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Letter

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Reversal of Salt Concentration Dependencies of Salt and Water Diffusivities in Polymer Electrolyte Membranes

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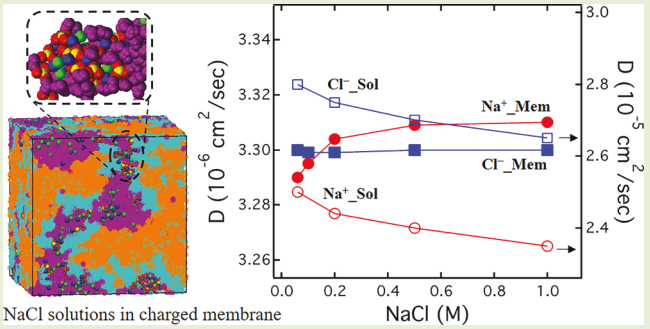
Supporting Information

ABSTRACT: Recent experimental results have shown that transport properties of salt ions and water in charged polymer membranes exhibit an intriguing dependence on salt concentration that is opposite to that seen in electrolyte solutions. Motivated by such observations, in this study we have used atomistic molecular dynamics simulations to investigate the molecular level mechanisms underlying the transport properties of salt solutions in charged polymer membranes. Our results are in qualitative agreement with experimental results and suggest that the mobility of the salt ions is influenced by electrostatic interactions with the charged groups in the polymer membrane. The mobility of water molecules is shown to arise as a consequence of the influence of salt on the hydration characteristics in solution and polymer electrolyte systems.



In the quest for clean water, polyelectrolyte desalination membranes have emerged as a focal area of research. In such a context, sulfonated polystyrene-containing copolymers such as commercial cation exchange polymer (CR61)[1] shown in Figure 1 have been developed as a promising candidate for advancing a variety of applications from clean energy to water purification[2−4] and reverse osmosis.[5,6] The ionic domains in the membrane and their assembly in the presence of salt ions and water are expected to influence the transport of salt ions and water, and developing a molecular understanding of their interrelationship is expected to be crucial to the design and optimization of desalination membranes.

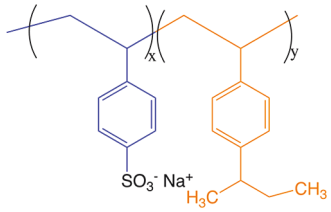


Figure 1. Chemical structure of sulfonated polystyrene-*co*-divinylbenzene polymer.

Only relatively few studies have examined in detail the transport properties of salt and water in polyelectrolyte membranes. For instance, Geise et al.[7,8] studied the impact of salt concentration on the diffusion of ions and water for sulfonated pentablock copolymers and reported an increase in the salt diffusion coefficient and a decrease in the membrane's water content with increasing salt concentration. Of specific interest to the present study is the recent work by Kamcev et al.,[9] which extracted the individual diffusivities of the cation (Na^+) and the anion (Cl^-) of salt solutions in fixed charge CR61 membranes as a function of external NaCl salt concentrations (ranging from 0.01 to 1 M). Surprisingly, they observed that the Na^+ diffusion coefficients in the membrane were greater than the diffusivity of Cl^- ions. Such results contrast with the behavior in aqueous salt solutions, wherein both experiments and simulations have demonstrated that the Cl^- ions exhibit higher mobilities than the Na^+ ions.[10−12]

Motivated by the above experimental results, in this letter we report the results of atomistic molecular dynamics simulations which were used to probe the transport properties of salt ions and water molecules. We focused on the influence of NaCl concentration in the fixed charge (f = 0.30) un-cross-linked membranes upon the ion and water mobilities. This sulfonation fraction (f = 0.30) was chosen to match with the experimental study[9] referenced above. Such results are compared with diffusivities of salt ions and water in aqueous NaCl solutions. We invoke analysis of structural and dynamical characteristics to explain the mechanisms underlying our results.

