WATER HYDROGEN BONDING IN PROTON EXCHANGE
AND NEUTRAL POLYMER MEMBRANES

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by
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ABSTRACT

Understanding the dynamics of water sorbed into polymer films is critical to reveal structure-property relationships in membranes for energy and water treatment applications, where membranes must interact with water to facilitate or inhibit the transport of ions. The chemical structure of the polymer has drastic effects on the transport properties of the membrane due to the morphological structure of the polymer and how water is interacting with the functional groups on the polymer backbone. Therefore studying the dynamics of water adsorbed into a membrane will give insight into how water-polymer interactions influence transport properties of the film. With a better understanding of how to design materials to have specific properties, we can accelerate development of smarter materials for both energy and water treatment applications to increase efficiency and create high-flux materials and processes. The goal of this dissertation is to investigate the water-polymer interactions in proton exchange and uncharged membranes and make correlations to their charge densities and transport properties.

A linear Fourier Transform Infrared (FTIR) spectroscopic method for measuring the hydrogen bonding distribution of water sorbed in proton exchange membranes is described in this thesis. The information on the distribution of the microenvironments of water in an ionic polymer is critical to understanding the effects of different acidic groups on the proton conductivity of proton exchange membranes at low relative humidity. The OD stretch of dilute HOD in H₂O is a single, well-defined vibrational band. When HOD in dilute H₂O is sorbed into a proton exchange membrane, the OD stretch peak shifts based on the microenvironment that water encounters within the nanophase separated structure of the material. This peak shift is a signature of different hydrogen bonding populations within the membrane, which can be deconvoluted rigorously for dilute HOD in H₂O compared to only qualitative observations that can be made with pure D₂O or H₂O. The theory and experimental practice of determining the hydrogen
bonding distribution of water in a range of proton exchange membranes bearing aromatic sulfonate and perfluorosulfonate groups using this OD stretch technique is discussed.

The OD stretch of dilute HOD in H$_2$O absorbed in a series of sulfonated syndiotactic poly(styrene) and sulfonated poly(sulfone) membranes was studied using FTIR spectroscopy to measure how the character of the sulfonate headgroup and the backbone polarity influenced the water-membrane interactions. Using a three-state model, the OD stretch yielded information about the populations of absorbed water participating in hydrogen bonds with polymer-tethered sulfonate groups, water in an intermediate state, or water hydrogen bonding with other water molecules. The perfluoroalkyl sulfonate moiety, which behaves as a superacid, consistently displayed the largest fraction of headgroup-associated water due to its strong acidic character. Measurements of the OD stretch gave insight to the strength of the hydrogen bonds formed between water and the sulfonate groups. Water associated with the superacid displayed an OD stretch peak position that was blueshifted by 39 cm$^{-1}$ compared to the aryl sulfonate associated water with an OD stretching frequency that was centered at 2547 cm$^{-1}$. The polarity of the polymer backbone also affected the OD stretch peak position. As hydration increased, the OD peak stretching frequency in poly(styrene)-based membranes displayed a redshift from 2566 cm$^{-1}$ to 2553 cm$^{-1}$, whereas there was no OD peak maxima shift in poly(sulfone)-based membranes due to the greater amount of intermediate water in the more polar poly(sulfone) backbone system.

To further understand how the acidity of the sulfonate can be altered and how the acidity affects the hydrogen bonding network of water in a polymer membrane, various polymers with small chemical differences in the perfluorosulfonate sidechain were studied. In addition to the vibrational spectroscopy measurements using HOD as a probe, the partial charges of the sulfonate groups were calculating using DMol3 DFT calculations. The calculations and the experimentally determined peak position of the OD stretch both correlated to give a ranking of acidity for the various sidechains. It was found that having a thioether linkage instead of an ether linkage
(typical linkage for perfluorosulfonates) increased the acidity of the sulfonate group due to the capability of sulfur to expand its octet and more readily accept additional electron density. Through DFT geometry optimization, it was discovered that the thioether linkage prefers a kinked configuration while the ether linkage gives a more linear sidechain structure. This structural configuration correlated to experimental findings allowing more water to interact with the sulfonate group containing the ether linkage than the thioether linkage due to the sulfonate group being more easily accessible, even though the thioether sidechain is more acidic.

Three sulfonated poly(arylene sulfone) based polymers were studied using FTIR and DFT calculations to better understand how the acidity of the sulfonate groups were affected by the placement on the backbone. By increasing the number of sulfone groups, which have electron withdrawing properties, flanking the sulfonated aromatic ring, the acidity was increased. The charge density of a sulfonate group flanked by two sulfone groups was -1.626 (in units of fundamental charge), while the charge density of a sulfonate group flanked by one sulfone group increased to -1.703. Additionally, if the subsequent ring was unsulfonated, the charge density further increased to -1.737, indicating that some stability is gained by both available rings being sulfonated. The differences in charge density are reflected in the water uptake and conductivity measurements, where the samples with the lowest charge density had the highest water uptake and conductivity. The deconvoluted OD peak revealed that the sample with two sulfone groups flanking the sulfonated aromatic ring contains the highest amount of bulk-like water, which led to the increased conductivity.

The polyamide active layer of commercially available reverse osmosis membranes was studied at various relative humidities to better understand how the structure of the active layer changes when hydrated. The fingerprint region was used to analyze changes in the vibrational signature of specific functional groups and to understand how different chemical moieties interact with water. Using the difference spectrum, the water-polymer interactions could be quantified and
correlated to transport properties of the membrane. Increasing the amount of free carboxylic acid groups on the backbone will lead to an active layer that is less crosslinked and contains a greater number of larger pores, which results in a higher flux. Active layers that contained a smaller concentration of free carboxylic acids were more highly crosslinked and had a higher amount of smaller pores, resulting in a lower flux.

In summary, by studying the water hydrogen bonding network in various proton exchange membranes and neutral polyamide membranes, a new understanding of structure-property relationships has been developed. This will lead to a greater understanding of transport properties and conductivity in various polymer membranes. Expanding this fundamental knowledge will lead to the development of smarter materials for energy and reverse osmosis applications, and the ideas developed here can be extended to new types of materials used for various needs.
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beginning.
Chapter 1
Introduction

1.1 Background

Hydrogen fuel cells are a part of the crucial technology advancements that are needed to reduce our dependence of fossil fuels. Proton exchange membranes fuel cells (PEMFC) provide a means of alternative energy production by converting chemical fuel into electricity while emitting only water and heats as byproducts. Vast improvements to the lifetime and power outputs have been made to PEMFC since their mass production introduction during the Gemini space program in the 1960’s. However, for PEMFC to become a viable power source for vehicles, electronics, production plants, and even our homes, their performance must be improved and the cost must be reduced before they can be considered a competitor to petroleum-based processes.

According to the DOE, since 2006 the automotive fuel cell system cost has dropped from $124/kW to $55/kW.\(^1\) Much of this cost reduction has come from advances in the design of the membrane electrode assemblies (MEAs) which now contain less platinum nanoparticles.\(^2\) Little change has been made to the proton exchange membrane (PEM) since the late 1960s when NAFION®, a polyperfluorosulfonic acid, was first introduced. The PEM acts as a separator between the two electrodes, allowing only the transport of protons to complete the half reactions. NAFION® based membranes provide outstanding oxidative and chemical stability while also possessing high conductivity at low relative humidity compared to its alternatives.\(^3\) The major drawback of NAFION® is its high cost of production and degradation at high temperatures. Therefore, in order to reduce the cost of PEMFCs even further, to a level that is comparable to the kW price of combustion engines, development of novel PEM materials is a necessity.
There have been numerous efforts to displace NAFION® with PEMs that are not fluorinated. PEMs based on aromatic polymer backbones have been shown to have high modulus, low methanol and hydrogen crossover and longer open circuit hold lifetimes due to their low oxygen crossover.\textsuperscript{4,5} Additionally, many aromatic PEMs are based on engineering thermoplastics that are synthesized at large scale and have the potential to provide very cost-effective membrane materials. There is a huge range of potential chemical compositions that can be employed to tune the properties of these materials and the community has surveyed the structure-property relationships of aromatic PEMs extensively. Despite their interesting properties, in the majority of studies the low humidity and low hydration number ($\lambda$) proton conductivity of aromatic PEMs is too far below the low relative humidity performance of NAFION® to meet low humidification cell operation. The conduction properties of PEM are determined by the material’s volumetric ion content, chemical composition, morphology, and water uptake. These factors are often dependent on one-another. For instance, with greater water uptake a PEM’s ion concentration declines and the chemical composition of the material can have a distinct influence on the nanophase separated morphology of the ionic domains.\textsuperscript{6} The morphology of PEMs has received great attention with NAFION®, a poly(perfluorosulfonic) acid, as the conventional and most-studied PEM.\textsuperscript{7} The goal of these morphology studies is to arrive at a mechanistic understanding of how NAFION® achieves its high proton conductivity. Through this work, the “ideal morphology” may be arrived at and emulated in new materials.

While advanced technologies must be developed to achieve a sustainable energy supply, another issue that is closely related, but often overlooked, is the global need for water. In many areas around the world, such as the Middle East, India, and Africa, water shortages are becoming a more pressing issue. Less than one percent of the freshwater on earth is suitable for human consumption.\textsuperscript{8} As fresh water resources grow scarce, the process of reverse osmosis (RO) has become increasingly important for the production of clean water. Reverse osmosis is a
membrane-facilitated filtration process that involve applying a hydrostatic pressure greater than the osmotic pressure of the solution to a semipermeable membrane. This pressure creates a chemical potential difference across the membrane, driving the solvent to the low concentration side of the membrane while the solute remains on the high concentration side of the membrane.9 For RO membranes to be a low-cost, high-efficiency means of water purification, they must possess high flux and salt rejection. Currently, thin film composite membranes (TFC) made from aromatic polyamides dominate the market for RO applications.10,8 TFCs rely on the thin, dense polyamide layer for their superior transport properties, but because the layer is so thin, characterization is limited. In order to develop better membranes, characterization of the polyamide layer in TFC membranes needs to improve.

