Molecular Dynamic Study of Water-Cluster Structure in PFSA and PFIA Ionomers

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Molecular-dynamics simulations were used to study the structure of water clusters in different perfluorinated ionomers. The ionomers included in this work were Perfluorosulfonic Acid (PFSA) and Perfluoroimide Acid (PFIA). Different shapes and sizes of water domains in PFSA and PFIA were observed. In PFSA, ionomer water domains have spherical-like shape while water domains have complicated branch structure in PFIA ionomer. The mean water-cluster size for PFSA and PFIA ionomers as a function of water content lie on one universal curve, which indicates that the size of water clusters depends primarily on water content and weakly on ionomer chemistry. In PFSA, almost all hydronium ions are located predominantly close to the water cluster/backbone interface for both large and small values of water content; while in PFIA a relatively large fraction of hydronium ions are distributed within the bulk of the water clusters. A similar distribution of acidic groups was observed in both ionomers. In PFSA ionomer, all sulfonic groups are located in the surface water layer at the distance from 3 Å to 6 Å from the backbone. In PFIA ionomer, approximately 60% of sulfonic groups are located in the surface water layer and 40% of sulfonic groups are immersed into the bulk of water cluster.

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Perfluorinated ion-exchange membranes are widely used in both fuel cells and flow-battery cells. Flow batteries, such as vanadium redox batteries (VRBs), are promising devices for the large-scale Electrical Energy Storage (EES) applications1 and are receiving increasing interest due to the demand for grid-scale EES solutions and recent improvements in VRB cell performance.2 The ion-exchange membrane is a critical component in these different types of electrochemical flow cells, which conducts the charge-carrier ions (e.g., protons) while preventing the flow of electrons through it. Additionally, in a flow-battery cell, the membrane separates the positive and negative liquid electrolytes containing the active redox-species ions. For example, in a VRB cell, it is desirable to prevent the crossover of vanadium ions through the membrane since the result is a decrease in both the energy efficiency and energy capacity of the VRB system.2,3 In VRBs, this energy-capacity loss is recoverable, since the vanadium can be simply rebalanced by pumping some of the electrolyte with the excess V to the other electrolyte tank (albeit with an additional energy loss due to self-discharging that results from mixing the two reactants). In flow-battery chemistries with dissimilar active-species ions (e.g., Fe-Cr systems), crossover can also cause contamination of the electrolytes and/or electrodes, which can result in additional adverse effects on the flow-battery system.4 In any case, the active-species ions are transported through the membrane in the hydrophilic phase (i.e., the water clusters) of the membrane. Therefore, the study of the water-cluster structure is required to understand and model the transport of different ions in the membrane. One of the ultimate goals of this work is to understand how different types of ion-exchange membranes may impact the crossover of the active-species ions relative to the transport of the desired charge-carrier ions. Therefore, in this work, Molecular Dynamics (MD) simulations are used to study the structure of water clusters in two different types of perfluorinated ionomers; namely, the Perfluorosulfonic Acid (PFSA) ionomer from E. I. du Pont de Nemours and Company (i.e., Nafion) and the Perfluoroimide Acid (PFIA) from the 3M Corporation. As mentioned in recent review5 fluorinated ionomers (PFSA and PFIA) are still “the first-choice for the PEM fuel cells”.

