Atomistic Simulations of Structure of Solvated Sulfonated Poly(ether ether ketone) Membranes and Their Comparisons to Nafion: II. Structure and Transport Properties of Water, Hydronium Ions, and Methanol

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The results of extensive all-atom molecular dynamics (MD) simulations of water- and methanol-solvated SPEEK (sulfonated poly(ether ether ketone)) are reported. In this Part II of the two-part article, we present results elucidating the spatial distributions of hydronium ion (vehicular proton) and methanol and the transport properties of water, hydronium ions, and methanol. Our results suggest that hydronium ions escape attraction shells of sulfonic groups with increasing water and methanol contents but move closer to sulfur with an increase in temperature. The localization of the hydronium ion near sulfonate anion was seen to be significantly more pronounced than in Nafion, suggesting stronger basicity of sulfonate anion and therefore weaker acidity of its conjugate acid in SPEEK than in Nafion. In contrast with Nafion, methanol competes with hydronium ions and water to solvate sulfonate anion and also lies closer to aromatic backbone. Water diffusion coefficients follow experimentally observed trends where they are lower in SPEEK than in Nafion at low water weight percent but approach the Nafion values at higher water weight percent. The vehicular proton diffusivity, as quantified by hydronium ion diffusivity, was found to be an order of magnitude lower than that in Nafion. The transport results are rationalized based on the structural insights presented in Part I and the present article.

I. Introduction

Sulfonated poly(ether ether ketone) (SPEEK) in pure, blended, or cross-linked form is emerging as an alternative to Nafion as a candidate membrane material for polymer electrolyte membrane fuel cells (PEMFCs).[2–5,28] In comparison with Nafion, the advantages of SPEEK include reduced water, methanol crossover, and low cost. However, these attractive features are mitigated by reduced proton conductivity, swelling at low temperatures (occurring in SPEEK at 80 °C compared with Nafion at 140 °C), resulting in reduced morphological stability.[1–5]

Much experimental research in the past has probed the performance of hydrogen and direct methanol fuel cells, particularly the transport properties of permeants such as proton, water, and methanol in dry and solvated SPEEK and compared them with the corresponding properties of Nafion.[1–5,22,26] In particular, Kreuer[1,2] presented transport data for proton and water in SPEEK and compared them with Nafion. They reported that the diffusivities of water and proton are similar for Nafion and SPEEK at high water volume fractions but are lower in SPEEK at lower water contents. Other experiments by Li et al.[5] found that proton conductivity of SPEEK is similar to that of Nafion above 80 °C. Li et al.[5] and Xue et al.[22] reported lower methanol permeability in SPEEK than Nafion.

In Part I of this work,[29] we presented results from classical molecular dynamics (MD) simulations quantifying the structural characteristics of SPEEK. We described the nanostructure of the hydrophilic and hydrophobic domains and their variations with water, methanol contents, temperature, and methanol concentration. We found less phase segregation and larger hydrophilic–hydrophobic interfaces, less structured water, and less pronounced aqueous cluster sizes and percolation in SPEEK

as compared with Nafion. These observations were broadly consistent with experimental results.[1,2,4] However, unlike the situation of Nafion, which has been well studied by simulations,[9–11,13–16,21] very few simulation studies have concerned with the distributions of hydronium ions and methanol as well as the transport coefficients of the permeants such as water, hydronium ion, and methanol in SPEEK membranes.[24]

In this second part of the two part article, we report results of extensive all-atom simulations of water- and methanol-solvated SPEEK. We studied the distributions of hydronium ion and methanol with respect to the polymeric chain elements such as sulfur and the backbone, and the transport coefficients of the permeants (water, methanol, and hydronium ion) as a function of weight percent of water, methanol concentration, and temperature. We have further drawn insight into the transport properties in SPEEK and their comparison with Nafion using the structural comparisons. The results presented are consistent with experimental observations and provide new insights into the origins of the specific properties of SPEEK such as low methanol crossover and low proton conductivity.