In brief, copolymers,[13−16] Na^+ ions, and Cl^- ions[17] were modeled using the Optimized Potentials for Liquid Simulations - All Atoms (OPLS-AA) force field. Water molecules were modeled by TIP4P/2005.[18,19] A system with 40 sulfonated CR61 polymers with 80 monomers/chain for f = 0.30 was built in a cubic simulation cell $L \sim 100$ Å. The counterion for the polymers was Na^+ ions. The simulations were performed in the

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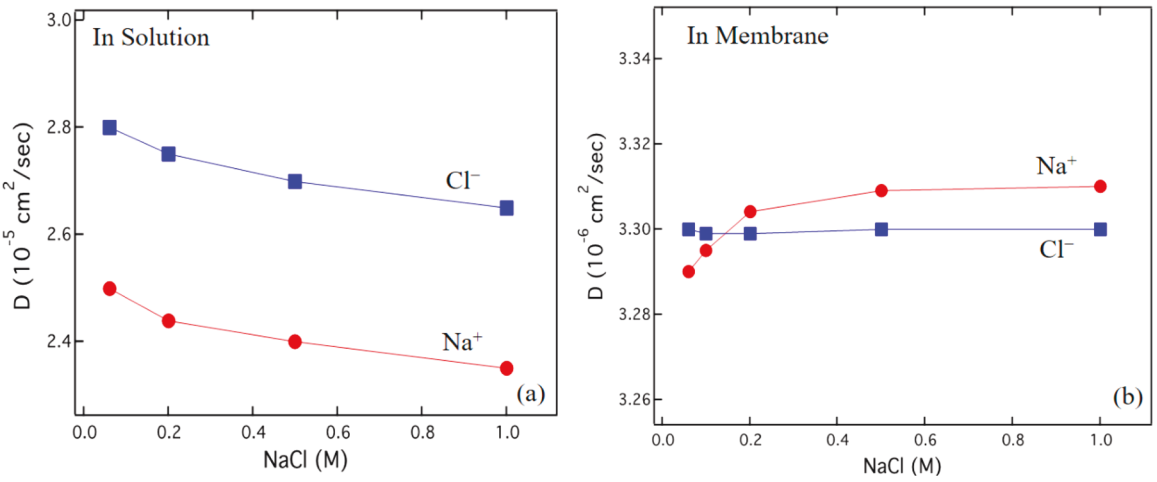

Figure 2. Diffusion coefficients of Na^+ and Cl^- both (a) in solution and (b) in membrane as a function of NaCl concentration. The lines represent a guide to the eye.