1.2 Motivation

Aromatic-based PEMs have struggled to compete with NAFION® for decades. This perceived deficiency of aromatic PEMs has been rationalized by their many differences, mostly notably the lack of a superacid chain in the aromatic polymers. It is thought that NAFION®’s superior sidechain chemistry is linked to increased phase segregation and leads to higher conductivity.11 The morphology of NAFION® has long been considered ideal, however, recently, the advent of superacid PEMs based on aromatic polymers has concerted efforts by a number of groups.12–14 These materials are interesting because they combine the robust mechanical and low crossover properties of aromatic PEMs with a conductivity performance that, in many cases, is nearly equivalent to NAFION® at low relative humidity. Reasonable conductivity at low λ has been achieved in a few cases for aromatic PEMs without superacids, but usually block copolymer15 or other morphological or hydration16 strategies are required, which adds complexity to the synthesis of these materials. Computational simulations of the hydration of a superacid
versus a non-superacid moiety have shown that the increased acidity (decreased charge density) is pivotal for weak hydrogen bonding between water and polymer. Superacids form weaker hydrogen bonds to the surrounding water molecules therefore allowing for faster water dynamics and proton transport. It is the goal of this dissertation to characterize both sulfonate acidity and charge differences and understand how structure-property relationships will affect the hydrogen bonding network in novel superacid containing PEM membranes using vibrational spectroscopy and HOD as probe.

The thin polyamide layer of TFCs governs the transport properties of the membrane. Currently, little is known about how the physicochemical properties of the polyamide layer affect the transport properties. The average thickness of the polyamide layer is ~100 nm and it is attached to a thick layer of porous poly(sulfone) making it difficult to isolate and characterize this thin layer. Researchers have previously used various microscopy techniques to study commercial membrane’s surface characteristics, such as surface roughness and cross-sectional geometry. In order to isolate the polyamide layer, researchers have synthesized the thin layer in their laboratories and have gained valuable insight into how reactant concentration can affect functional group and crosslinking density using various techniques. However, the transport properties of these laboratory synthesized films cannot be measured because they are too thin. Little research has been conducted on the isolated polyamide layer of commercial membranes and how these films interact with water when hydrated. Here we aim to study commercial membranes provided by The Dow Chemical Company in order to better understand the structure-property relationships within the isolated polyamide layer and how they impact the transport properties. By using FTIR and HOD as a probe, we were able to observe functional group density changes while also monitoring the water-polymer interactions. The findings could be correlated to the transport properties measured by Dow in order to relate structure-properties relationships to transport properties in commercial films.
1.3 References


Chapter 2

Literature Review

2.1 Introduction

Polymeric membranes have wide applications in energy technologies and membrane-facilitated water treatment applications. To be successful, the membranes must interact with water and facilitate or inhibit the transportation of ions. The chemical structure of the polymer directly impacts the transport properties of the membrane because water must interact with the functional groups tethered to the polymer backbone. Observing the dynamics of water adsorbed into a membrane will give insight into how water-polymer interactions influence transport properties of the film. By gaining insight about structure-property relationship, we can design materials to have specific properties and develop advanced materials for both water treatment and energy applications.

Proton exchange membrane fuel cells (PEMFC) are one of the most promising technologies for green energy conversion.¹ Their energy density and power density fill an important niche in automotive and portable power applications, and their use of energy dense chemical fuels gives them great potential compared to batteries. Currently, the membranes in PEMFCs are constructed from perfluorosulfonic acid (PFSA) polymers, such as NAFION®. PFSA are unique due to their hydrophobic, fluorinated backbones and hydrophilic, superacidic sulfonate side chains. This juxtaposition causes the sulfonate moieties to cluster together and form interconnected water-filled nanochannels,² enabling proton transport from the anode to the cathode of an electrochemical cell, allowing the desired half-reactions to occur. For example,
high proton transport rates are needed to facilitate hydrogen oxidation (H₂ → 2H⁺ + 2e⁻) and oxygen reduction (½O₂ + 2H⁺ + 2e⁻ → 2H₂O) in a hydrogen/air fuel cell where current densities can approach 1 A/cm² in the projected area of a 10 μm thick porous electrode. Water is an ideal solvent for proton transport because of its amphotericity³, fast rotational dynamics⁴, and ability to form dynamic hydrogen bonds⁵. These factors influence the hydrogen bonding network established in polymers films. Therefore, understanding the behavior of water in polymers and how the water contributes to the polymer’s proton conductivity is crucial to developing better-performing materials for membrane-based applications.

Reverse osmosis (RO) is the most commonly used process for producing fresh water from seawater or brackish water. As freshwater grows increasingly scarce, the efforts to increase the efficiencies of RO membranes become of amplified importance. Currently, aromatic polyamides are the industry standard because their unique interfacial polymerization gives high rejection of ions, on the order of 99.5% and higher. High rejection and low salt permeability are desirable qualities in RO membranes. Aromatic polyamides are highly cross-linked due to their polymerization method and it is hypothesized that the crosslinking provides size sieving capabilities, allowing small molecules, like water, to pass through the network while rejecting larger particles, such as hydrated ions. However, little is known about the structure-properties relationships of aromatic polyamide membranes. This chapter will discuss the current state of RO membranes, specifically aromatic polyamides, and how we can study the water within the membranes to learn more how structure-properties relationships correspond to transport measurements in hopes to development smarter materials for membrane-mediated water treatment applications.
2.2 Current State of Proton Exchanges

2.2.1 Proton exchange membrane fuel cells

Proton exchange membrane (PEM) fuel cells are a viable energy conversion device for sustainable energy systems because they convert hydrogen fuel into energy and water. Unlike lithium-ion based batteries, where ions must move through a polymer matrix that is deprived of water due to high reactivity of the lithium ions, PEMs rely on the water produced as byproduct of the two half-reactions to transport protons from the anode to the cathode. The presence of water increases the absolute conductivity of a material because transport can occur via the fast dynamics of water ($10^{-4}$ to $1 \text{ S cm}^{-1}$) instead of relying on transport via the slower dynamics of polymer segmental motion ($10^{-11}$ to $10^{-3} \text{ S cm}^{-1}$). PEM fuel cells operate using hydrogen as fuel and the only chemical product is water, making them attractive for applications including providing energy for vehicles and for stationary and portable devices. Fuel cells containing a proton exchange membrane operate at a lower temperature, between 60-120 °C, than fuel cells that use alternative separating materials, which operate between 200-800 °C, and typically PEM cells have higher power density, making them an great alternative. A schematic of a PEMFC is shown below in Figure 2-1. Simply put, the device consists of an anode and a cathode, which provide the oxidation and reduction half reactions, a gas diffusion layer (GDLs), catalyst layers and a PEM, which acts as a separator to prevent the mixing of the reactants, a conductor for protons, and provides structural support.
Figure 2-1. Schematic of a PEMFC. The proton exchange membrane is shown in blue, the catalyst layer is shown in grey, the gas diffusion layer is shown in black and the anode and cathode are labeled.

2.2.2 Structure-property relationships for PEMs

NAFION®, a perfluorosulfonic acid ionomer (PFSA) membrane produced by DuPont, is the most common PEM and serves as a benchmark for membrane performance due to its robust electrochemical stability and high proton conductivity. PFSA have unique structures that consist of a poly(tetra-fluoroethylene)- like backbone and a pendant sidechain with sulfonic acid groups. The structure of NAFION® can be found in Figure 2-2.
The combination of a Teflon-like backbone, which is extremely hydrophobic and provides structural integrity, with the very hydrophilic sulfonic acid, creates well-defined nanochannel within the membranes when hydrated. The sulfonic acid groups provide protonic charge carries via dissociation, and proton conductance is assisted by water dynamics through the percolating water-filled cavities. However, NAFION® has its shortcomings. PFSAs are expensive to produce and suffer from low conductivity at low water contents temperatures above 80°C, both of which are desirable for many applications. Researchers have been searching for alternative polymer systems that mimic the desirable of PFSA, namely high conductivity and large water-filled nanochannels.

The most commonly explored alternatives to PFSAs are aromatic based polymer systems that contain poly(phenylene)⁹⁻¹¹, poly(ketone)¹²,¹³, poly(imide)¹⁴⁻¹⁶ and poly(sulfone)¹⁷,¹⁸ backbone structures. While all these backbones can be used to create PEMs, the fundamentals as to how they function and compare to PFSA are of interest. Kreuer thoroughly compared the morphology and transport properties of NAFION® and sulfonated poly(etherketone) (PEEKK). Small angle X-ray scattering (SAXS) data showed that when hydrated, the ionomer peak for sulfonated poly(etherketone) was broader and shifted towards higher scattering angles compared to the ionomer peak from NAFION®. This result indicated that the hydrophilic/hydrophobic phase segregation in PEEKK was less-than that in NAFION®, or that the aromatic polymer contained narrower water-filled channels. Kreuer also found that the aromatic polymer had more
branching and more dead-ends than NAFION®. A schematic comparing the morphology can be found in Figure 2-3.

Kreuer also measured the dielectric constant and the water self-diffusion coefficient of each system. Once again, NAFION® outperformed PEEKK by displaying a higher dielectric constant and a faster self-diffusion coefficient at both high and low water volume fraction. Similar comparisons have been conducted on many different types of sulfonated aromatic polymers, and conclusions are analogous. Aromatic based polymer backbones do not provide the same juxtaposition between the backbone and sidechain to achieve ordered, large interconnected water filled channels to produce transport properties like PFSA membranes.

Sulfonated multi-block copolymers have been a popular alternative because the content of the hydrophobic (unsulfonated) and hydrophilic (sulfonated) units can be finely tuned to create
self-assembled continuously connected channels. These materials have been shown to have higher conductivity than their random counterparts and have increased conductivity at low relative humidity. However, the conductivity achieved at low humidity is not at the level needed for applications. Multi-block copolymers also suffer from poor mechanical stability and complicated synthesis routes.