We note that in a recent study, Brunello et al.[24] have also used MD simulations to study the distributions of hydronium ion near sulfonate anion and the transport properties of water in SPEEK membranes. In Part I of this article, we highlighted the main systemwise differences between their study and the present one. More specific to this article, we note that our system differs with regard to the presence of methanol and hence we are able to quantify the methanol transport characteristics as well as the influence of the presence of methanol upon the transport of water and hydronium ions. In addition, we also present the diffusivity values for hydronium ions (determined in a classical framework) and rationalize it based on the

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structural data. The diffusivity information for hydronium ions were not quantified in the work by Brunello et al.[24]

The following is the outline of the rest of the article: In Section II, we present details of the simulation methodology and the force fields used. In Sections IIIA and IIIB, we present results quantifying the influence of water weight percent, methanol concentration, and temperature on the distributions of hydronium ion and methanol with respect to SPEEK chain elements. In Section IIIC, we discuss the dynamics of water, hydronium ion, and methanol and analyze these results in the context of structural information. Our results for SPEEK are compared with the previous simulation studies on Nafion and related benchmark experimental studies for both membranes. Finally in Section IV, we summarize the important conclusions.

II. Simulation Details

Article I elaborates most of the simulation details pertinent to our work. Below, we briefly discuss the aspects most pertinent to this article.

A. Framework of Classical Simulations. Despite SPEEK being a reasonably strong acid, it is not completely dissociated in aqueous solution.[2] Because of the ensuing dynamical acid—base equilibrium, simulating the properties of SPEEK requires, in principle, quantum mechanical simulations that can account for bond breaking and formation.[25] As a preliminary step to modeling transport properties, we have adopted a classical formalism with assumptions that were detailed in article I. Specifically, as mentioned in article I, we assumed the pK_a of SPEEK to be −1.0 and that it remains unchanged as a function of temperature, water content, and methanol concentration. We also assumed that each dissociated H^+ combines with a water molecule to form a hydronium ion whose identity remains fixed throughout the simulation. This approach is similar to the track taken in some previous studies on Nafion.[11,13,14,21] The fact that we can reasonably reproduce experimental results for structural and dynamical behavior of solvated SPEEK suggests that the limitations of our assumptions are not too severe.

In view of the above assumption, we do note that the proton transport results presented in the subsequent sections need to be interpreted with caution. Explicitly, the classical framework we have used precludes quantification of transport occurring due to Grotthus proton hopping mechanism.[25] Recently, Petersen and Voth reported that in water-solvated Nafion membrane, the vehicular proton conduction (classical diffusion of hydronium ion) and proton diffusion due to Grotthus hopping are of the same order of magnitude.[23] Whereas it is not entirely clear if similar considerations quantitatively apply for nanostructured SPEEK—water—methanol mixtures, it may be concluded that the hydronium ion transport rate deduced in our simulations is one significant component of the transport processes for proton.

B. Potentials. Potentials used for the SPEEK units[18] and water[17] have been elucidated in Part I of this work. For hydronium ions, we used the force field parameters and charges from Jang et al.[14] We used combination of three-site model developed by Honma et al.[19] and OPLS-AA[20] (for force constants for intramolecular bending) for methanol.

C. Simulation Run Details. Most of the details of the simulation procedure have been elaborated in Part I.[6−8,29] Pertinent to this article is the fact that the diffusivity, D, of all permeants was calculated from mean square displacement to be

$$D = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle / 6t$$

where $\mathbf{r}(t)$ is the position vector of a permeant at time, t.

III. Results and Discussion

A. Spatial Distributions of Hydronium Ion. In this section, we discuss the distributions of hydronium ions with respect to sulfonic acid groups at different water, methanol contents (weight percent), and temperatures.

Figure 1a,b displays the changes in radial distribution functions (RDFs) of S(sulfonic acid)−O(hydronium) and O(sulfonic acid)−O(hydronium), respectively, with varying water content. With an increase in the weight percent of water, we observe that the hydronium moves away from the sulfonic acid groups. This behavior is also reflected in the results plotted in Figure 2, which demonstrates that the coordination numbers deduced from the RDF monotonically decrease with the increase in the water content.

The above observations may be rationalized as arising from the increased water solvation of the sulfonic acid groups with increasing water content. One may expect that water competes with hydronium ions to solvate sulfonate anions (reported in Part I, section IIIE1). In turn, this may lead to an enhanced screening of the electrostatic pull exerted by sulfonic group, thereby allowing for the hydronium ion to become less localized.