During the last thirty years a large number of theoretical and experimental work has focused on the investigation of the overall structure of PFSA and related ionomers (e.g., see Refs. 5–7 and references therein). Understanding PFSA-type structures is challenging due to both the complexity of these multi-phase structures and by the sensitivity of the ionomer structure to preparation details (see excellent review of A. Kusoglu and A.Z. Weber6 where recent progress and developments on PFSA membranes are summarized). Nevertheless, considerable insight into the basic structure of these complex materials has been obtained from this vast body of prior work. For example, the structure of PFSA ionomers has been studied at different scales, including small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS), small-angle neutron scattering (SANS),8–18 quasi-elastic neutron scattering (QENS),19,20 infrared (IR)21,22 and Raman spectroscopies, time-dependent Fourier-transform IR (FTIR),23 NMR,24,25 analytical electron microscopy,26 positron-annihilation lifetime spectroscopy,27 tapping-mode atomic-force microscopy,28,29 scanning-electrochemical microscopy,30 and electrochemical-impedance spectroscopy,31,32 which has established that the PFSA structure consists of micro-phase separation of a hydrophobic matrix and hydrophilic clusters. It has also been established that the hydrophobic phase contains crystallites with PTFE-like crystallinity, which is associated with the perfluorocarbon backbone of PFSA. However, the size and structure of these crystallites are still widely debated in the literature. It is also clear that water molecules, protons, and anionic side chains form the hydrophilic clusters, and the size of these ionic clusters varies from 1 nm to 4 nm depending on water content. The shape of the clusters (e.g., spherical vs. cylindrical) and connectivity of the cluster network also continue to be a subject of debate in the literature. Therefore, in spite the large amount of experimental data, there is no commonly-held theory of the complete structure of PFSA ionomers. More exhaustive reviews of experimental studies of PFSA and related ionomers are available in the literature.1,5,33

A large number of PFSA models are also available in the literature (e.g., see Refs. 5–7,31,33 and references therein). In 1970, Eisenberg proposed clustering of ions in organic polymers.34 Mauritz and Hopfinger incorporated dipole-dipole interaction into the Eisenberg model to treat water distribution in PFSA.35 A variety of PFSA-structure models were further developed. One of the most popular models was proposed by Gierke and co-authors.11,36–40 In this model, the hydrophilic phase of PFSA is modeled by spherical hydrophilic clusters connected through cylindrical channels. Hydrophilic clusters are inverse micelles that are formed by water cluster surrounded by

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sulfonate groups. The mean clusters diameter is approximately 4 nm and diameter of cylindrical channels are about 1 nm in fully-hydrated PFSA. Yarusso and Cooper proposed a modified hard-sphere model,\(^{41}\) in which ionics are coated with a layer of polymer backbone whose electron density is the same as the matrix. In the core-shell model, ionic clusters consist of ion-rich core surrounded by an ion-poor shell (depleted zone) formed by fluorocarbon chains.\(^{6,62,63,64}\) A three-phase model of PFSA was proposed by Yeager and Steck,\(^{49}\) where one phase consists of fluorocarbon chains, the second phase is low-density interfacial region formed by side chains, and the third phase is spherical water cluster with ionic groups confined in pores. More recently, a fibrillar structure of PFSA has been proposed,\(^{44}\) where the fibrils are formed by aggregated polymer chains and water organized in a continuous medium surrounding the fibrils. Alternatively, parallel cylindrical water nano-channels in PFSA have been proposed.\(^{31}\) Another model assumes a lamellar (or slab) structure with an alternation of layers consisting of water or polymer chains.\(^{45}\)

With the development and availability of improved computational capabilities, PFSA structures have been studied utilizing more complicated computational models (e.g., see review\(^{5}\) and references therein). The first fully atomistic MD studies of ionomers were based on polyelectrolyte analogues.\(^{46-48}\) A large body of work was devoted to MD simulation of hydrated PFSA\(^{49-64}\) Atomic-level MD simulations of PFSA-based polymer materials, Hyflon/Dow, Nafion and Aciplex, were reported in Refs.\(^{60-64}\). Phase separation into hydrophilic and hydrophobic regions was observed in these simulations. The phase separation results in formation of water channel network. Calculated with an alternation of layers consisting of water or polymer chains.\(^{45}\)