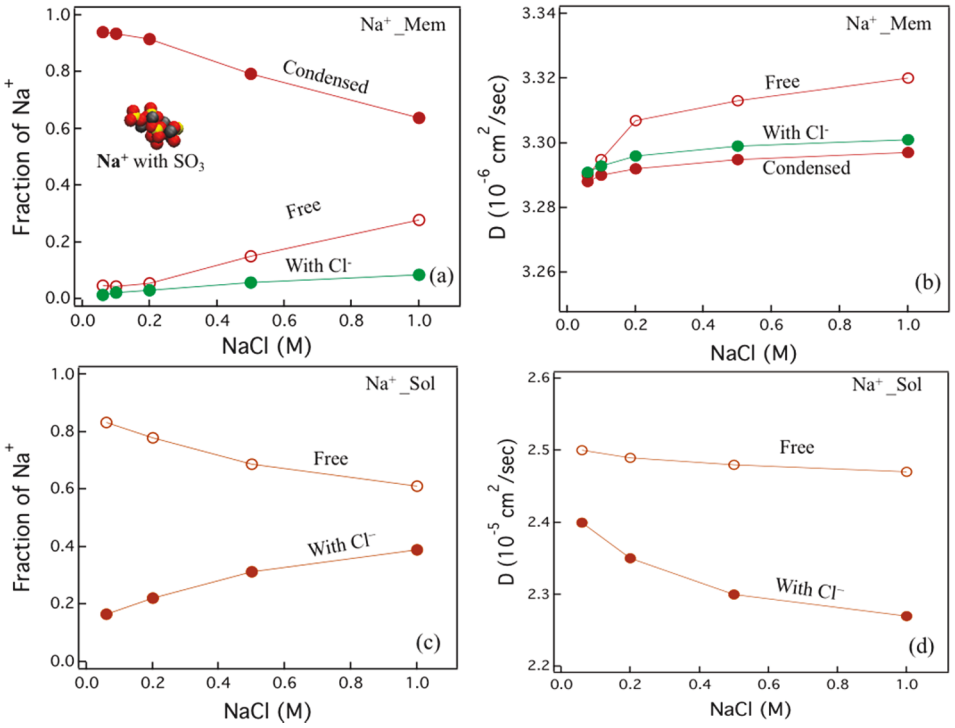

Figure 3. Na^+ in membrane: (a) The fraction of Na^+ ions *condensed* with sulfonate groups, *paired with* Cl^- *ions*, and *free* ions. Inset snapshot shown as an example of the ionic cluster where Na^+ ions are associated with sulfonated groups. (b) Diffusivity of condensed, *paired with* Cl^-, and free Na^+ ions as a function NaCl concentration. Na^+ in solution: (c) The fraction of Na^+ ions that are paired with Cl^- ions and free Na^+ ions. (d) Diffusion coefficients of Na^+ ions that are paired with Cl^- ions and free ions as a function of NaCl concentration. The lines represent a guide to the eye.

membrane with five different concentrations of NaCl ranging from 0.04 to 1 M, which is similar to the range explored in the experimental study. Table S1 in the Supporting Information presents further details of number of molecules present in the systems. A fixed number of water molecules (4800 molecules) is placed in all systems to probe the impact of salt concentration on the transport of ions/water. The water volume fraction was fixed at 0.5 (which corresponds to 10 waters per sulfonate group or equivalently a hydration number (λ = 10)) and was selected to match with the experimental study.[9] The Supporting Information presents further details of interaction parameters, the simulation methodology, and equilibration procedure for the simulations. Snapshots of a system after equilibrating are shown in Supporting Figure S1.

We begin our discussion of results by presenting the diffusion coefficients of Na^+ and Cl^- ions (determined from the respective ion mean-squared displacements (MSDs) shown in Supporting Figure S2 for the selected salt concentration) as a function of NaCl concentration (Figure 2). In brief, we identify two main trends: (a) The diffusivity of Cl^- ions in electrolyte solutions (Figure 2a) is seen to be higher than those of Na^+ ions, whereas they are seen to be reversed in the polymer membrane (Figure 2b). (b) In aqueous electrolyte solutions (Figure 2a), we observe that the diffusivities of both Na^+ and Cl^- ions *decrease* with increasing NaCl concentration. In