In comparing our results for SPEEK with those reported for Nafion, we note that the change in the height and the breadth of the peaks in the RDFs of O(S)−O(H₃O⁺) and S−O(H₃O⁺) with change of water weight percent is much less pronounced in SPEEK when compared with results reported for Nafion.[13,21] These trends are seen quantitatively in the comparison of coordination numbers and their changes when the water content is increased from 5 to 40 wt % (Figure 2). (Values of coordination number higher than 1 may be rationalized as arising from adjacent sulfur atoms sharing same hydronium ion.) We observe that the coordination number of hydronium ions around sulfur at lower water contents in our system is lower compared with Nafion—an observation that may be due to the fact that methanol present in our system can compete with hydronium ions to solvate sulfonate anions. (See Section IIIB of this article.) More interestingly, we observe that at higher water contents, more hydronium ions are held to sulfur atoms in our SPEEK system compared with results reported for Nafion. Additionally, the relative decrease in the coordination number with increase in water content is quite mitigated in our SPEEK system against a significantly steeper change in the case of Nafion. These observations suggest that hydronium ions get trapped in the electrostatically attractive binding with sulfonate anions more strongly in SPEEK than Nafion. The observation is consistent with the stronger basicity of sulfonate anion (arising from weaker acidity of the conjugate sulfonic acid) and the lower dielectric constant of water in SPEEK relative to Nafion.[2]

In comparing the results of our work with those of Brunello et al.,[24] we note that there are differences. Although Brunello et al. have used the same potential parameters and charge equilibration procedure as ours, the coordination numbers they have obtained are closer to that in Nafion systems than in our model. At lower hydrations, Brunello et al. report higher coordination numbers than our work. These differences, may be rationalized as arising from the methanol present in our system. At higher hydrations, coordination numbers in the work by Brunello et al. decrease at the faster rate and reach values lower than our model. Whereas we do not have a conclusive explanation for these differences, we do note that the system parameters (the size of the chain, number of chains, and the degrees of sulphonation) in their work are significantly different

SPEEK Membrane Structure and Comparison to Nafion

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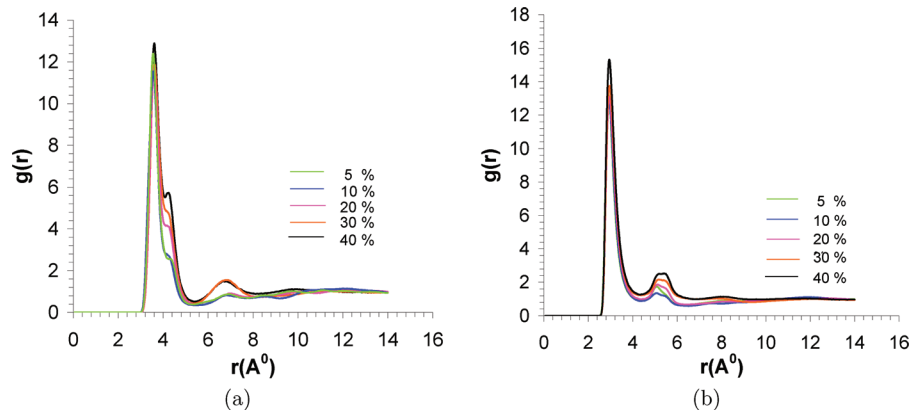
Figure 1. RDFs plotted at different water weight percent for: (a) S(sulfonic acid)−O(hydronium ion) and (b) O(sulfonic acid)−O(hydronium ion).
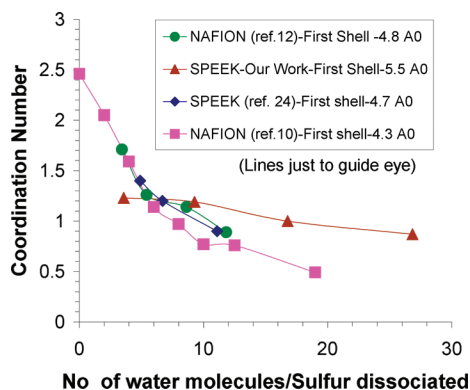
Figure 2. Comparison between SPEEK and Nafion of coordination numbers of hydronium ion around sulfur at different hydration levels.

compared with our simulations, and hence it is not straightforward to isolate the physical reasons underlying such differences.

Figure 3a displays the RDFs of S−O(hydronium) with changing methanol concentration. From the results presented in Table 1, we observe that the coordination numbers display a small but perceptible decrease with increasing methanol concentration. These results indicate that increasing methanol concentration facilitates the breakup of hydronium ion coordination with sulfur. These results may again be rationalized as arising from the shielding of the electrostatic pull exerted by sulfonic group due to the build-up of solvent (methanol) layer between hydronium ion and sulfonic group.