To decrease computational efforts, and thereby increase the size of the modeled system, different simplifications were applied; such as the “united-atom” approach\(^{53,54}\) and a “coarse-grained” force-field model.\(^{55}\) Khoklov and co-workers proposed a mesoscale model of the modeled system, different simplifications were applied; such as the “united-atom” approach\(^{53,54}\) and a “coarse-grained” force-field model.\(^{55}\) More recently, a fibrillar structure of PFSA has been proposed,\(^{44}\) whose electron density is the same as the matrix. In the core-shell model, ionic clusters consist of ion-rich core surrounded by an ion-poor shell (depleted zone) formed by fluorocarbon chains.\(^{6,62,63,64}\) A three-phase model of PFSA was proposed by Yeager and Steck,\(^{49}\) where one phase consists of fluorocarbon chains, the second phase is low-density interfacial region formed by side chains, and the third phase is spherical water cluster with ionic groups confined in pores. More recently, a fibrillar structure of PFSA has been proposed,\(^{44}\) where the fibrils are formed by aggregated polymer chains and water organized in a continuous medium surrounding the fibrils. Alternatively, parallel cylindrical water nano-channels in PFSA have been proposed.\(^{31}\) Another model assumes a lamellar (or slab) structure with an alternation of layers consisting of water or polymer chains.\(^{45}\)

Comparative study of correlations in hydrophilic phase of DuPont’s PFSA (i.e., Nafion) and 3M PFSA ionomers have been published in.\(^{59}\) The radial-distribution functions (RDF) between sulfonate groups, between sulfonate group and water molecules, and between sulfonate group and hydronium ions were calculated as functions of both hydration level and temperature. Three different water models were used; F3C, SPC/Fw, and SPC/Fw with reactive MS-EVB (multi-state empirical valence bond) potential that takes into account both hydration level and temperature. Three different water models were used; F3C, SPC/Fw, and SPC/Fw with reactive MS-EVB (multi-state empirical valence bond) potential that takes into account the formation and breakup of O-H bonds. It was found that the model predictions are sensitive to the water model used in simulation. Analysis of the coordination number of water around the sulfonate group indicates that the water clusters in DuPont’s PFSA tend to be bigger and farther apart than the clusters in 3M’s PFSA.

Recently, PFIA ionomer was proposed as possible new Proton Exchange Membrane (PEM) for PEM fuel cells.\(^{65,66}\) Comparison of hydrophilic domains structure and proton conductivity for 3M PFIA, 3M PFSA and Nafion were experimentally investigated in Ref.\(^{67}\). An ab initio study of proton dissociation and the energetics of proton transfer is presented in Ref.\(^{68}\) for three 3M ionomers with multi-acid side-chains including PFIA.

This work is motivated by the eventual goal of being able to obtain the ability to predict how different ionomers may impact the transport of different ions within the hydrophilic phases of the membrane. Therefore, the detailed structure of individual water clusters in PFSA and in PFIA ionomers was undertaken using MD simulations. The PFSA ionomer contains one acidic group, the sulfonic group, per pendant chain. The PFIA ionomer contains two acidic groups per pendant chain, namely, a sulfonic group at the end of the side chain and a sulfonimide group in the middle. Two acidic groups and two protons per one pendant chain increase proton concentration in the membrane and can offer higher proton conductivity than that for PFSA membrane. Additionally, two acidic groups per one pendant chain make the pendant chain more hydrophilic. It is expected that more hydrophilic pendant chain with two acid groups should penetrate deeper into the water cluster, which might reduce transport of larger positive ions through the membrane by geometrical constraint.

**Figure 1.** The schematic structures of PFSA and PFIA side chains.

**Molecular Dynamics Model**

**MD model of perfluorinated ionomers: PFSA and PFIA.—** The schematic structures of PFSA and PFIA ionomers are presented in Figure 1. The PFSA is a copolymer consisting of hydrophobic fluorinated backbone and fluorinated side chains with sulfonic acid group. The PFIA ionomer is also a copolymer with the same fluorinated backbone. The fluorinated side chain of PFIA contains two acidic groups; namely, sulfonic acid group at the end of the side chain and sulfonimide group in the middle. We estimated acidities of these groups through pKa of model compounds similar to ionomer side chains. For the sulfonic group the model compound is triflic acid with pKa = −12 and for the sulfonimide group the model compound is bis-perfluoroethyl sulfonimide with pKa < −2.\(^{69}\) From these values of pKa we conclude that for typical values of pH of ionomer membranes (that is around 0) most of both sulfonic and sulfonimide acidic groups are dissociated. Thus, the charge of the PFSA side chain is −1 and the charge of the PFIA side chain is −2. Consequently, the number of hydronium ions in PFSA system is equal to the number of PFSA side chains in the system. The number of hydronium ions in PFIA system is equal to the doubled number of PFIA side chains.