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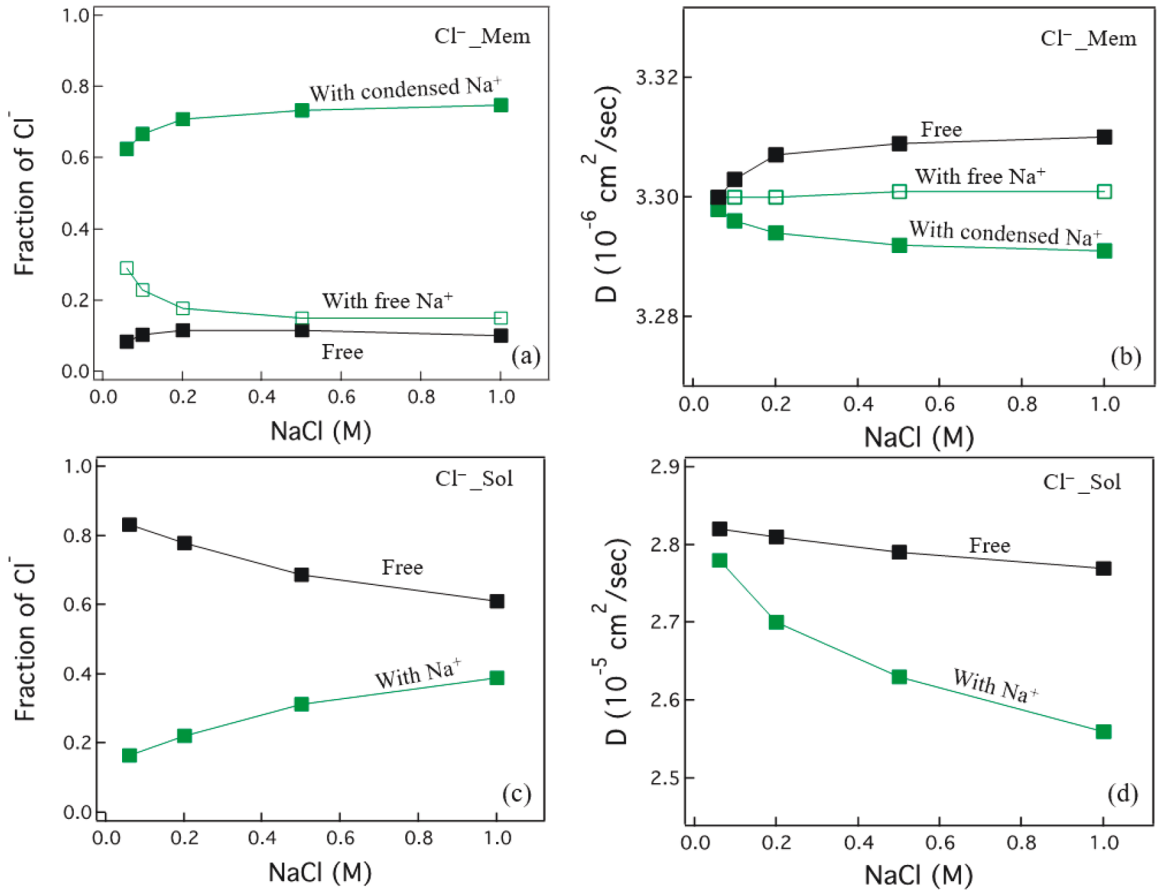

Figure 4. Cl^- in membrane: (a) The fraction of Cl^- ions associated with condensed Na^+ ions, with free Na^+ and free Cl^- ions. (b) Diffusion coefficients of Cl^- ions associated with condensed Na^+ ions, with free Na^+ and free Cl^- as a function of NaCl concentration. Cl^- in solution: (c) The fraction of Cl^- ions associated with Na^+ ions and free Cl^- ions. (d) Diffusion coefficients of Cl^- ions associated with Na^+ ions and free Cl^- as a function of NaCl concentrations. The lines represent a guide to the eye.

contrast, the diffusivity of Na^+ in the polymer membrane is observed to increase with NaCl concentration, whereas the diffusivity of Cl^- in the polymer membrane is almost insensitive (slightly decreases, based on numerical values) with NaCl concentration (Figure 2b).

To unravel the mechanisms underlying the above results, we effected a number of structural and dynamical characterizations, and in a longer article, we plan to present the detailed results of such analysis. In the present letter, we focus on the fundamental mechanism that emerged as the outcome of the above analysis, viz., the fraction and mobilities of the "condensed" and "free" ions in the systems.

Specifically, we categorized the Na^+ ions into three groups: "condensed" with the sulfonate groups; "paired" with Cl^- ions; and as "free" if it was neither condensed nor paired. The Na^+ ions were considered as "condensed" with sulfonate groups if they were within a cutoff distance of 4.25 Å (the location of the peak of the first coordination shell between S−Na^+ ions as shown in Supporting Figure S3). If Na^+ ions are associated with Cl^- ions within a cutoff distance of 3.5 Å (first hydration shell from $g(r)$ between Na^+−Cl^- ions as shown in Supporting Figure S4(a)) they were considered as "paired". Subsequent to identification (at $t = 0$) of condensed, paired, and free Na^+ ions, their dynamics was used to characterize the diffusivities of the distinct populations of the ions.