Figure 3b displays the S−O(hydronium) RDF with change in temperature. It is observed that the peak at short distances of 3.5 Å intensifies (correspondingly, the coordination numbers up to 4 Å increase from 0.42 at 298 K to 0.51 at 353 K), suggesting that with increasing temperature, the hydronium ions move closer to sulfur. This may be rationalized by noting that with the increase in temperature, the water of hydration moves away from the sulfur (Part I, section IIIE1). The latter may be expected to lead to a reduced screening effect by water, thereby increasing the electrostatic pull exerted by the sulfonate anion upon hydronium ions. We would like to note that similar results have been reported by Venkatnathan et al. in case of Nafion.[27] Specifically, they have reported an increase in hydronium ion coordination and a decrease in water coordination around sulfur with an increase in temperature from 300 to 350 K at three hydration levels (3.5, 11, and 16).

B. Spatial Distributions of Methanol. Lower methanol crossover is one of the attractive features of SPEEK for DMFC application. The results for water cluster characteristics (section IIIA of Part I), which indicated smaller cluster sizes, and percolating fractions provide an explanation for these trends. In this section, we present results for the distributions of methanol around solvation sites such as sulfonate anion and the aromatic carbon to provide more insight into the transport properties and their comparisons to Nafion.

Figure 4a displays the results for S−O (methanol) RDF with varying water content. The coordination numbers for the ranges up to 6, 6−10, and 10−14 Å change from 0.049, 0.125, and 0.244 at 5 wt % water to 0.23, 0.79, and 2.4 for 40 wt % water. In light of the substantial increase in the largest shell, the results suggest that with increasing water content, methanol molecules are more likely to be localized further away from the sulfur atoms. Similar to the arguments used to rationalize our results for hydronium ion−sulfur RDF, we may explain this trend as being due to the increased screening effect and the enhanced mobility of aqueous phase due to the addition of water.

Figure 4b depicts the change in S−O(methanol) RDF with changing methanol concentration. With increasing methanol concentration, the coordination number of methanol increases from 0.38 to 4.5 (for the shell extending up to 7 Å). This increased localization of methanol to sulfur is expected to be a consequence of methanol competing with water to solvate sulfonate anion/sulfonic acid group. It is interesting to note that this behavior is in contrast with the corresponding results for Nafion, where Urata et al.[15] reported negligible change in the peaks under similar conditions. (We note that the potential field for methanol is the same in both the studies.) In addition, the increase in coordination number relative to the increase in solvent amount is higher for methanol than water. The latter can be established by noting that in water−methanol solution, coordination number (up to 7 Å) of water increases from 8.48 to 11.65 with increase in water concentration (of water−methanol solution) from 60 to 90%. Moreover, the above result for methanol in Figure 4a can be compared with the observation that in a 1 M methanol solution, an increase in water from 10 to 40 wt % results in a change in the water coordination number in the first shell (up to 5.8 Å) from 2.8 to 6.1 (as reported in IIIE1 of the Part I of this work).[29] This is in stark contrast with that in Nafion, where water was observed to associate with sulfur preferably to methanol.[15] These results may explain the trends observed in section IIIE1 of Part I of this article, where it was argued that the presence of methanol in our system may push water molecules away from the sulfonic acid groups and thereby explain the differences noted with the results reported in studies of methanol-free Nafion membranes.
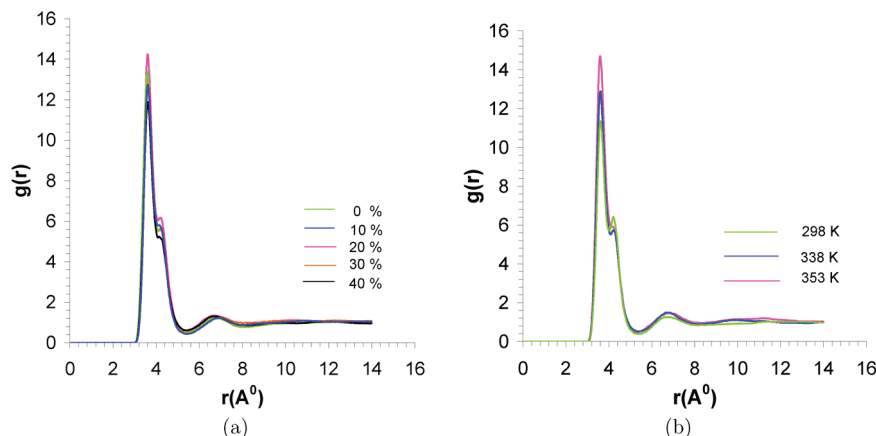
Figure 3. RDFs for S(sulfonic acid)−O(hydronium ion) plotted at (a) different methanol weight percent and (b) different temperatures.
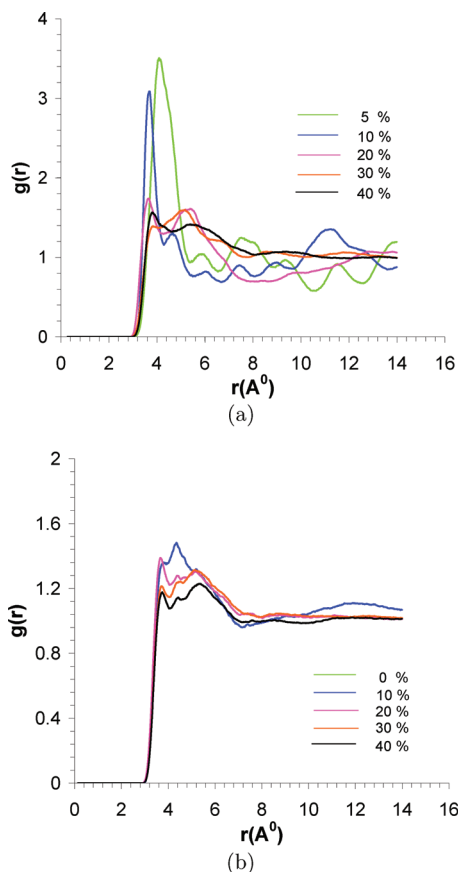
TABLE 1: S−OH Coordination for Changing Methanol Concentration