In Molecular Dynamics calculations we employed the all-atom TEAM ab initio force field developed by Huai Sun and co-workers.\(^{71}\) This force field has the Amber functional form:

\[
E = \sum_{\text{bonds}} K_b (b - b_0)^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \frac{6}{2} K_\phi \left[1 - \cos(n)\right] + \sum_{\text{nonbond}} \left[6v_i[\sigma_i/r_i]^2 - 2(\sigma_i/r_i)^6\right] + q_i q_j / r_{ij}
\]

The energy of long-range coulomb interactions is calculated by PPPM method\(^{72}\) while Van der Waals interaction is taken into account only within the cutoff distance, \(r_\text{cutoff} < 12\ \text{Å}\). Intramolecular 1–4 non-bonded interaction energies are scaled by factors of 0.5 and 0.8333 for Van der Waals and Coulomb terms respectively as accepted for Amber functional form. The Lennard-Jones parameters for atoms of different types are calculated according to Lorentz-Berthelot mixing
rules:

\[ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}; \quad \sigma_{ij} = (\sigma_i + \sigma_j)/2 \]

Molecular-dynamics simulation of equilibrium water uptake of PFSA membrane was also performed with TEAM force field.\(^7\) Calculated water uptake is in close agreement with the experimental data, which justifies application of this force field for molecular dynamics simulations of perfluorinated proton-exchange membranes. The force-field parameters for atoms of sulfonimide group in PFIA were chosen according to Lopes and Padua.\(^7\) The list of force field parameters are presented in Appendix. The TIP4P model for water molecules\(^7\) and the force field by Kusaka\(^7\) for hydronium ions (\(H_3O^+\)) were used in current work. Simulations were performed in LAMMPS software package.\(^7\)

**Formation of initial structure for MD simulation.**—The initial molecular configuration for MD modeling of ionomer + water was prepared in the following way. The ionomer chains were constructed on the basis of the ideal PTFE chains with helical symmetry and a period of 13 CF\(_2\) groups. One PFSA chain consists of 150 CF\(_2\) backbone monomers and 10 side chains, which results in a correct equivalent weight (1100 g/eq). One PFIA chain consists of 136 CF2 backbone monomers and 10 side chains, which corresponds to an equivalent weight of 625 g/eq.

Two hydration levels of PFSA ionomer were modeled: \(\lambda = 12\), which correspond to hydration level of PFSA ionomer in equilibrium with saturated vapor, and \(\lambda = 22\), which corresponds to hydration level of PFSA ionomer in equilibrium with liquid water (see Ref. 5 where huge data for water-uptake behavior of Nafion membranes are summarized, as well as in Ref. 76). We define \(\lambda\) as the number of water molecules per side chain. The same definition of \(\lambda\) is also used by the 3M Corporation (supplier of PFIA). The PFIA membrane in equilibrium with liquid water demonstrates hydration level of \(\lambda = 50\).\(^7\) The system that corresponds to this hydration level of PFIA ionomer was modeled in this work. For comparison, we also modeled the system with hydration level of \(\lambda = 22\) that corresponds to hydration level of PFIA ionomer in equilibrium with vapor at relative humidity RH = 90%. Note that we did not calculate the water content in the membrane in equilibrium with vapor and liquid water. Those parameters are input for our simulations and were taken from experimental data. The number of water molecules in membrane was fixed during simulation and was not changed during one trajectory.

In the case of PFSA, the initial configuration for thermalization consisted of 27 ionomer chains, 270 \(H_3O^+\) ions and 2970 or 5670 water molecules for \(\lambda = 12\) or 22, respectively. In the case of PFIA, the initial configuration for thermalization consisted of 27 ionomer chains, 540 \(H_3O^+\) ions and 11340 or 26460 water molecules for \(\lambda = 22\) or 50, respectively.