From the results displayed in Figure 3(a) we observe that the fraction of condensed Na^+ ions decreases, while the fractions of paired and free ions increase with increasing NaCl concentration (also seen in the radial distribution function $g(r)$ between S−Na^+ ions as shown in Supporting Figure S3.). Complementary to such results, Figure 3(b) displays the individual mobilities of condensed, paired, and free Na^+ ions in the membrane as a function of salt concentration. Therein, it can be seen that with an increase in the salt concentration the diffusivity of free Na^+ ions monotonically increases, whereas the mobility of both condensed and paired Na^+ ions remains relatively insensitive to the salt concentration.

The above results can be understood by noting that there is a competition for the sulfonate groups between the Na^+ ions arising from the salt and the Na^+ ions present as the original counterions of the polymer membrane. With the addition of salt, the total number of Na^+ ions is increased, which frees up a larger fraction of Na^+ ions from coordination with the sulfonate groups. Since the probability of coordination with sulfonate ions is reduced, the mobility of both the free and condensed ions (we note that condensed ions are identified only by their state at $t = 0$) is expected to be enhanced. Together, the increase in the fraction of free ions and the higher mobility of such a population can be attributed as responsible for the salt concentration dependence of Na^+ ions in polymer membranes.

The above trends are seen to contrast with the behavior in aqueous solutions (Figures 3c and 3d). In the latter context, we considered Na^+ ions as condensed if they are paired with Cl^- ions within a cutoff distance of 3.5 Å (first hydration shell from

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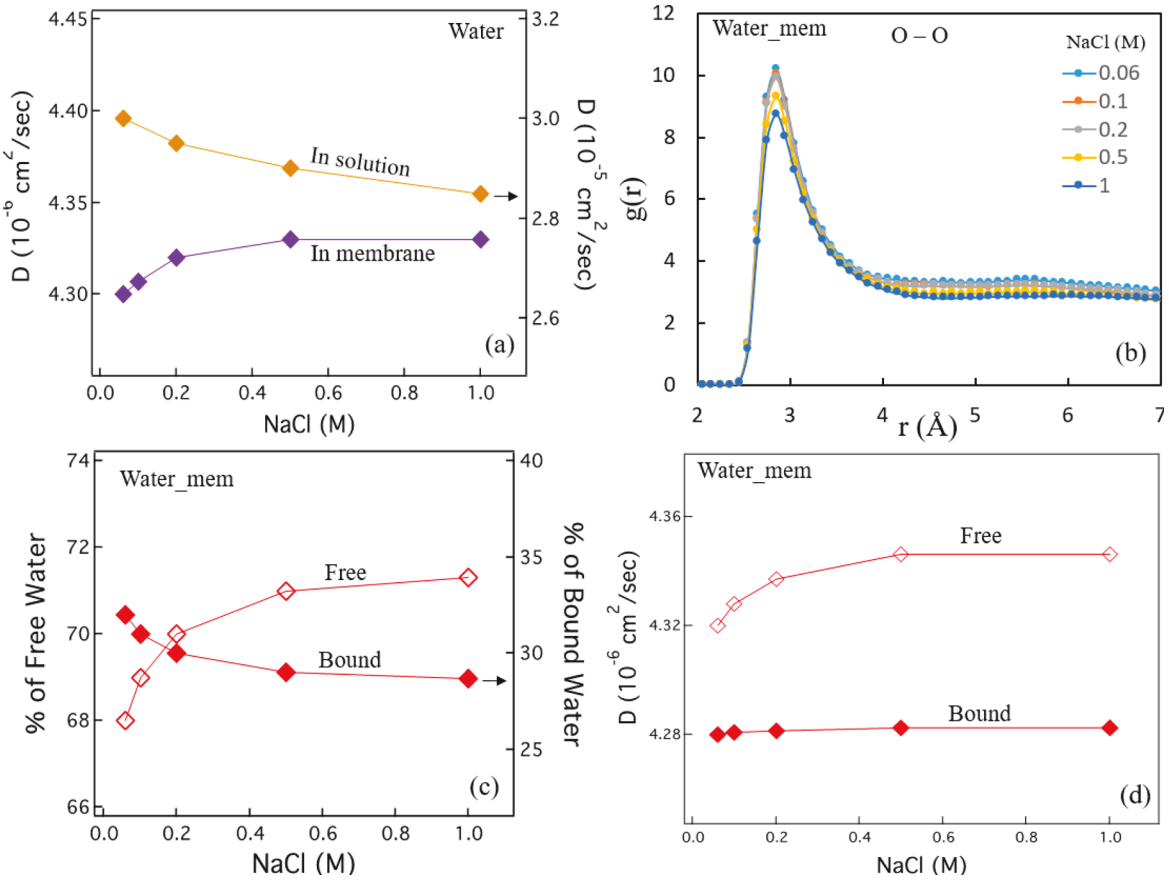