methanol wt %	coordination number-first shell up to 5.2 Å
0	0.82
3.33	0.8
10	0.77
20	0.8629
30	0.78
40	0.74

Figure 5 displays the changes in RDF of aromatic carbon−oxygen of methanol at different methanol concentrations. With the increase in methanol concentration, the coordination number decreases from 3.32 at 3.33 wt % methanol to 0.28 at 40 wt %
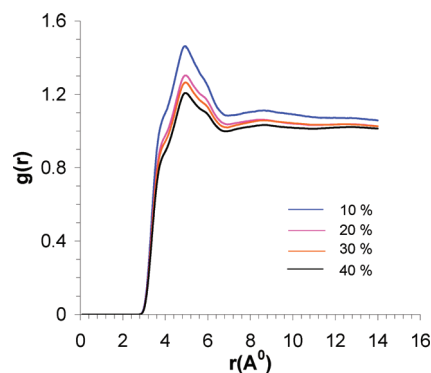
Figure 5. RDFs for aromatic carbon−O(methanol) at different (a) water weight percent and (b) methanol weight percent.
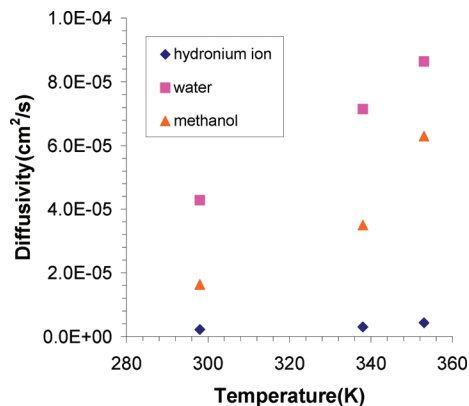
methanol. These results indicate an overall movement of methanol away from the aromatic carbon, which can be rationalized as arising from the increased mobility due to the increase in the number of methanol molecules. These trends are consistent with the results reported for coordination between CF2 of Nafion backbone and methanol in Urata et al.[15] However, the peak at 4.8 Å in the RDF for SPEEK is observed to be stronger and closer to the backbone compared with the peak reported at 6.5 Å for Nafion. These trends suggest that methanol lies closer to aromatic carbon of SPEEK than the CF2 units of the Nafion backbone.

In summary, the above results suggests an enhanced localization of methanol around sulfur and aromatic carbons of SPEEK compared with Nafion. In addition to the diminished nanophase segregation effects discussed in Part I of this article, the above features may be expected to contribute to lower methanol crossover (relative to Nafion) noted in SPEEK membranes.