A cube of size \((612 \times 612 \times 612 \, \text{Å}^3)\) with periodic boundary conditions was chosen as the initial simulation box. Water molecules and \(H_3O^+\) ions were randomly distributed in the simulation box. Ionomer chains were oriented along \(x\) or \(y\) or \(z\) axis with randomly distributed coordinates of the chain centers.

The thermalization was performed in an isothermal–isobaric (NPT) ensemble. The number of molecules (\(N\)), pressure (\(P\)) and temperature (\(T\)) are conserved in an NPT ensemble. The external pressure was kept constant and equal to 1 atm. The temperature was changed during the thermalization process. The initial temperature of the system was set to \(T_0 = 50\, \text{K}\). Then the system was heated up to \(T_1 = 500\, \text{K}\) for 1 ns. After that the system was equilibrated at \(T_1 = 500\, \text{K}\) for 10 ns, and then was cooled to \(T_2 = 300\, \text{K}\) for 10 ns. At fixed volume at \(V = 500\, \text{K}\) and water vapor pressure increased up to 25 bar, water should leave the membrane. However, we run our simulations in NPT ensemble, with a fixed the number of particles. An increase of instant pressures is damped by the increase of the simulation box with the boundary conditions used here.

The simulation volume was automatically adjusted to correspond to the desired pressure. As a result, the initial low-density structure transforms into a system with realistic density. Namely, in the system with PFSA ionomer, the final density was 1.73 g/cm\(^3\) for \(\lambda = 12\) and 1.59 g/cm\(^3\) for \(\lambda = 22\). These values are in good agreement with experimental data, which are approximately 1.75 and 1.65 g/cm\(^3\) for \(\lambda = 12\) and \(\lambda = 22\), respectively.\(^7\) In the system with PFIA ionomer, the final density was 1.46 g/cm\(^3\) for \(\lambda = 22\) and 1.24 g/cm\(^3\) for \(\lambda = 50\). It is well known that the polymers are not thermodynamically equilibrium systems due to very long equilibration time, except small ideal polymer crystals. We believe that we obtain realistic system that corresponds to the micro-structure of real polymer from comparison of obtained density of the system with the density of real polymer. For calculation of different statistical properties of the system, the MD trajectory in the NPT ensemble at 300 K was simulated for 8 ns.

**Results and Discussion: Water Clusters Structure**

Snapshots of the systems after thermalization are shown in Figure 2. For better visualization, water molecules and hydronium ions are removed. The systems shown in Figure 2 correspond to full hydration of the two different ionomers in liquid water. Micro-phase separation is evident in these snapshots. One phase is non-polar and formed by backbone molecules. The second phase is polar and formed by water molecules and hydronium ions. This phase manifests itself in the snapshots by shadowed caves.

The different shapes of the water domains in PFSA and PFIA are clearly evident in Figure 2. In PFSA, water domains have spherical-like structure. In PFIA, water domains have complicated branch structure. Below we analyze the systems structure with the help of radial distribution functions (RDFs) and probability distributions, which are distributions of the distance from chosen atom of one type to the nearest atom of another type. Although water clusters in PFIA have branch structure, we estimate water-cluster size and find average radius of water domains.

**Water-cluster structure.**—To estimate the size of water clusters, the distribution of the distance from water molecule to the nearest backbone atom was constructed for four systems under consideration. Polymer backbone atoms nearest any water molecules form the wall of the water cluster; which is why they are valuable for determination of the water-cluster size. Water molecules in the center of the cluster are the most distant from the wall. The distance from these molecules to the wall (i.e., to the nearest backbone atoms) is equal to the cluster “radius”. One might think that water forms spherical clusters around the anionic groups. However, visualization of the molecular dynamics trajectories shows that it is not the case. As a rule, water clusters contain several anionic groups, and the distribution of the anionic groups within the cluster is quite chaotic. Thus, the inspection of the solvation shells is not helpful in estimation of the water-cluster size.