Figure 5. (a) Diffusivity of water in the membrane (left axis) and in solution NaCl (right axis) as a function of NaCl concentration. (b) Radial distribution function of O−O of water in membrane as a function of NaCl concentration. (c) Percentage of free (left axis) and bound water (right axis) molecules as a function of NaCl concentration. (d) Diffusivity of bound and free water molecules as a function of NaCl concentration. The lines represent a guide to the eye.

$g(r)$ between Na^+−Cl^- ions as shown in Supporting Figure S4(b)). It is seen from the results in Figure 3c that the fraction of free ions decreases with increasing salt concentration. Similar to the results for the polymer electrolytes, the mobility of condensed Na^+ ions is seen (Figure 3d) to be lower than that of the free Na^+ ions. The results for the mobility and fraction of condensed ion pairs mirror those reported in earlier studies.[11,20−24] Pertinent to the present context, since the population of condensed ions *increases* with salt concentrations in electrolyte solutions, the overall mobility of the Na^+ ions decreases with increasing salt concentrations.

Why does the pairing between Na^+ and Cl^- ions not influence the diffusivity of Na^+ ions in the polymer electrolyte? The main reason is that the mobilities of both the free Na^+ ions and the free Na^+ ions condensed with Cl^- ions are still higher than Na^+ ions condensed with the sulfonate groups. Since the fraction of Na^+ ions condensed with sulfonate groups decreases with salt concentration, the average mobility of Na^+ ions increases with increasing salt concentration.

What are the mechanisms underlying the diffusivities of Cl^- ions? In this context, we classified the Cl^- ions in the polymer membrane into three populations: (I) Those which are associated with the condensed Na^+ ions; (II) those which are associated with free Na^+ ions; and (III) free Cl^- ions. The results displayed in Figure 4b conform to intuitive expectations and demonstrate that the diffusivities of these populations follow the order $D_I < D_{II} < D_{III}$. However, a more surprising observation is found in the results displayed in Figure 4a. Therein, it is seen that the relative fraction (f) of the different populations satisfies the trend: $f_I > f_{II} > f_{III}$. While the *initial* relative populations of I, II, and III can be seen to mirror the condensed and free Na^+ ions (Figure 3a), the more surprising observation is the increase in the fraction f_{III} despite a reduction in the fraction of condensed Na^+ ions (Figure 3a). While we do not have a conclusive explanation for this observation, we speculate that the polymer backbone near the condensed Na^+ ions presents a local environment with lower dielectric constant which facilitates enhanced ion pairing between the cations and anions. As a consequence, the majority of the Cl^- ions resulting from the addition of salt is seen to become associated with the Na^+ ions "condensed" with sulfonate groups.