2.2.3. A new perspective on structure-property requirements for PEMs

Much attention has been given to mimicking the unique morphology of PFSAs believed to provide this class of membrane with its high performance capabilities. Conversely, another important characteristic of PFSA polymers is their strongly acidic pendant sulfonate group. The electron withdrawing properties of fluorine cause the sulfonate moiety to be extremely acidic and categorized as a superacid. A superacid is defined as having a $pK_a$ that is more negative than 100% sulfuric acid ($pK_a = -3$), the estimated $pK_a$ of a perfluoroalkyl sulfonate group is $-14.1$. There are reports of ionomers that contain the superacid sulfonate$^{21-25}$, but most PEMs rely on the much less acidic alkyl sulfonate group as a proton conduction moiety despite their low conductivity at low humidity. Aromatic polymers containing superacidic sulfonate sidechains have only recently begun to be explored due to complicated synthetic routes leading to low ion exchange capacities. Recently, Bae et al., were able to synthesize a set of sulfonated syndiotactic poly(styrene) membranes, one of which contained a superacidic fluoroalkyl sulfonic acid sidechain, in order to probe how the acidity of the sidechain will affect the membranes properties.$^{23,24}$ The structures of the three sidechains along with their measured conductivities are shown in Figure 2-4. The conductivity of the sPS-S1 sample is very similar to the conductivity of the NAFION® membrane, while the sPS-S2 (classic aromatic sulfonate) only reaches similar conductivity at higher humidity values. TEM images of the sPS-$S_n$ set compared
to NAFION® are shown in Figure 2-5. The sPS-S_n series shows little phase segregation compared to NAFION® even though the sPS-S1 sample gave similar conductivity values. The results are in stark contrast to the previous idea that controlling the morphology to have wide and interconnected hydrophilic domains would result in higher conductivity at low RH conditions, suggesting that more attention should be placed in studying the sidechain chemistry.

Figure 2-4. The chemical structure and conductivity measurements of sPS-S_n ionomer series showing sPS-S1 and NAFION® have similar conductivity.²⁴
Figure 2-5. TEM images of sPS-S\textsubscript{n} ionomers and NAFION\textsuperscript{®} show differences in morphology.\textsuperscript{24}

2.3 Water binding and correlation to transport properties

2.3.1 Proton transport in pure water

Proton transport in water relies on the strong hydrogen bonds formed between water molecules and the rapid breaking and forming of these bonds. Proton mobility in water is ~9 times higher than Li\textsuperscript{+} and 5 times higher than K\textsuperscript{+} because of hydrogen’s ability to hydrogen bond to water molecules and “tunnel” between them. This type of transport, described as “structural diffusion”, is well studied and depicted in Figure 2-6. A protonic defect is formed as a Zundel ion (H\textsubscript{5}O\textsubscript{2}\textsuperscript{+}), and is then disrupted by the formation of another hydrogen bond as an Eigen ion.
(H$_2$O$_3^+$). The Eigen ion is disrupted by a hydrogen bond breaking; another Zundel-ion is formed, resulting in the proton defect being transferred. This type of transport is also referred to as the Grotthuss (hopping) mechanism, where protons move through an infinite network of hydrogen bonds.

![Diagram](image_url)

Figure 2-6. Mechanism for proton conduction in pure water. Grey area highlighting the region with protonic defect.

Protons (and other ions) can also be transported by the vehicle mechanism. The proton diffuses through the network via a vehicle, this case H$_3$O$^+$, while the pure water molecules (unprotonated) diffuse in the opposite direction allowing for a net transport of protons. The relative contributions of the two types of transport depends on temperature, pressure and the concentration of ions present. At high temperatures, the contribution from structural diffusion lessens as hydrogen bonds weaken and the opposite is true as pressure increases, strengthening the hydrogen bonds. The hydrogen bonding network regulates proton transport and the following
sections will discuss means to studying the hydrogen-bonding network and its effect on transport in hydrated acidic membranes.

2.3.2 Proton transport in acidic polymer membranes

Water sorbed into polymeric ion conductors does not behave as bulk water because it is both confined and interacting with ionic tethers of the polymer; therefore studying the water in these membranes is crucial to understand how protons are transported. Absorbed water is slowed in these membranes, affecting the relative contributions from the two types of transport discussed previously. Zawodzinski, et al. demonstrated this phenomenon by comparing the self-diffusion coefficient (determined by Pulsed-Field Gradient (PFG)-NMR) of water in a hydrated NAFION® film to the diffusion coefficient calculated from the conductivity, essentially separating the two types of transport (hopping and vehicle). Figure 2-7 shows that at low water content, the two diffusion coefficients were similar, but as the water content increased, the protons start to diffuse faster than the water molecules. At low water content, transport is occurring predominately via the vehicle mechanism because the water molecules are likely solvating the sulfonate groups of NAFION®. As the water content increases and the sulfonate groups are fully solvated, the amount of bulk-like water increases and proton diffusion by structural diffusion (hopping) dominates.
Dynamics of water absorbed into ion-containing polymers is slowed due to the hydrogen bonding of water to the polymer sidechains, thus altering the hydrogen bonding environment. Much work has been dedicated to studying and analyzing water-polymer interacting by studying the hydrogen-bonding network within ion-containing polymers as means to understand proton conduction. The next section will explore various methods that have been used to study water-polymer hydrogen bonding in ion-containing polymers.

2.3.3 Probing the water-polymer hydrogen bonding in ion-containing polymers

Nuclear magnetic resonance (NMR) has been used to characterize water dynamics in various polymer films by measuring the spin-lattice relaxation times, $T_1$, and diffusion coefficients.\textsuperscript{29-32} $T_1$ measurements of $^2$H$_2$O provides insight about the rotational diffusion occurring in the polymer film on the nanometer length scale. Using a quadupolar nucleus, such as $^2$H, has
distinct advantages because the quadrupolar interactions dominate and allow for direct interpretation of rotational dynamics. Liquid water at ambient pressure has a $T_1$ value of 400 ms, but when liquid water is supercooled to temperatures near 200 K and under high pressures, the $T_1$ value drastically decreases to 2-20 ms, indicating that the rotational mobility is slowing.

Figure 2-8 shows that PFSA (NAFION® and Aquivion®) membranes yield $T_1$ values that range from 5-200 ms, depending on hydration, while sulfonated aromatic polymers, such as S-Radel, display much faster $T_1$ values, ranging from 5-20 ms. The drastic difference in rotation mobility is due to PFSAs having more well-defined, phase-separated domains, resulting in larger, wider interconnected water channels than aromatic-based polymers. These large channels allow the water molecules to be farther away from the polymer-water interface and have more liquid like character. To understand how water is diffusing on a longer length scale, PFG-NMR is used to determine the translational diffusion coefficient. When NAFION® is hydrated, the diffusion coefficient is about 2.5 times lower than that of bulk water ($D_{eff}=2.3 \times 10^{-5}$ cm$^2$ s$^{-1}$), indicating that the water is moving slower. The diffusion coefficient of water in sulfonated aromatic polymers is slower than the diffusion coefficient in NAFION®. Water in sulfonated aromatic polymers consistently has slower water dynamics than PFSAs due to the aromatic polymers’ inability to form a percolating network of wide, water-filled channels.
Ultrafast spectroscopy has been employed to study water’s hydrogen bonding network to better understand the behavior of water when it is confined within a reverse micelle. The vibrational relaxation of water is sensitive to the molecules’ environment because local forces (i.e. perturbed hydrogen bonds by solvation) cause the vibrational energy levels to shift, altering the vibrational lifetime. In reverse AOT (sodium bis(2-ethylhexyl) sulfosuccinate) micelles, it was found that water behaved differently in these microenvironments than bulk water. The vibrational lifetime plots for various size micelles could be fit with a biexponential function, indicating the confined water experiences two different environments: tightly bound, confined water that is hydrogen bonded to the sulfonate anion, and bulk-like water. These results are similar to what has been observed in NAFION® where Moilanen, et al., concluded that water occupied two distinctly different environments within the polymer. By studying the vibrational
lifetime of the OD stretch of dilute HOD in H₂O, they characterized how the hydrogen bond network changes as a function of hydration or increased water content in NAFION® films. Moilanen, et al. noticed drastic changes in the OD stretch lifetime measurements as hydration of the polymer increased. When NAFION® was initially hydrated, an OD stretch with a slow relaxation on the order of 11 ps was assigned to water that occupied the solvation shell of the sulfonate group. The remaining water in the sample displayed fast relaxation on the order of 5 ps, which is similar to bulk water (1.7 ps lifetime), displayed in Figure 2-9.

![Figure 2-9. OD vibrational lifetime decays of NAFION® hydrated at various water content, λ.](image)

The hydrogen bonding network of water can also be examined by linear FTIR spectroscopy, using dilute HOD in H₂O as an easily interpretable probe of the water’s behavior in the material. Both the OH fundamental stretching modes (v₁ and v₃) have shown temperature-dependence by shifting to lower wavenumbers at lower temperatures, due to stronger hydrogen bonds, whereas the bending frequency shifts to higher frequencies. The bending mode is not
used to study the hydrogen bonding network because the shift is much smaller than the fundamental stretching mode. Fermi resonance and overlapping bands cause the vibrational spectrum of pure water (H₂O) to be very complicated. Band clusters result from overlapping bands and result in single peaks that represent many different modes. Fermi resonance leads to intensity borrowing between different modes or overtones within a cluster, again resulting in peaks that represent more than a single vibrational mode. The vibrational spectrum of pure D₂O is equally as complicated for the same reasons, however, to simplify the spectrum, dilute HOD in H₂O or D₂O is used. By breaking the symmetry of H₂O/D₂O, the bands in the vibrational spectrum of dilute HOD are well separated because overlapping bands and Fermi resonance are eliminated. This allows for a single vibrational stretching mode to be analyzed.