The distribution was averaged over all molecules through 800 snapshots of MD run. The location of water molecule was defined as

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![Image](https://example.com/image.png)
location of O atom of the water molecule. The distance from the water molecule to the nearest backbone atom was considered as the distance from the water molecule to the interface between water cluster and hydrophobic domain. The probability distribution of the distance from water molecules (solid lines) and hydronium ions (dashed lines) to the nearest backbone atom for all four systems under consideration are shown in Figure 3. All curves for water molecules demonstrate two peaks. The first distinct peak at 3.2 Å corresponds to the molecules at the surface of the water domains. The surface water molecules are separated by the Van-der-Waals radius from outer backbone atoms, which is approximately 3 Å. These molecules form the first solvation shell of backbone atoms. The second peak is diffusive and almost indistinguishable for PFIA with $\lambda = 50$.

The distributions of the distance between hydronium ion and the nearest backbone atom are shown by dashed lines in Figure 3. The first observation from Figure 3 is that for both PFSA and PFIA systems the distributions for small and large water content are very similar (i.e., compare dashed lines in Figure 3a and Figure 3b or dashed lines in Figure 3c and Figure 3d). The second observation is that the distributions of hydronium ions for PFSA (see Figure 3a and Figure 3b) have one distinct peak at 3.0 Å that corresponds to hydronium ions in the surface layer of water cluster. The distributions of hydronium ions for PFIA demonstrate two peaks. The first distinct peak at 3.0 Å also corresponds to hydronium ions in the surface layer of the water clusters. The second diffusive peak at approximately 7.5 Å corresponds to hydronium ions in the bulk of the water cluster.

The fraction of hydronium ions in the surface layer of the water clusters was calculated by integration through the first peak (from 3 Å to 5 Å) of the distribution of hydronium ions. Calculated fraction of hydronium ions in the surface layer of the water clusters for PFSA is 0.61 and 0.56 for $\lambda = 12$ and $\lambda = 22$, respectively. Calculated fraction of hydronium ions in the surface layer of the water clusters for PFIA is 0.38 and 0.33 for $\lambda = 22$ and $\lambda = 50$, respectively. Therefore, relatively large fractions of hydronium ions are distributed within the bulk of the water clusters of PFIA ionomer, unlike PFSA where they are primarily on the surface of the water clusters. In PFIA ionomer, hydronium ions penetrate into the water clusters up to 10 Å depths.

To estimate the size of water domains we analyzed the cumulative probability distribution of the distance from water molecule to the nearest backbone atom in (a) PFSA and in (b) PFIA at the two different hydration levels specified.
nearest backbone atom, which are presented in Figure 4. The radius of water clusters was defined as a value at which cumulative probability reaches 0.99. The average radii of water clusters in PFSA are estimated as 12 Å and 17 Å for λ = 12 and 22, respectively. The average radii of water clusters in PFIA are estimated as 21 Å and 26 Å for λ = 22 and 50, respectively. The mean water cluster sizes in PFSA and PFIA ionomers are plotted in Figure 5 as a function of weight water content. The calculated values of mean cluster size for both ionomers lie on one universal curve. This result indicates that the size of water cluster depends mostly on water content and weakly depends on the ionomer chemistry. It also confirms that water absorption is proportional to the equivalent weight of the ionomer.

The probability distributions of the minimal distance between acid group atom and backbone atom are shown in Figure 6 for all systems under consideration. As in the case of hydronium ions, the distributions for acid groups are almost the same for small and large water content for both PFSA and PFIA. In PFSA ionomer, all sulfonic groups are located in the surface water layer at the distance from 3 Å to 6 Å from the backbone. In PFIA ionomer, the distribution of sulfonic groups is much broader than that in PFSA ionomer. Approximately 60% of sulfonic groups are located in the surface water layer and 40% of sulfonic groups are immersed into the bulk of water clusters. The distribution of sulfonic groups for PFIA ionomer is consistent with distribution of hydronium ions; the sulfonic groups in the bulk of water cluster are required for neutralization of negative charge of hydronium ions in the bulk of the cluster. The distributions of sulfonimide groups have one distinct peak at 3.2 Å and the major fraction of sulfonimide groups are located in the surface water layer at the distance from 3 Å to 6 Å from backbone as the sulfonic groups in PFSA ionomer.