Taken together, the above results for the diffusivities and the relative fractions of I, II, and III serve to explain the observations of Figure 2. Specifically, it is seen that the mobility of Cl^- ions in the membrane is influenced by the diffusivities of population III, which, due to the low mobility of the condensed Na^+ ions, also possesses the lowest mobilities. We recall that in contrast the salt concentration dependence of the mobility of Na^+ ions was dominated by the mobility of the free Na^+ ions. As a consequence, the Na^+ ions in the membrane exhibit average higher diffusivities than Cl^- ions. Moreover, the mobility of Na^+ ions in the membrane increases with increasing salt concentration due to an increase in the free Na^+ ions, whereas the mobility of Cl^- ions reflects an interplay of the

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mobilities of the populations I and III and is relatively insensitive to the salt concentrations.

In contrast to the above trends in polymer membranes, the diffusivity and fraction of associated Cl^- ions *in aqueous solutions* follow intuitive expectations. Overall, the fraction of associated Cl^- ions increases with increasing salt concentrations, and the mobility of such ion pairs is indeed lower than the free ions. The relative diffusivities of Na^+ and Cl^- ions agree with earlier simulation reports[11,12,20,25] and have been rationalized based on the presence of the hydration shell surrounding the Na^+ ion in aqueous solutions, which hinders the mobility of such ions. To maintain the focus on polymer membranes, we refer to the earlier works for the mechanisms underlying aqueous electrolyte solutions.

We also examined the effect of salt concentration on the mobility of water molecules in the polymer membrane (Figure 5a) and observed a similar reversal of salt concentration dependencies relative to the aqueous solutions. Explicitly, the diffusivity of water molecules is seen to increase with salt concentration in the polymer membrane, whereas the water mobilities decrease with increasing salt concentrations in aqueous solutions. We rationalize these observations by invoking two features: (i) Internal structure and coordination of water: We calculated the radial distribution function $g(r)$ of O−O (oxygen atoms of water) and display the results in Figure 5b for membrane and in Supporting Figure S5 for aqueous electrolyte. Within polymer membranes, it can be seen that with increasing salt concentration the intensities of the first peak become less pronounced, and the second solvation shell becomes flatter. These trends are indicative of salt-induced breaking of the water structure in the polymer membrane and are expected to enhance the mobility of the water. In contrast, we observe for aqueous electrolyte (Figure S5) that the addition of salt increases the intensities of the first and second peaks. Such an observation is consistent with earlier reports where salt has been suggested to enhance the structure of water in electrolytes.[26−28] Pertinently, we expect such enhanced coordination will reduce the mobility of water molecules. (ii) A second origin of water mobilities relates to the relative fraction of free water and water bound to the sulfonate groups (we considered water molecules are bound with sulfonated groups if they are within a cutoff distance of 4.6 Å and first hydration shell from $g(r)$ between S−O of water as shown in Supporting Figure S6). The corresponding results displayed in Figure 5c demonstrate that the fraction of free water molecules increases with increasing salt concentrations. Since such a population is likely to possess higher mobilities, we expect for the overall diffusivities of the water molecules to become enhanced with increasing salt concentrations. We argue that the above two features underlie the salt-induced enhancement in the mobility of water molecules in polymer membranes.

In summary, we presented atomistic molecular dynamics simulation results for the mobilities and structure of salt ions and water in charged polymer membranes and compared them with the trends in aqueous electrolyte solutions. In polymer electrolytes, we found a reversal in the trends relative to aqueous electrolytes of the salt ions and water mobility with respect to the salt concentration. We find that such results arose from the influence of the charged polymer membrane on the water structure and ion pairing tendencies. Together, our results highlight the complexities of ion transport phenomena in solvated charged membranes and reinforce the need to accurately capture the local electrostatic phenomena and structures in such systems for prediction of ion and water mobilities.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.8b00333.

Details of the simulation methodology and supplementary results relating to the radial distribution function (PDF)

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Notes

The authors declare no competing financial interest.

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