The frequency of the OD stretch is indicative of the strength of the hydrogen bond. When HOD is in the solid state, exhibiting very strong hydrogen bonds, the OD stretch is centered around 2440 cm⁻¹. Whereas in the vapor phase, the faint absorption peaks due to non-hydrogen bonded OD groups are located at 2719 cm⁻¹. In the liquid state, a single Gaussian peak centered at ~2509 cm⁻¹ is observed for 5 mol % HOD in liquid H₂O. When NAFION® is hydrated with dilute HOD in H₂O, the vibrational spectrum displays a broad, non-Gaussian peak spanning ~2700-2400 cm⁻¹. The broad Gaussian of HOD in NAFION® encompasses the distribution of hydrogen bonding environments that adsorbed water experiences in the polymer and this distribution can be rigorously deconvoluted to disclose the percentage of water in various microenvironments. Previous studies on dilute HOD adsorbed into NAFION® showed that the OD peak position was blueshifted by ~85 cm⁻¹ compared to bulk water. The large shift was attributed to water participating in a weaker hydrogen bond with the sulfonate groups of the polymer side chain compared to the stronger water-water hydrogen bonds in bulk-like water. More recently, Moilanen, et al. hydrated NAFION® at varying levels of hydration to understand how the hydrogen bonding network varied as a function of water content. The researchers were
able to develop a peak fitting routine comprised of the weighted sum of two water distributions and extract quantitative population values corresponding to bulk and polymer. As shown in Figure 2-10, they found that as NAFION® adsorbed more water, the OD peak redshifted ~40 cm⁻¹, revealing that the hydrogen bonding network depends on the amount of water in the polymer.

![Figure 2-10. FTIR normalized spectra of water absorbed in NAFION® at various water content, λ. The spectrum of bulk water is shown for comparison.](image)

It is interesting to think about water-polymer interactions and how they influence the hydrogen bonding network and proton transport, but these measurements can also be used to estimate the charge density of the ions tethered to the polymers. The next section will highlight different vibrational and computational studies and how they are used together estimate charge density and how that relates to the water-polymer hydrogen bond strength.
2.4 Measuring hydrogen bond strengths and charge density

2.4.1 Charge density measured with FTIR

Early vibrational spectroscopy studies aimed to understand the forces between solvent molecules and ions in aqueous solutions as a way to better understand ionic mobility. Researchers studied the vibrational signature of isotopically dilute HOD in electrolyte solutions to determine trends for various anions based on their size, charge and electronegativity. Waldron first studied a series of halide salts (excluding bromide) and found that the OD peak frequency increased with decreasing charge density. A solution of potassium iodide (KI) gave an OD peak position of 2559 cm$^{-1}$ while a solution of potassium fluoride (KF) gave a peak position that was redshift from pure water at 2470 cm$^{-1}$. The frequency shifts correlated with theoretically calculated hydration enthalpy values, indicating the relationship between frequency, charge density and hydrogen bond strength. In 1986, Mikenda correlated frequency (O-D) and hydrogen bond lengths (O-D···X$^-$) measured by neutron or X-ray diffraction and concluded that there is a correlation between these two intrinsic characteristics for a broad set of anions. More recently, Kropman and Bakker used both linear and nonlinear vibrational spectroscopy to study aqueous halide salt solutions. Their findings, supported by those found by Waldron and Mikenda, and are shown in Figure 2-11. Anions I$^-$, Br$^-$, and Cl$^-$ all gave peaks that were blueshifted compared to the pure OH vibrational mode because their charge densities (electronegativity) are lower than oxygen and therefore the hydrogen bonds formed are weaker. Fluorine has the highest charge density of the series and as a result displays an OH peak that is redshift from the pure state because the hydrogen bonds formed are stronger than those in pure water. It is also useful to think about this trend in terms of acidity, as it is a direct result of charge density, where hydrogen iodide (HI) behaves as a superacid (p$K_a$= -10) because of the low electronegativity of its
conjugate base, I. The low charge density of the iodine anion is attributed to its large electron cloud, allowing the negative charge to be easily dispersed.

Figure 2-11. The linear OH stretch absorption spectrum of solutions of KF, NaCl, NaBr and NaI in isotopically dilute D$_2$O.\textsuperscript{44} The peak corresponding to pure water is shown using a dotted line.

2.4.2 Charge density and hydrogen bonding geometry calculated using density functional theory (DFT)

Paddison used first principle studies to examine the differences between the two types of anions commonly used in proton exchange membranes, \textit{para}-tolunesulfonic acid and triflic acid. The partial charges of each atom of the sulfonate anion were calculated and the total sum of the oxygen charges was used to determine the charge density. When the anions were hydrated ($\lambda=6$), triflic acid had a charge of -1.438, while \textit{para}-tolunesulfonic gave a charge density of -1.602 (in units of elementary charge).\textsuperscript{45} Triflic acid consistently had a lower charge density than \textit{para}-tolunesulfonic at all hydrations levels. Triflic acid has a lower charge density on the sulfonate group because once the proton has dissociated from the sulfonate anion, the excess electron
density is stabilized more readily by the -CF₃ group of triflic acid compared to the aromatic ring of para-toluenesulfonic acid, due to the strong electron-withdrawing properties of fluorine. The additional stabilization allows the triflic acid to behave as a weak conjugate base and results in the hydrogen bond between the sulfonate anion and the hydrated proton being longer than para-tolunesulfonic acid. Paddison concluded that in a perfluorinated material, once the first hydration shell forms around the sulfonate ion, the proton is effectively shielded from the anion by water molecules, allowing the dissociated proton to be more readily transported through the ionic channels.

The hydrogen bonding distances were calculated by Paddison. Minimum energy conformations of both hydrated triflic acid and para-toluenesulfonic acid showed complete dissociation of the acid proton once the sixth water molecule was added. However, the calculated distance between the oxygen of the sulfonate group and the acidic proton was greater for triflic acid (3.679 Å) compared to para-toluenesulfonic acid (3.196 Å). Again, this is due to the -CF₃ groups better stabilizing the excess negative charge of the sulfonate anion produced upon proton dissociation. Once the proton is dissociated it is observed to participate in a hydrogen bond with two water molecules, forming a Zundel ion. The binding energies were also calculated for both acids and it was found that the binding energy was consistently lower (more negative) for triflic acid compared to para-toluenesulfonic acid, indicating that the water was more loosely bound or formed weaker hydrogen bonds.

The hydrogen bonding geometry of a single water molecule to triflic acid was modeled using a gradient method. The minimum energy structure of the triflic-acid-water molecular pair consists of a doubly hydrogen-bonded water molecule to the triflic acid proton and oxygen atoms. A schematic of the optimized geometry is shown in Figure 2-12. The hydrogen bond between the acid proton and the oxygen of the water molecule is shorter (2.606 Å) than the hydrogen bond
between the oxygen of the sulfonate and the proton of a water molecule (which is a more typical hydrogen bonding length, 2.842 Å).46

Figure 2-12. Optimized geometry of the triflic-acid-water molecular pair, displaying the doubly hydrogen-bonded water molecule.46

2.5 Probing microstructure reverse osmosis (RO) membranes

2.5.1 Current state of RO membranes

As the need for clean water grows, reverse osmosis (RO) membranes have become increasingly used in wastewater reclamation and water treatment due to advances in technology and decrease in cost. Current RO membranes are predominately thin film composite (TFC) aromatic polyamide membranes. Their success is attributed to the TFC design, where three distinct layers are finely tuned to achieve various mechanical, transport and filtration properties. A cartoon illustration of the three layers is shown in Figure 2-13. The first layer is the polyamide active layer, which is about 100 nm thick. This layer can be tuned for specific selectivity and
rejection properties. Because the layer is ultrathin, it also has high water flux. The second layer is a microporous poly(sulfone) support that is about 50 μm thick. This layer provides additional support and aids in filtration. Finally, the woven polyester layer is about 120 μm in thickness and provides mechanical stability.

Figure 2-13. Illustration of a thin film composite aromatic polyamide reverses osmosis membrane.

In most commercial applications, the thin polyamide layer is formed by interfacial polymerization of amine monomers and aromatic acid chloride monomers. The polymerization occurs directly on top of the poly(sulfone) layer. First, the poly(sulfone) layer is coated with an aqueous solution containing the water soluble monomers, and then a water immiscible organic solution containing the second monomer is applied. Currently the most successful monomers are 1,3-benzenediamine (m-phenylenediamine, MDPA) in an aqueous solution and 1,3,5-benzentricarbonyl chloride (trimesoyl chloride, TMC) in an organic solvent. Because of the immiscibility of the two solvents, the polymerization reaction shown in Figure 2-14 will only occur at the interface, yielding a thin and dense polymer layer. Many different factors, ranging from reactant concentration to post-reaction treatments, affect the composition and morphology of the thin polyamide layer.\(^{47,48}\) Transport is controlled by the active layer, therefore it is critical
to better our understanding of how microstructural changes affect the efficiency and performance of thin polyamide membranes.

![Chemical structures](image)

Figure 2-14. Synthetic scheme of cross-linked fully aromatic polyamide via interfacial polymerization. 47

2.5.2 Probing the structure of polyamide based membranes

Little work has been done to study water adsorbed into aromatic polyamide RO membranes because the active layer is very thin and difficult to isolate. It is useful to first examine the work that has been done on the similar aliphatic polyamide systems (nylons), which have been studied more readily. Early work by Puffr and Sebenda used sorption isotherms and infrared adsorption at various relative humidity to study water in amorphous polyamide membranes to better understand the mechanism for sorption of water into the polymer. For
Nylon-6, they concluded that water binds to the amide groups, first forming a double hydrogen bond between carbonyl group (termed firmly bound water) and then forming bridging hydrogen bonds between amide C=O and N-H groups (termed loosely bound water), illustrated in Figure 2-15.49

![Figure 2-15](image)

Figure 2-15. The mechanism proposed by Puffr and Sebeda for water sorption into aliphatic polyamide, nylon, membranes. The dry membrane structure is shown in the left (A) and the hydrate membranes on the right (B), where two types of water are proposed, (1) firmly bound water, and (2) loosely bound water, and (3) sites for capillary condensed water.49

Evidence from vibrational spectroscopy indicating that water was binding to two function groups of the amine because both the C=O and N-H peaks shift when the samples is hydrated.50 A third site was added for capillary condensed water, when hydration levels increased close to liquid levels, water would start to cluster in these areas and condense.

