advance the nanoscale picture of water diffusion in the hydrophilic domains of PFSA membranes. Both geometric confinement and molecular environment are related with  $E_a$  of diffusion. In order for nanoconfinement to significantly alter  $E_a$  of diffusion (Figure 8), the size of the confinement needs to be small enough (around 1 nm based on simulations). When water molecules are in confining structures of this size, the potential energy surface governing water molecule motion is such that water molecules become trapped in potential energy minima and acquire partial ordering. The correlated motion of ordered water creates a larger energy penalty for a water molecule to move out of the shell of its neighbors, significantly increasing the  $E_a$  for diffusion. The nontrivial difference in  $E_a$  between lithiumform PFSA and lithium triflate solutions at low  $\lambda$ , as shown in **Figure 3**, likely results from the formation of partially ordered, slow-diffusing water under membrane nanoconfinement. This effect cannot exist in fully dispersed and well-mixed salt solutions. In addition, the fixed nature of the polymer sidechains may contribute to the elevation of the  $E_a$  of diffusion, although this effect is minimized under the phase-separated environment of PFSA membranes. At high hydration, we observe a characteristic feature in the experiments: The  $E_a$  of water diffusion in PFSA becomes lower than that in salt solutions. We suggest that this feature results from nanoscale phase separation and formation of bulk-like water regions. As discussed in the previous section,  $E_a$  disproportionately weights toward the fast diffusing species in a multi-

component system. In the hydrophilic domains of PFSA membranes, there exist water molecules closely associated with the sidechains as well as bulk-like water molecules surrounded by only water molecules. While the average  $D_{water}$  depends on the molar ratio of the two components, the average  $E_a$  depends on the product of the molar ratio *and* the diffusion coefficient of the two components. The fast diffusing bulk-like water molecules therefore contribute more heavily to the overall diffusion process, making the resulting  $E_a$  closer to that of bulk liquid water. We cannot observe this effect in the aqueous LiOTf solutions due to the lack of phase heterogeneity. When the membrane becomes highly hydrated (**Figure 8**), bulk-like water dominates the overall water population, which makes the aforementioned effect even stronger. As a result,  $E_a$  in the membrane drops below that of aqueous salt solutions and approaches that of liquid water.



**Figure 8.** Conceptual figure of water channels in PFSA membrane. At low hydration, the size of water regions reaches the critical value for nanoconfinement effects to take place, markedly increasing  $E_a$  for diffusion. With increasing hydration, the hydrophilic domain expands. Nanoscale phase separation leads to the formation of bulk-like water in the hydrophilic domain, which gives rise to low  $E_a$ .

## Conclusions

In summary, we have shed light onto how the nanoscopic effects in a PFSA membrane are related with the  $E_a$  of water diffusion through its conducting hydrophilic domains. The main experimental results show two distinctive regimes of behavior for the  $E_a$  of diffusion. At high hydration,  $E_a$  is lower in the membrane than in salt solutions with identical water/ion ratio, but the trend strongly reverses at low hydration. This pattern results from a combination of geometric nanoconfinement and local molecular environment, and each of these effects influences water diffusion behavior over different  $\lambda$  regimes. At low hydration, MD simulations show the size of the hydrophilic domains might reach the critical value beyond which water becomes ordered and solid-like. The ordered water has a much higher  $E_a$  than bulk water and is responsible for the steep elevation of  $E_a$  at low  $\lambda$ . In the heterogeneous PFSA membrane, there will be a distribution of sizes of hydrophilic domains. Thus, water molecules may be ordered in some regions of the membrane but remain disordered in other regions. The transition from ordered to disordered water likely happens smoothly over decreasing  $\lambda$  values, and the  $E_a$ consequently increases gradually. At high hydration, the hydrophilic domain sizes are dominantly above the critical size, so formation of ordered water is limited. Meanwhile, the population of bulk-like water becomes dominant due to nanoscale phase separation of ionic sidechains. We believe that  $E_a$  weights more toward fast diffusing species, bulk-like water in this case, so the ensemble average  $E_a$  approaches that of liquid water at high  $\lambda$ .

We would like to emphasize here the rich implications and general applicability of the  $E_a$  of diffusion for understanding local diffusion processes. We have managed to show that  $E_a$  of diffusion serves as a probe for local molecular environment, which includes both a confinement effect and intermolecular interactions between water and confining medium. The confinement effect on water dynamics becomes dominant only when the size of the confinement is close to the size of the molecules undergoing transport. The fact that water at the nanoscale can have an  $E_a$  close to that of liquid water illustrates the importance of water-rich domains in membranes.

Creating regions for transport that are larger than 1 nm in size seems crucial to obtain fast water and ion transport with low activation energy of diffusion. We can apply the same reasoning to diffusing ions in membranes, which are more challenging to measure and simulate due to their low density, and we are exploring ions in ongoing work. While these results and understanding are based on polymer membranes, we can obtain  $E_a$  of diffusion for any diffusive process. Thus, we can use  $E_a$  of diffusion to study transport not only in polymer membranes but also in other nanoporous materials such as metal organic frameworks, zeolites, porous silica, natural minerals and biological structures.

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## **Supporting Information**

Experimentally measured D and  $E_a$  of bulk water and membrane water. Force-field parameters in MD simulations. Snapshots of confined water in carbon nanotube. Potential energy plots of confined water. Change of energy, density, and RDFs during equilibration of simulation models. Extract front factor  $lnD_0$  from Arrhenius equation.

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