To study the configurations of the side chains we calculated the probability distributions of the distance between the carbon at the joint of the backbone and side chain and the center of acid groups. Position of the sulfur was defined as a center of sulfonic group, and position of the nitrogen was defined as a center of sulfonimide group. The calculated probability distributions are shown in Figure 7. The distributions for small and large water content are almost identical for both PFSA and PFIA. All distributions have one distinct peak. In PFSA ionomer, the peak is at 8.8 Å; whereas the distance between the carbon at the joint of the backbone and side chain and the sulfur of sulfonic group is 9.2 Å in the lowest energy state of a single side-chain in a vacuum. This indicates that side chains in PFSA are almost straight. In PFIA ionomer, the peaks in the distribution for sulfonimide and sulfonic groups are at 9.0 Å and 13.7 Å, respectively. The distances between the carbon at the joint of the backbone and side chain and the sulfur of sulfonic group or the nitrogen of sulfonimide group in PFIA optimized geometry are 9.8 or 17.1 Å, respectively. This indicates that a portion of PFIA side chain is rather straight (from joint carbon atom to sulfonimide group); whereas the remaining portion of the PFIA side chain, from sulfonimide group to sulfonic group, is curved.

Observed localization of hydronium ions near the water cluster surface agrees with results of Ref. 61 where the hydronium ions were localized around the sulfonate groups near the water-channel surface. We speculate that the reason for location of hydronium ions near the surface is electrostatic interaction of the ions. Hydronium ions repel each other and are pushed to the water cluster surface. On the other hand, hydronium ions are attracted by negative acid groups of the side chains that are located at the water-cluster surface. The side chains are located at the water cluster surface due hydrophobic interaction of hydrophobic part of the side chain with water molecules. The distribution of hydronium ions in PFIA cluster is more uniform compared to PFSA, as seen in comparing distributions in Figure 3.

![Figure 5](image1.png)

**Figure 5.** The mean water cluster size as a function of weight water content for both ionomers.

![Figure 6](image2.png)

**Figure 6.** Probability distribution of the minimal distance between acid group atom and backbone atom: (a) PFSA and (b) PFIA (sulfonimide groups and sulfonic groups) for two different hydration levels for each acid group.

![Figure 7](image3.png)

**Figure 7.** Distribution of the distance from the carbon at the joint of the backbone and side chain to the centers of acid groups (PFSA sulfonic group - solid line, PFIA sulfonic group - dashed line, PFIA sulfonimide group - dotted line).
This is consequence of the relatively deep immersion of the sulfonic group into the cluster, which results in positive charge within the bulk of the cluster. This positive charge is neutralized by the penetration of hydronium ions into the water cluster.

**Aggregation of acid groups.**—The aggregation of acid groups was studied through calculation of coordination number as a function of the distance, $R$, for a given acid group. The coordination number is the number of acid groups within the sphere of radius $R$ centered at the given acid group. The coordination number is calculated by integration of radial distribution functions (RDF) between the acid groups from 0 to the given value $R$. The RDFs were calculated between $S$ atom of sulfonic or $N$ atom of sulfonimide groups (below we abbreviate sulfonimide as “imid”) for all four systems. All RDFs were averaged over 800 snapshots of MD trajectory. Coordination numbers for considered systems are shown in Figure 8. Coordination numbers for PFSA calculated in this work are similar to those calculated in Ref. 59.