Most recently, researchers have used vibrational spectroscopy to study noncommercial aromatic polyamide films synthesized by interfacial polymerization to better understand how reaction conditions and monomer concentration might affect the crosslinking structure. Using FTIR to study the fingerprint region (1730-1350 cm⁻¹), Su et al. were able to track the ratio of unreacted carboxylic acid groups that remained in the system after interfacial polymerization with different monomer ratios. When the 1,3-phenylenediamine (MPDA) monomers are present at
higher concentrations in the aqueous phase, the amount of pendant carboxylic acid groups decreased, as shown by the decreasing peak intensity at 1720 cm\(^{-1}\) in Figure 2-16.\(^{51}\) A lower MPDA/TMC yields more unreacted acid chloride groups, which undergo hydrolysis to form free carboxylic acids. Increased carboxylic acid content has been hypothesized to increase the flux of the membranes because they cause the membranes to be more hydrophilic.\(^{52}\) The monomer ratios will also affect the amount of crosslinking in the active layer, which has implications on salt permeability and flux.

Researchers at the National Institute for Standards and Technology (NIST) have developed a system to synthesize thin polyamide films using a layer-by-layer technique where dilute solutions of a single monomer are spin coated onto a substrate (typically an alcohol functionalized surface) and allowed to react with the available functional groups. The substrate is rinsed to remove unreacted monomer and then the second monomer is applied and the process is repeated until a desired thickness is achieved.\(^{53}\) An illustration of the process is shown in Figure 2-17. The layer-by-layer (LbL) technique has made studying the swelling behavior of highly cross-linked polyamides synthesized using different monomer chemistries possible. Using both the Flory-Rehner and Painter-Shenoy models for polymer swelling behavior, researchers were able to extrapolate interaction parameters and estimate the distance between crosslinking junctions.\(^{54}\) While it is useful to study noncommercial membranes to understand general concepts about synthesis, structure, and properties, these membranes are very thin and therefore measuring the transport properties is extremely difficult.
Figure 2-16. The FTIR spectra of polyamide films prepared at different MPDA concentrations (50°C, 1% TMC); (a) 2% MDPA, (b) 4% MPDA and (c) MPDA. The dashed lines represent the deconvoluted peaks.\(^5\)

Figure 2-17. Illustration of the molecular layer-by-layer deposition of polyamide starting from an alcohol functionalized surface. Cycle can be repeated until desired thickness is achieved.\(^5\)
NIST has advanced with their LbL technique to make supported membranes where the transport properties can be measured, but these membranes are much thinner and have a vastly different surface morphology than the commercial interfacially polymerized samples. To deeply understand the structure-property relationships of the active layer polyamides, the interfacially polymerized system must be studied systematically.

Recently, a method for delamination has been developed by Freger and has allowed researchers to study the active layer of commercial membranes. The structure of the polyamide network has been studied using many different techniques; most interesting is positron annihilation lifetime spectroscopy (PALS) used to measure the free volume cavity size. RO membranes are so highly cross-linked that the pore sizes are on the angstrom length scale and are responsible for both flux and salt passage parameters. Work by Suzuki et al. determined that there are two types of pores in commercial RO membranes, on the order of ~2 Å and 3.5-4.5 Å, and that as the distribution of type of pore changes, so do the transport properties. A larger number of large pores led to higher flux, but lower rejection. Interestingly, much attention has been given to probing the morphology and membrane characteristics and how differences in these parameters affect transport properties, but little attention has been devoted to actually studying the water inside the membrane and how the polymer-water interactions might be influencing the transport properties. We know from work on ion-containing membranes that these water-polymer interactions are very important for ion and water transport, therefore Chapter 7 of this thesis will discuss work to further understand water-polymer interactions in neutral polyamide membranes for reverse osmosis applications.
2.6 Conclusion

In order to design smarter polymer membranes for energy and water treatment applications we must study how the water is interacting within the polymer by probing the hydrogen bonding network. Wide-ranging research has shown that aromatic sulfonate tethers do not produce adequate proton transport; therefore we must explore different sidechain chemistry. Superacid sulfonate tethers have been synthesized on aromatic based polymers and have started to be studied; however the water in these novel membranes has yet to be studied. The remainder of this thesis will explore various superacid sidechains attached to aromatic polymer backbones to better understand their charge density and hydrogen bonding dynamics. The techniques and experience that were developed by studying sulfonated systems can be extended into neutral aromatic polyamide membranes. Little is known about the water dynamics in this class of membranes and this thesis will demonstrate how changes in chemistry and composition of these membranes affect the hydrogen bonding network and transport properties.
2.7 References


(10) Ghassemi, H.; McGrath, J. E. Synthesis and Properties of New Sulfonated Poly(p-Phenylene) Derivatives for Proton Exchange Membranes. I. *Polymer (Guildf).* 2004, 45 (17), 5847–5854.


Chapter 3

Materials and Experimental Procedures of Characterization

3.1 Introduction

This chapter introduces the materials that will be discussed throughout this dissertation and the procedures used to characterize the materials. The details for preparing and/or casting are described in this chapter. The majority of the work for this dissertation was completed by using linear Fourier transform infrared (FTIR) spectroscopy to carefully measure the change in the vibrational signature of dilute HOD adsorbed into the system. This chapter will discuss in-depth how the samples were exposed to dilute HOD, how the spectra were obtained and how the data was analyzed and deconvoluted using a custom peak fitting routine. Density functional theory (DFT) modeling was used to assign the charge density and configurations of many of the sidechains. Water uptake was measured using relative humidity-controlled thermogravimetric analysis (RH-TGA). Conductivity was measured using electrochemical impedance spectroscopy (EIS). In some cases, morphology and domain spacing was studied using small angle x-ray scattering (SAXS).
3.2 Materials

3.2.1 Sulfonate Membranes

Sulfonated syndiotactic poly(styrene) (PS-S1 and PS-S2 of Figure 3-1a) and sulfonated poly(sulfone) samples (PSU-S1 and PSU-S2 of Figure 3-1b) were synthesized and provided by our collaborators in Dr. Chulsung Bae’s research group in the Department of Chemistry and Chemical Biology at Rensselaer Polytechnic Institute.\textsuperscript{1,2}

\begin{center}
\begin{tabular}{c|c}
R Group & Sample \\
\hline
-OCF\textsubscript{2}CF\textsubscript{2}SO\textsubscript{3}\textsuperscript{−}Na\textsuperscript{+} & S1 \\
-SO\textsubscript{3}\textsuperscript{−}Na\textsuperscript{+} & S2 \\
\end{tabular}
\end{center}
Figure 3-1. Repeat units of the (a) syndiotactic poly(styrene) (PS) or (b) poly(sulfone) (PSU) backbones where R is fluoroalkyl (S1) or aryl (S2) tethered sulfonated group.

Additional sidechains were synthesized onto poly(sulfone) by members of Dr. Bae’s research group. These additional sidechains provided materials to study how finer changes of the sidechain chemistry might affect the transport properties and water hydrogen bonding. The materials are shown in Figure 3-2.

![Figure 3-2](image)

<table>
<thead>
<tr>
<th>R Group</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>-SCF₂CF₂SO₃⁻ Na⁺</td>
<td>PSU-S4</td>
</tr>
<tr>
<td>-OCF₂SO₃⁻ Na⁺</td>
<td>PSU-S5</td>
</tr>
<tr>
<td>F₃C(\text{OCF₂CF₂SO₃⁻ Na⁺})</td>
<td>PSU-S6</td>
</tr>
</tbody>
</table>

Figure 3-2. Repeat unit of the poly(sulfone) (PSU) backbone where R represents various tether structures.

To investigate how the backbone structure affects the acidity of the sulfonate group, three varieties of poly(phenylsulfone) were examined. Figure 3-3 shows the three materials used.
SES-0206 (a) was provided by YanJin™ Technology Co. and contains a sulfone group between the two phenyl rings with the attached sulfonate group. sPSO2-360 (b) is a sulfonated poly(p-phenylene sulfone) where all the ether linkages are replaced with sulfones.³ Lastly, sPS-V (c) is the sulfonated form of RADEL®, a commonly used material for cation exchange membranes.

![Diagram of SES-0206](image)

![Diagram of sPSO2-360](image)

![Diagram of sPS-V](image)

Figure 3-3. Repeat unit of sulfonated (a) poly(ethersulfone) (SES-0206), (b) poly(p-phenylene sulfone) (sPSO2-360), and (c) poly(phenylsulfone) (sPS-V).

It is important that all samples be in sodium form. The reason for this will be discussed in more depth when describing the FTIR experiments. To convert any samples that were not in sodium form, the membranes were soaked in a 1 M solution of sodium chloride (Aldrich, 99%) for 24 h. To remove excess sodium the membranes were soaked in deionized water for 24 h and then rinsed with additional DI water. The rinse processed was repeated a total of three times.
3.2.2. Polyamide thin film composite membranes

Commercial reverse osmosis (RO) membranes were provided by the Dow Chemical Company to study the cross-linked polyamide active layer, shown in Figure 3-4. The supported active layers of the membranes were removed from the nonwoven fabric such that just the poly(sulfone) and polyamide layer remained. The remaining two-layered membrane was placed in a funnel lined with filter paper and washed with sufficient dimethylformamide (DMF) to remove the poly(sulfone) layer. To remove the DMF, the remaining polyamide layer was washed with water and then methanol. The polyamide fibers were placed onto a calcium fluoride crystal and allowed to dry at 50 °C under vacuum for 20 h.

Figure 3-4. Repeat unit of cross-linked fully aromatic polyamide.

3.3 Fourier transform infrared spectroscopy (FTIR) of HOD

Observations of the OD stretch of HOD in dilute H$_2$O have been employed for a long time in physical chemistry to study the hydrogen bonding behavior of water in a wide range of systems. The first experimental studies using this technique were conducted by Waldron, who used HOD to study the differences in hydrogen bonding lengths of various halide salts. Waldron discovered that the OD peak is blueshifted in the order I$^-$, Cl$^-$, and F$^-$. The fluoride salt actually redshifts the OD peak from the pure liquid value, which has been reported by others. This shift is
due to the electron density of fluorine being extremely high where the hydrogen bond formed is stronger than the hydrogen bond between two water molecules. The blueshift found in salts containing I⁻ and Cl⁻ is explained by the decreased strength of the hydrogen bond between iodine and chloride anions and is supported by heats of hydration calculations.⁴

The OD stretch falls in an advantageous region of the FTIR spectrum in many of the polymers we have measured. In many of these aromatic materials that do not contain N-H, S-H, P-H bonds, the infrared absorption spectrum between 2000 cm⁻¹ and 2800 cm⁻¹ is relatively flat. In a few samples that contain large portions of unfunctionalized poly(styrene), we have observed a cluster of three small peaks at 2630 cm⁻¹, 2602 cm⁻¹ and 2582 cm⁻¹. These peaks are only present when the film thickness is greater than 3 µm, which is sometimes desired when attempting to increase the absorbance of the OD peak if the sample does not uptake much water. These peaks are observed in literature spectra of poly(styrene), but are often not addressed as they are relatively weak. We hypothesize they are either a result of an overtone or combination bands arising from the A₂ and B₂ modes of the mono-substituted benzene rings of poly(styrene).⁶,⁷ These peaks can be eliminated by using a thinner film of poly(styrene).