C. Transport Properties of Permeants. In this section, we report the diffusion coefficients of water, methanol, and hydronium ions as a function of water content, temperature, and the amount of methanol. We use the structural characteristics presented in Part I of this article and the preceding sections of this article to provide insight into our results. In Figure 6, we display the diffusion coefficients of water, methanol, and hydronium ions as a function of temperature. As may be intuitively expected, the diffusion coefficients increase with increasing temperature. A fit of these diffusion coefficients with an Arrhenius functional form $D = D^0 \exp(-E/RT)$ yields activation energy (E) values of 9.82, 11.04, and 20.02 kJ/mol for hydronium ions, water, and methanol, respectively. The corresponding value for hydronium ion in the case of Nafion[14] has been reported 10.32 kJ/mol, which is higher than that in

Figure 4. RDFs for S(sulfonic)−O(methanol) at different (a) water weight percent and (b) methanol weight percent.

Figure 6. Diffusivity of permeants in the SPEEK system plotted against temperature.

SPEEK. A possible rationalization for this lower temperature sensitivity of vehicular proton diffusivity in SPEEK may be identified in the more pronounced localization of the hydronium ions near the sulfur groups (Section IIIA). One may envision that this localization may reduce the overall mobility and its temperature dependence, as reflected in the activation energies.

In Figure 7a, we display the diffusion coefficients of water, methanol, and hydronium ion as a function of water weight percent. Overall, the diffusion coefficients are seen to increase with an increase in water weight percent, a result that can be rationalized as a consequence of the growth of aqueous phase clusters, which facilitates enhanced mobilities (sections IIIA, IIIC, and IIID of Part I). In Figure 7b, we compare the preceding results with those reported for Nafion for the same water contents (expressed as weight percent).[9,11−14] We note that the simulations on Nafion were done at 298 K, whereas our results are for 338 K. However, the results presented in Figure 6 indicate that with 40 wt % water and 1 M methanol solution, the diffusivity at 338 K is about 70, 214, and 40% higher than that at 298 K for water, methanol, and hydronium ions, respectively. When this temperature dependence is accounted (strictly speaking, the preceding activation energy is valid only for a water content of 40 wt % water), it is seen that at 5 and 10 wt % water, the diffusivity of water in SPEEK is about 2 to 4 times lower than that in Nafion. As the water content is increased, the values for SPEEK become comparable to the corresponding values in Nafion.

The above results are consistent with the experimental observations, which have indicated that crossover and transport coefficients of water in SPEEK become comparable to Nafion at higher water contents but are lower at lower water contents.[2] As discussed in Part I (sections IIIA, IIIC, and IIID of Part I), less phase segregation resulting in lower water cluster sizes and less efficient percolation of water in SPEEK compared with Nafion may contribute to lower water diffusivity values at lower water contents. At higher water contents, the phase segregation in SPEEK increases along with the growth of water clusters and percolating fraction and becomes comparable to Nafion, and this could explain the fact that values of the diffusivities in SPEEK approach closer to Nafion.

In comparing our simulation results on SPEEK with that of Brunello et al.,[24] the latter reported water diffusivity to be 0.07 × 10⁻⁵ at 10 wt % water and 0.13 × 10⁻⁵ at 20 wt % water at 353 K, which is lower than our results. However, our results are more consistent with the experimentally observed trends of the SPEEK transport coefficients approaching the Nafion values at higher water contents.

In Figure 8a,b (with respect to weight percent and hydration level, respectively), we present the results for vehicular proton diffusivity of SPEEK and Nafion at various water contents. At all water contents, we observe that the values for SPEEK are an order of magnitude less than that in Nafion.[9,11−14] When considered with respect to hydration level, the values in SPEEK are observed to be a few times lower than those of Nafion. Moreover, at all water contents, our hydronium ion diffusivity is seen to be at least 20−30 times lower than that of water. In contrast, in Nafion, water diffusivity has been reported to be only 2 to 8 times higher than hydronium ion (within classical MD approach). In addition, the increase in hydronium ion diffusivity with water content is less significant in SPEEK system than that in Nafion. These results are consistent with the localization of hydronium ion in SPEEK discussed in Section IIIA. Indeed, stronger binding of hydronium ions to sulfonate anions in SPEEK than Nafion is expected to reduce the diffusivity of hydronium ions and also lead to a less significant increase in the hydronium ion diffusivities with increasing water content.