All coordination numbers shown in Figure 8 demonstrate reasonable dependence on water content (i.e., aggregation decreases with increase of water content for all acid groups). Aggregation of all acid groups in PFIA ionomer (see Figures 8b–8d) is lower than those in PFSA ionomer (see Figure 8a) because PFIA side chain is longer than PFSA side chain. Aggregation between sulfonic groups in PFSA with $\lambda = 12$ and $\lambda = 22$ is not very different. For PFSA ionomer, aggregation is unity at a distance of approximately 6.5 Å, which indicates that in PFSA every sulfonic group is coupled with another sulfonic group through a water molecule or a hydronium ion. We consider sulfonic and sulfonimide groups in PFIA separately as the aggregation for these groups can be different. The aggregation between sulfonic groups in PFIA with $\lambda = 22$ is about 0.25 at 6.5 Å; whereas the aggregation between sulfonimide groups is about 0.5 at the same distance. This difference can be explained by the larger size of sulfonimide group relative to the sulfonic group, which is the primary reason the total coordination number of sulfonic and sulfonimide groups in PFIA is less than coordination number for sulfonic group in PFSA at the same distance. We define the total coordination number of sulfonic or sulfonimide group as the number of all (sulfonic or sulfonimide) acid groups within the sphere of radius $R$ centered at the given acid group.

The total coordination number of sulfonic group is the sum of the curves in Figures 8b and 8d. The total coordination number of sulfonimide group is the sum of the curves in Figures 8c and 8d. The total coordination numbers of sulfonic and sulfonimide groups are about 0.85 and 0.7 at 6.5 Å, respectively. The coordination number of sulfonic group in PFSA at the same distance is about 1.0. We explain the lower aggregation in PFIA than those in PFSA by longer side chain and larger size of sulfonimide group.

**Conclusions**

A comparative molecular dynamics study of water domain structure in hydrated PFSA and PFIA ionomers was performed. Two hydration levels were modeled for each of the ionomers. The smaller hydration levels correspond to ionomer in equilibrium with vapor at high relative humidity ($\lambda = 12$ for PFSA and $\lambda = 22$ for PFIA). The larger hydration levels correspond to ionomer in equilibrium with liquid water ($\lambda = 22$ for PFSA and $\lambda = 50$ for PFIA).

Different shapes and sizes of water domains were observed in PFSA and PFIA ionomers. In PFSA ionomer, water domains have spherical shapes, while water domains have complicated branch structures in PFIA ionomer. The average radii of water clusters in PFSA are estimated to be 12 Å and 17 Å for $\lambda = 12$ and 22, respectively. The average radii of water clusters in PFIA are estimated to be 21 Å and 26 Å for $\lambda = 22$ and 50, respectively. The mean size of water cluster in PFSA and PFIA ionomers were plotted as a function of weight water content and the values for both ionomers lie on one universal curve, which indicates that the size of water cluster depends mostly on water content and weakly depend on the ionomer chemistry.

Different distributions of hydronium ions in water clusters of PFIA and PFSA ionomers were also observed. In PFSA, almost all hydronium ions are located predominantly close to the water cluster/backbone interface for both large and small values of water content.
In PFIA, a relatively large fraction of hydronium ions is distributed within the bulk of the water clusters. The fraction of hydronium ions in the bulk of water clusters for PFSAs is 0.39 and 0.44 for $\lambda = 12$ and $\lambda = 22$, respectively; while the fraction of hydronium ions in the bulk of water clusters for PFIA is 0.62 and 0.67 for $\lambda = 22$ and $\lambda = 50$, respectively.

The distribution of acid groups in the water domains is also different in PFSA and PFIA. In PFSA ionomer, all sulfonic groups are located in the surface water layer at the distance from 3 Å to 6 Å from the backbone. In PFIA ionomer, the distribution of sulfonic groups is much broader than in PFSA ionomer. Approximately 60% of sulfonic groups are immersed in the bulk of the water clusters. The sulfonic groups in the bulk of PFIA water cluster are required for neutralization of negative charge of hydronium ions in the bulk of the cluster.

The presented model captures the major physics that governs the distribution of ions within a water cluster and thereby provides a reasonable approximation of the structure of the hydrophilic regions within these two different ionomers. These clusters are the domain where the transport of ionic species occurs in ion-exchange membranes made from these materials, which are utilized in various electrochemical cells, such as fuel cells and flow batteries. This understanding can therefore be used to assess the impact of the water-cluster structures on the transport of various types of ions within these membranes, which will be the subject of future publications.

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