The OD stretch of HOD in dilute H₂O has been used extensively in studies of water hydrogen bonding because of the well-defined vibrational mode of OD centered at 2509 cm⁻¹ in liquid H₂O. Attempts have been made to understand the hydrogen bonding populations of water in liquid H₂O and D₂O, but the closely clustered bands around 3400 cm⁻¹ (in H₂O) or 2500 cm⁻¹ (in D₂O) lead to Fermi resonance and band sharing which precludes rigorous analysis of these peaks to recover the molar populations of water in different hydrogen bonding environments.⁸ Studying HOD solves these issues because the three fundamental bands of the HOD (v₁, v₂, and v₃) are widely separated, eliminating Fermi resonance and intermolecular coupling of vibrations, depicted in Figure 3-5. One can study either the OH (dilute H₂O in D₂O)⁹,¹⁰ or the OD (dilute D₂O in H₂O) stretch of HOD and gather similar results. Temperature-dependent studies of HOD show
that as the temperature is increased the symmetric and asymmetric modes ($\nu_1$ and $\nu_2$) are blueshifted.\textsuperscript{8,11} As the temperature of water increases, the hydrogen bonds start to weaken, therefore a blueshift of the symmetric and asymmetric modes indicating the weakening of the hydrogen bonding network. In the solid state, when hydrogen bonds are the strongest, the OD peak has a frequency centered around 2440 cm\textsuperscript{-1}. In the gaseous state, when the hydrogen bonds are far weaker than in a liquid or solid, there is a faint OD peak centered around 2719 cm\textsuperscript{-1}.\textsuperscript{8} These two measurements mark the two extremes of the OD peak position and give us an idea how the OD stretch shifts correspond to hydrogen bond strengths.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-5.png}
\caption{Intramolecular vibrations of H\textsubscript{2}O, D\textsubscript{2}O and HOD in liquid water.\textsuperscript{5}}
\end{figure}
3.4 FTIR sample preparation and experimental procedure

Samples were prepared by casting a thin film of polymer solution in sodium from various solvents onto CaF\textsubscript{2} windows. The films were dried under vacuum and placed in an FTIR transmission flow cell (depicted in Figure 3-6) (Model 64100-F, New Era Enterprises, Vineland, NJ). Estimated film thicknesses ranged from ~1-3 \( \mu \text{m} \). Humid air containing 5 mol \% D\textsubscript{2}O was flowed (20 std. cm\textsuperscript{3} s\textsuperscript{-1}) through the cell while spectra were recorded using a Bruker (Billerica, MA) VERTEX 70 spectrometer with a nitrogen-cooled mercury-cadmium-telluride (MCT) detector.

Figure 3-6. Flow cell schematic used to introduce humidified air, containing HOD, to the cast polymer membrane sample while collecting FTIR spectra.
Humidification of the flowing air through the FTIR cell was achieved by dewpoint mixing of fully-humidified and dry air streams. Air at dewpoint was produced by a water sparging system, and was then mixed with a dry air stream at controlled mass flow ratios to yield a range of relative humidities. The relative humidity of the mixed stream was measured using an RH probe (Omega HX15-W, Omega Engineering, Inc., Stamford, CT) before being introduced to the measurement cell at the same temperature as the system. Each RH corresponded to a different hydration number ($\lambda = \text{mole of water/mole of sulfonate group}$) depending on the polymer sample. In scoping experiments, we equilibrated the samples for up to 1 h at each RH while taking spectra every 5 min. After 20 min, the spectrum did not change, so we used an equilibration period of 20 min at each RH. The polymer was equilibrated for 20 min at each RH and a spectrum was acquired every 5 min. Each spectrum was recorded at 2 cm$^{-1}$ resolution and 100 scans. Spectra were extracted from 2700 cm$^{-1}$ and 2400 cm$^{-1}$ and baselined by setting the absorbance equal to 0 at those two points. Peak fitting was performed using Origin 8.0 (OriginLabs, Northhampton, MA) data analysis software. As required, rotational bands resulting from excess water vapor were subtracted using an experimentally measured pure HOD vapor spectrum. Otherwise water signatures from the chamber were eliminated during background subtraction from measurements made on the empty chamber at each RH.

3.5 FTIR Data analysis

3.5.1 Peak deconvolution for sulfonated membranes

Recently, Fayer and colleagues have performed extensive studies on water’s behavior in NAFION® using linear FTIR, fluorescence, visible absorption, and ultrafast vibrational relaxation
measurements.\textsuperscript{19–23} This excellent body of work on NAFION\textsuperscript{®} has drawn on studies of water in reverse micelles.\textsuperscript{24,25} In the reverse micelle work, it has generally been observed that the experimental data can be deconvoluted using a two-population core-shell model.\textsuperscript{26} In NAFION\textsuperscript{®}, the data can also be reproduced with a two-population model\textsuperscript{19,26}, reminiscent of the reverse micelle studies. The two-population model is alluring because the line shape for each of the microenvironments can be directly measured. The OD stretch of HOD in dilute H\textsubscript{2}O is centered at 2509 cm\textsuperscript{-1} with fwhm of 170 cm\textsuperscript{-1}. The lineshape is not Gaussian but has a low frequency tail starting at 2400 cm\textsuperscript{-1} caused by a combination of the bending and a libration mode (\(\nu_2 + \nu_L\)).\textsuperscript{4,5} This mode is usually centered around 2117 cm\textsuperscript{-1} but is very broad and its high frequency tail causes the lower frequency end of the OD peak to have a tail. Evidence of this tail can be seen in Figure 3-7 where the experimental OD peak (black) is plotted with a Gaussian peak that was fit to the experimental data. The real lineshape of the OD stretch complicates our three-population model discussed below, so we approximate the OD lineshape with a Gaussian. Previous studies have been able to fit the OD peak in NAFION\textsuperscript{®} using experimental spectra of bulk water and water hydrating the sulfonate group at all hydration levels by adjusting the intensity of the peaks.\textsuperscript{6} We were unable to produce adequate fits using this method and found that using Gaussian peaks along with our three-population model gave the best results.
Figure 3-7. Experimental OD peak (black) plotted with its equivalent Gaussian fit (red). The low frequency shoulder in the experimental curve is the product of a combination band centered at 2117 cm\(^{-1}\).

The basis for the three-population model is derived from the previously used two-population core-shell model. The two-population model relied on the notion that in a reverse micelle there only two types of water; water molecules that interact with the sulfonate headgroup (shell water) and bulk-like water that interacts with other water molecules (core water).\(^{26}\) This concept was then applied to water sorbed into NAFION\(^{®}\) membranes due to NAFION\(^{®}\)’s ability to strongly phase segregate resembling a reverse micelle. However, poly(styrene) based polymers such as those studied here and poly(sulfone) materials from our previous work do not phase segregate as strongly as NAFION\(^{®}\) does and the two-population model was altered to deconvolute the OD peaks.\(^{29}\) A third peak was added to the water population model to account for water in an intermediate population. There is significant evidence for this type of water in the literature, usually referred to as loosely bound water.\(^{30,31}\) There is also evidence to support this third population of water in reverse micelles using ultrafast infrared spectroscopy to study the
hydroxyl stretch. As the micelles become smaller ($\lambda = 2-10$), the dynamics of the core water starts to slow due to the collective nature of water reorientation.\textsuperscript{32} This means that water that is not directly interacting with the sulfonate group are still perturbed and their dynamics are slowed. Water in both the first and second hydration shell of the sulfonate group must be accounted by employing a three-population model. A schematic of the three types of water is shown below in Figure 3-8.

![Schematic of the three different populations of water sorbed into a polymer membrane.](image)

Figure 3-8. Schematic of the three different populations of water sorbed into a polymer membrane. Bulk-like water is furthest from the sulfonate group (blue), intermediate water is in the second hydration shell (green) and headgroup water is directly bound to the sulfonate group (orange). Number of molecules shown in the schematic is not meant to represent the actual relative populations.

Experimental results from our three-population model are shown in Figure 3-9. Peaks are fit starting with lowest RH samples. The peak is fit using the three-population model where the peak position for the headgroup and intermediate water are allowed to vary and the parameters
for bulk water are held constant (2509 cm\(^{-1}\) and fwhm of 170 cm\(^{-1}\)). Headgroup associated water will always have a peak position that is at a higher frequency than intermediate water because headgroup water is directly interacting with the sulfonate group and the hydrogen bond formed is weak.\(^{29,33}\) The established parameters from the low \(\lambda\) fit are held constant for samples measured at increasing RH. The peak positions and fwhms will change as the polymer chemistry changes, but the parameters for bulk water will remain constant. It was sometimes necessary to let the fwhm of the intermediate water peak vary with increasing hydration. This variation is needed because of the hydrogen bonding network reorientation as hydration increases. As the hydrogen bonding changes, the fwhm of the entire OD peak changes and the only peak that can be justified to change is the intermediate water.

Figure 3-9. The OD stretch deconvolution of PSU-S1 at a \(\lambda\) of 2.0 and 8.5. Hydration numbers were obtained by introducing the samples to 100\% and 30\% RH, respectively.