We should point out that because our study includes only the classical, vehicular mode of proton transport, our above results represent only a lower bound to the actual proton diffusivities (and conductivities) that may be observed. Recently, research reported from Petersen and coworkers and Voth and coworkers indicates that in water-solvated Nafion membrane, the relative magnitudes of vehicular proton conduction (classical diffusion of hydronium ion) and proton diffusion due to Grotthus hopping are the same but with negative correlation.[23] In situations involving even lower hydronium ion vehicular mobility (such as our results), the Grotthus mechanism may become even more relevant and need to be accounted more accurately with the quantum mechanical aspects of proton conduction. We hope to pursue these issues in more detail in a future article.

Figure 9 displays the variations in the diffusivities of water, hydronium ion, and methanol with increasing methanol concentration. The diffusivity of water is seen to decrease with the increase in methanol concentration, due to both the decrease in the number of water molecules and also the reduction in the water cluster sizes (section IIIB of Part I). In contrast, the changes in methanol diffusivity are seen to be very small. It initially decreases, and from there onward it increases and then decreases slightly. The initial decrease in methanol diffusivity may be explained as being due to the increased localization of methanol near sulfur (Section IIIB), and the subsequent behavior may be rationalized by the increase in the number of methanol molecules. We also note that the trends in diffusivity of water and methanol are similar to those noted in corresponding study on Nafion by Urata et al.[15] However, quantitative comparisons are not possible because of the different weight % of solvent in our simulations.

IV. Summary

We used atomistic simulations of SPEEK to study the effects of changing water weight percent (or equivalently varying the hydration level, while maintaining 1 M methanol concentration), methanol concentration, and temperature on the distribution of hydronium ions, methanol and the dynamics of water, methanol, and hydronium ions. The prominent conclusions presented in this article include:

(1) Hydronium ions move away from sulfonate anion with an increase in water content and methanol concentrations, and it moves toward sulfur as temperature increases. The localization of hydronium ion in SPEEK was much more pronounced than

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(a)

(b)
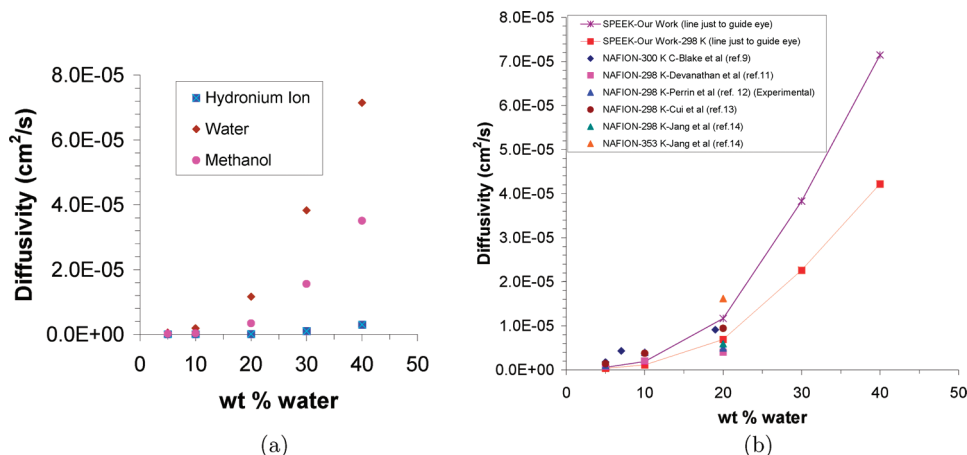
Figure 7. Diffusivity with change in water weight percent of (a) permeants in SPEEK and (b) water in SPEEK (this work) compared with corresponding values for Nafion membranes reported in literature.

(a)