\subsection*{3.5.2 Non-Condon Effects}

To obtain population distributions, the deconvoluted peak area in the OD stretch region must be corrected for non-Condon effects, which are amplified by strong hydrogen bonding environments, like that of water.\(^{34}\) The non-Condon effect results in an increase of the transition dipole strength with decreasing frequency. Therefore, the area of the two peaks were corrected for
the frequency dependence of the transition dipole moment,\(^{19,35}\) by determining the transition
dipole \((\mu)\) at each wavenumber using Equation 3-1, where \(\mu_g\) and \(\omega\) represent the gas-phase
transition dipole and the frequency of the vibration, respectively. In linear IR spectroscopy,
absorbance depends on \(\mu^2\). To obtain the correct absorbance value using the newly acquired
transition dipole, Equation 3-2, was used and the area of the new curve was calculated.

\[
\frac{\mu}{\mu_g} = 31.27 - (1.09 \times 10^{-2} \text{cm})\omega
\]  

(3-1)

\[
A_{\text{corrected}} = \frac{A_{\text{fit}}}{\mu^2}
\]  

(3-2)

3.6 Density functional theory calculations

Density functional theory provides an alternative method to solve the Schrodinger
equation for a many-body system. Kohn, Hohenberg and Sham were able to describe a real
system by an effective one-body system by replacing the complex many body wave function,
which is the solution to the Schrodinger equation and depends on 3N variables, with the electron
density which only depends on the three spatial coordinates \((x, y, \text{and} \ z)\).\(^{36}\) Therefore, the ground-
state electronic energy \(E_0\) is a functional of the function \(\rho(r)\). Charge densities were computed by
calculating the partial charge of the sulfonate group using DMol\(^3\) DFT calculations.\(^{37,38}\) Full
geometry optimizations were performed using the general gradient approximation (GGA) with a
PBE functional. Electrostatic potential derived atomic charges were obtained by using the B3LYP
method with a DNP basis set.
3.7 Water Uptake

Water uptake (WU) was measured using a TA instruments Q5000SA water vapor sorption microbalance at 30 °C between relative humidity of 30% and 95%. The hydration number (λ), or number of water molecules per ionic group was calculated from Equation 3-4.

\[
\lambda = \left( \frac{m_{RH} - m_0}{m_0} \right) \times \left( \frac{1000}{M_{H2O} \times IEC} \right)
\]  

(3-4)

Here, \( m_{RH} \) is the sample mass at a given RH, \( m_0 \) is the mass of the dry samples, \( M_{H2O} \) is the molar mass of water, 18.02 g, and IEC is the ion exchange capacity with units of milliequivalents of ions per gram of polymer.

3.8 Conductivity Measurement

Conductivity was measured using electrochemical impedance spectroscopy (EIS) with a Solartron 1260A impedance/gain-phase analyzer. The conductivity of the free-standing membranes was obtained using a two-probe, in-plane geometry cell, at frequencies between 1 MHz and 100 Hz scanning from high to low frequencies. A schematic diagram of the membrane conductivity cell is shown in Figure 3-10. All conductivity measurements were performed on membranes in the protonated form. To achieve this, the membranes were soaked in 1 M H₂SO₄ for 24 hr and then rinsed with DI water. Membranes were soaked in DI water for one week, changing the water every 24 hr to ensure excess protons were removed.
Figure 3-10. Schematic of the cell used for conductivity measurements of free-standing membranes\textsuperscript{39,40}, with securing screws (1), Teflon\textsuperscript{®} blocks (2), stainless steel electrodes (3), equilibration windows (4) and the membrane (5).

Membrane conductivity was measured in a controlled relative humidity environment using an Espec SH-241 environmental chamber. The relative humidity was varied from 30\% to 95\% while the temperature was held at 30°C. These parameters correspond to the environment used to measure the FTIR spectra and the water uptake values. The proton conductivity is computed by extrapolating the impedance line to the x-axis (real impedance). The extrapolated value of the real impedance (where the imaginary impedance is zero) is taken as the resistance of the membrane. Proton conductivity ($\sigma_+$) was calculated from equation 3-5,

$$\sigma_+ = \frac{L}{RA}$$ (3-5)
where $L$ is the length between the electrodes, $R$ is the resistance (real impedance extrapolated to x-axis) and $A$ is the cross sectional area of the membrane available for ionic current.

3.9 Small angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS) for domain spacing

SAXS patterns of dry acid-form membranes were collected on a Rigaku (formerly Molecular Metrology) instrument equipped with a pinhole camera with an Osmic microfocus Cu K$_\alpha$ source and parallel beam optic. Measurements were obtained under vacuum at ambient temperature. Typical counting times for integration over a multiwire area detector were 20 to 40 min with typical membrane thicknesses on the order of 100 μm. Scattering intensities were normalized for background scattering and beam transmission. Interdomain spacing were calculated using Equation 3-5, where $d$ is the interdomain spacing and $q$ is the scattering vector in inverse angstroms. All SAXS experiments were conducted by Melanie Disabb-Miller.

SANS data were collected using the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. Prior to measurement, samples were equilibrated in liquid D$_2$O for at least 24 h. SANS data were taken while the sample was immersed in liquid D$_2$O using a copper cell with quartz windows. Scattering intensities were corrected for background scattering from liquid D$_2$O, the quartz windows and the environment. The 2-D data were integrated to prepare the 1-D scattering curves using Igor Pro. Interdomain spacings were calculating using equation 3-5. SANS experiments were conducted by Lillin He at Oak Ridge National Laboratory (Oak Ridge, Tennessee).

$$d = \frac{2\pi}{q}$$

(3-5)
3.10 References


Chapter 4

Water Hydrogen Bonding in Sulfonated Polymers

4.1 Introduction

Polymer membranes with tethered acidic groups are important functional units of proton exchange membrane fuel cells and the properties of the membrane have a large influence on the operational performance of the cell.\textsuperscript{1,2} Poly(perfluorosulfonic acid)-based proton exchange membranes (PEM), such as NAFION\textsuperscript{®}, are the standard ion-conductive material in the fuel cell industry; however, there has been significant work on other types of PEMs that do not have the perfluorinated backbone structure.\textsuperscript{3-5} It is known that the hydrophilic/hydrophobic phase separation of these polymers drastically influences their conductivity and water transport properties.\textsuperscript{6,7} The phase separation of PEMs is determined by the chemical structure of the polymer, including the type of polymer backbone, its polarity, and the location and type of the tethered sulfonate group. Many of NAFION\textsuperscript{®}’s outstanding properties are due to the unique juxtaposition of the hydrophobic backbone and hydrophilic perfluoroalkyl sulfonic acid. The difference in polarity causes the sulfonate moieties to cluster and form interconnected water filled channels, allowing for high rates of proton transport.\textsuperscript{7-8} The perfluorinated backbone and sulfonic acid side chain tethers are also flexible, aiding the formation of the interconnected channels.

However, when analyzing a polymer with a more polar, less flexible backbone with sulfonate groups tethered directly to the aromatic backbone rings, such as in the case of sulfonated poly(ether ether ketone) (sPEEK), it was found that the water-filled channels were narrower and had more “dead-ends” due to the smaller hydrophobic/hydrophilic difference among the polymers.

constituents and poor self-assembly of the ionic groups.⁷ The effect of aromatic backbone stiffness has also been observed in sulfonated poly(phenylene),⁹ sulfonated poly(imide)₅,¹⁰, and other non-NAFION® PEMs based on engineering thermoplastics. There are subtle differences in the ionic domain morphology of different types of randomly sulfonated aromatic backbone-based PEMs, but the these differences are relatively minor compared to the differences observed between poly(perfluorosulfonic acid)-based membranes and aromatic-based PEMs.

The acidic group in PEMs can be connected directly to the backbone aromatic rings, as in sulfonated poly(ether ether ketone) or sulfonated poly(sulfone), or through a perfluoroalkyl tether or other extended linker group like what is found in NAFION®. While both types of moieties act as strong acids, the electron-withdrawing perfluoroalkyl tether in NAFION® causes the sulfonate group to behave as a superacid.¹² The superacidic nature of the perfluosulfonate is thought to be the key to NAFION®’s ability to achieve high proton conductivities at low relative humidity (RH) or low hydration numbers λ = number of water molecules per sulfonate group).¹³ Computational studies by Paddison comparing para-toluenesulfonic acid and triflic acid have shown that differences in acidity of the sulfonate moiety affects the proton mobility and conductivity.¹⁴ The results revealed that once the proton has dissociated from the sulfonate anion, the excess electron density is stabilized more readily by the -CF₃ group of triflic acid compared to the aromatic ring of para-toluenesulfonic acid, due to the strong electron-withdrawing properties of fluorine. This additional inductive stabilization causes the triflic acid to behave as a weak conjugate base, resulting a longer distance between the sulfonate anion and the hydrated proton in triflic acid than in para-tolunesulfonic acid. Therefore, in a perfluorinated material, once the first hydration shell forms around the sulfonate ion, the proton is effectively shielded from the anion by water molecules, allowing the dissociated proton to be more readily transported through the ionic channels.¹⁴ In the case of an aromatic sulfonate, which behaves as a strong conjugate base, the proton is more strongly attracted to the sulfonate group, impeding proton conductivity.
Experimental comparisons between NAFION® and sulfonated PEEKK support the computational results: at low hydration numbers the proton mobility and subsequent proton conductivity is higher in NAFION® due to the more acidic sulfonate moiety. The higher acidity causes the sulfonate group to have more ionic character and interact with more water molecules to achieve solvation. Currently, supercaids are being incorporated in polymers with aromatic backbones to develop membranes that are more cost-effective and safer to synthesize than fully perfluorinated materials. These structures are targeted as next-generation PEMs with the conductivity advantages of poly(perfluorosulfonic acid) membranes but better thermal and mechanical stability and lower gas crossover compared to currently available materials.