(b)
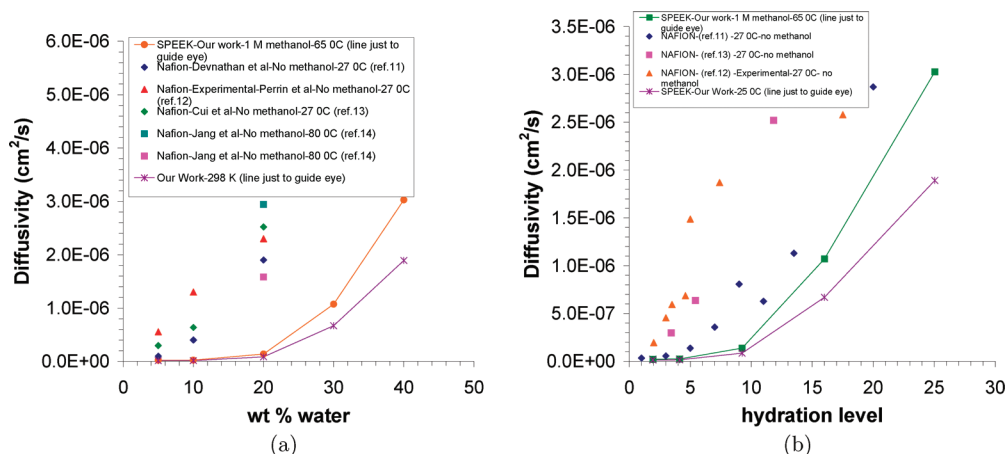
Figure 8. Diffusivity of hydronium ion in SPEEK (this work) compared with that in Nafion reported in literature with change in (a) water weight percent and (b) hydration level.
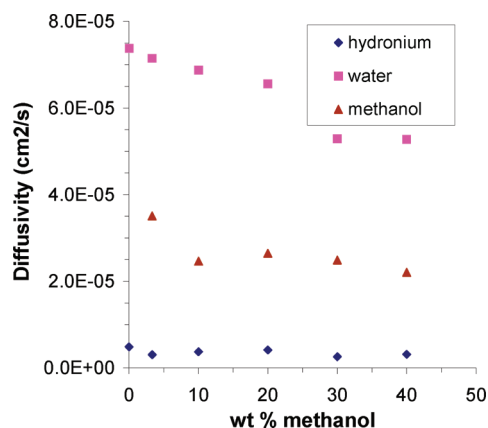
Figure 9. Diffusivity of permeants in SPEEK as a function of methanol weight percent.

that reported for Nafion, possibly indicating stronger basicity of sulfonate anion and the weaker acidity and less hydrophilicity of the conjugate sulfonic acid in SPEEK compared with Nafion. As discussed in Part I of this article, latter feature may be one of the factors leading to less phase segregation in SPEEK than Nafion and also might potentially contribute to hydronium ion competing with water to solvate sulfonate anion.

(2) Methanol moves away from sulfur with increasing water content. However, in contrast with results reported for Nafion, methanol moves toward sulfur with increasing methanol con-

centration. We suggested that the methanol competes with water to solvate sulfonic group in SPEEK. Moreover, methanol was found to lie closer to the aromatic backbone of SPEEK than fluorocarbon aliphatic backbone of Nafion. These results, in addition to the less pronounced water clustering effects reported in Part I, may contribute to lower methanol crossover in SPEEK than Nafion.

(3) The diffusivities of water, methanol and hydronium ions were found to increase with the increase in the water content and with temperature. The diffusivity of water in SPEEK was found to be comparable to Nafion at higher water contents but was lower than Nafion at lower water contents. The hydronium ion diffusivity in SPEEK is found to be lower than that in Nafion by an order of magnitude. Whereas the diffusivity trends for water and hydronium ion may be rationalized from smaller water cluster sizes and less efficient percolation (percolation becoming comparable at water contents of 20 wt % and higher), localization of hydronium ion near sulfonate anion may additionally explain at least the peculiarly lower hydronium ion diffusivity in SPEEK than Nafion. Whereas water diffusivity decreases with the increase in methanol concentration, both methanol and hydronium ion diffusivities exhibit only small variations with methanol content.

In a nutshell, the results presented in this two-part article suggest that less hydrophilic sulfonic acid and less hydrophobic and more rigid aromatic backbone lead to less nanophase segregation and more pronounced localization of hydronium ions

in SPEEK than in Nafion. These effects are also accompanied by smaller cluster sizes and less pronounced percolation, which lead to overall lower permeant mobilities in SPEEK than Nafion. Closeness of methanol to sulfonic group and backbone of SPEEK than Nafion may further contribute to lower methanol crossover (a property that has attracted the interest in SPEEK membranes).

Our study was intended to establish the benchmark results based on a classical framework for the structure and dynamics of solvated aromatic polymeric membrane. In future studies, we propose to integrate our simulations with a more realistic quantum mechanical treatment of proton diffusion and interactions. Having such a framework, we hope to extend it to other candidate membranes to study their structural and transport characteristics.

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