Water is an ideal solvent for proton transport because of its amphotericity, fast rotational dynamics, and ability to form dynamic hydrogen bonds. Therefore, understanding the behavior of water in polymers and how the water contributes to the polymer’s proton conductivity and other properties is crucial to developing better-performing materials for membrane-based applications. Nuclear magnetic resonance (NMR) has been used to measure relaxation times, $T_1$ and $T_2$ of water sorbed in various ionic polymers. Both types of measurements can be used to measure the different microenvironments of water quantitatively by mathematically deconvoluting the relaxation time into short and long components to account for tightly bound and loosely bound water, respectively. Dielectric relaxation spectroscopy has also been used to study various relaxation times of water in ionomers. Similar to NMR relaxation measurements, slow relaxation times are attributed to water associated with the ionic group and fast relaxation times are similar to bulk water where water-water interactions dominate. Ultrafast spectroscopy can also be employed to better understand water-polymer interactions by studying the dynamics of the hydrogen bonding network. By measuring the vibrational lifetime of the OD stretch of dilute HOD in H$_2$O, researchers have been able to characterize how the hydrogen bond network changes as a function of hydration in NAFION® films. Moilanen, et al.
concluded that drastic changes in the lifetime measurements as hydration increased indicated that water in NAFION® occupies two distinctly different states, bulk water and ionic headgroup-associated water. These two states differ due to the strength of the hydrogen bond they experience and thus they have different peak stretching frequencies and relaxation times. When NAFION® was initially hydrated, an OD stretch with a slow relaxation on the order of 11 ps was assigned to water that occupied the solvation shell of the sulfonate group. The remaining water in the sample displayed fast relaxation on the order of 5 ps, which is similar to bulk water (1.7 ps lifetime).

To complement the ultrafast measurements, the hydrogen bonding of water can be examined by linear FTIR spectroscopy, using dilute HOD in H₂O as an easily interpretable probe of the water behavior in the material. Temperature-dependent studies of the OH fundamental modes have shown that both stretching modes (ν₁ and ν₃) shift to lower wavenumbers at lower temperatures, due to stronger hydrogen bonds, whereas the bending frequency shifts to higher frequencies. However, the shift of the bending mode is much smaller than the stretching modes, thus studying any fundamental stretching mode will provide insight to the hydrogen bonding network. The FTIR spectrum of pure water (H₂O) and heavy water (D₂O) are complicated due to overlapping bands and Fermi resonance. To simplify the spectrum, dilute HOD in H₂O is used as a probe for water hydrogen bonding behavior. The bands in the vibrational spectrum of dilute HOD in H₂O are better separated, which eliminates overlapping bands and Fermi resonance.

The frequency of the OD stretch is indicative of the strength of the hydrogen bond. When HOD is in the solid state, exhibiting very strong hydrogen bonds, the OD stretch is centered around 2440 cm⁻¹. Whereas in the vapor phase, the faint absorption peaks due to non-hydrogen bonded OD groups are located at 2719 cm⁻¹. In the FTIR spectrum of NAFION® hydrated with dilute HOD in H₂O, a broad, non-Gaussian peak is evident ~2700-2400 cm⁻¹.
depending on hydration level, where a single Gaussian peak centered at ~2509 cm$^{-1}$ is observed for 5 mol % HOD in liquid H$_2$O.$^{28}$ The broad peak of HOD in NAFION® reflects the distribution of hydrogen bonding environments that water experiences in the polymer and this distribution can be deconvoluted to recover the percentage of water in different microenvironments.$^{24}$ Early work by Falk, et al. on dilute HOD in NAFION® showed that the OD stretch peak was blueshifted by ~85 cm$^{-1}$ compared to HOD in bulk H$_2$O.$^{28}$ This drastic shift was attributed to the water participating in a weaker hydrogen bond with the sulfonate groups on the polymer side chain, compared to the stronger water-water hydrogen bonds in bulk water. Moilanen, et al. performed a similar study over varying levels of hydration and were able to extract quantitative values corresponding to bulk and polymer-bound water using a curve fitting routine comprised of the weighted sum of two water distributions; polymer-bound water and bulk water.$^{24}$ Interestingly, as hydration was increased, the OD peak shifted by ~40 cm$^{-1}$ to lower wavenumbers, demonstrating that the hydrogen bonding network was dependent on the amount of water in the polymer, which correlates strongly to the polymer’s conductivity behavior with hydration.$^{29}$

The present report seeks to examine how backbone polarity and side chain electron withdrawing properties influence the binding of water within two types of polymer membranes with a variety of sulfonate groups. The OD stretch peak of water sorbed into series of sulfonated syndiotactic poly(styrene) (PS) and poly(sulfone) (PSU) films was analyzed to extract information about the populations of water in these materials. Additionally, the strength of the hydrogen bond formed between the sulfonate group and water was estimated based on the peak frequency of the OD stretch. Further understanding of how polymer structure influences function of these materials will assist in the development of new generations of ion-conducting polymers for fuels cell and other ion transport membranes.
4.2 Materials and Experimental Methods

4.2.1 Materials

Sulfonated syndiotactic poly(styrene) (PS-S1 and S2 of Figure 4-1a) and sulfonated poly(sulfone) samples (PSU-S1 and S2 of Figure 4-1b) were synthesized according to our previous reports using C–H borylation of aromatic polymers and subsequent Suzuki-Miyaura coupling of the borylated polymer side groups with phenyl bromides containing protected sulfonate side chains with fluoroalkyl or aromatic sulfonate tethers. Synthesis details and the basic properties of the polymers can be found in Refs. 13 and 15. The fluoroalkyl sulfonate (S1) sidechain in our system can be considered a superacid with an estimated pKₐ of -14. The aryl (S2) sidechain is much less acidic with an estimated pKₐ value of -2.5. It is difficult to accurately measure the pKₐ of aqueous superacid solutions; however, the trend of fluorinated acids having higher acidity has been observed in weaker acids, like carboxylic acid, where the pKₐ can be measured analytically by common methods. Therefore, it is reasonable to estimate the pKₐ value of perfluorosulfonic acid as being more negative than its aromatic analog.
4.2.2 Fourier transform infrared spectroscopy (FTIR)

Thin films of sulfonated PS and PSU in sodium form were cast from dimethyl sulfoxide onto CaF$_2$ windows, dried at 40°C for 24 h, then under vacuum at 80°C for 12 h and placed in an FTIR transmission flow cell (Model 64100-F, New Era Enterprises, Vineland, NJ). Estimated film thicknesses ranged from ~1-3 µm. Humid air containing 5 mol % D$_2$O was flowed (20 std. cm$^3$ s$^{-1}$) through the cell while spectra were recorded using a Bruker (Billerica, MA) VERTEX 70 spectrometer with a nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Humidification of the flowing air through the FTIR cell was achieved by dew-point mixing of fully-humidified and dry air streams. Air at dewpoint was produced by a water sparging system, and was then mixed with a dry air stream at controlled mass flow ratios to yield a range of relative humidities.
The relative humidity of the mixed stream was measured using an RH probe (Omega HX15-W, Omega Engineering, Inc., Stamford, CT) before being introduced to the measurement cell at the same temperature as the system. Each RH corresponded to a different hydration number \( \lambda = \text{mole of water/mole of sulfonate group} \) depending on the polymer sample. Hydration numbers were measured previously using a TA Instruments Q5000SA water vapor sorption analyzer and reported as a function of RH in Refs. 13 and 15. In scoping experiments, we equilibrated the samples for up to 1 h at each RH while taking spectra every 5 min. After 20 min, the spectrum did not change, so we used an equilibration period of 20 min at each RH for this work. The polymer was equilibrated for 20 min at each RH and a spectrum was acquired every 5 min. Each spectrum was recorded at 2 cm\(^{-1}\) resolution and 100 scans. Spectra were extracted from 2700 cm\(^{-1}\) and 2400 cm\(^{-1}\) and baselined by setting the absorbance equal to 0 at those two points. Peak fitting was performed using Origin 8.0 (OriginLabs, Northampton, MA) data analysis software. As required, excess water vapor rotational bands were subtracted using an experimentally measured pure HOD vapor spectrum. Otherwise water signatures from the chamber were eliminated during background subtraction from measurements made on the empty chamber at each RH. Three Gaussian peaks were used to fit the OD region from 2700 cm\(^{-1}\) to 2400 cm\(^{-1}\). One peak corresponding to bulk-like water was held constant for all samples and was centered at 2509 cm\(^{-1}\) with a constrained FWHM of 170 (signature of HOD in bulk water), while the headgroup-associated and intermediate water peaks varied by sample. For the superacid S1 samples, a weighted sum fitting routine was used. The peak positions and FWHM for headgroup-associated and intermediate water were determined by fitting the lowest RH samples with three peaks, the third peak being bulk water with peak position of 2509 cm\(^{-1}\) and FWHM of 170. Then the peak position and shape for all three peaks was held constant as the RH was increased and the fit was determined by varying the relative intensity of the peaks to match the experimental spectrum. The data from the aromatic sulfonic acid side chain samples could not be fit using the
weighted sum approach discussed above, and therefore only the peak positions (determined at the lowest RH) were held constant and the FWHM was allowed vary for the headgroup-associated and intermediate water over the range of RH studied.

4.2.3 Small-angle neutron scattering (SANS)

SANS data were collected using the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. Prior to measurement, samples were equilibrated in liquid D$_2$O for at least 24 h. SANS data were taken while the sample was immersed in liquid D$_2$O using a copper cell with quartz windows. Scattering intensities were corrected for background scattering from liquid D$_2$O, the quartz windows and the environment. The 2-D data were integrated to prepare the 1-D scattering curves using Igor Pro. Primary feature spacing, $d$, was calculated as using $d = 2\pi/q$, where $q$ is the scattering vector at maximum scattering intensity.

4.2.4 Small-angle X-ray scattering (SAXS)

SAXS patterns of dry acid-form membranes were collected on a Rigaku (formerly Molecular Metrology) instrument equipped with a pinhole camera with OsMic microfocus Cu K$_\alpha$ source and parallel beam optic. Measurements were obtained under vacuum at ambient temperature. Typical counting times for integration over a multiwire area detector were 20 to 40 min with typical membrane thicknesses on the order of 100 μm. Scattering intensities were normalized for background scattering and beam transmission.
4.3 Results and Discussion

4.3.1 OD peak shifts

In Figure 4-2, the FTIR spectrum of the OD stretch of both the PS-S2 and PSU-S2 is shown from 2700 cm\(^{-1}\) to 2400 cm\(^{-1}\). As the hydration number was increased from \(\lambda = 1.7\) to \(\lambda = 7.9\), the spectra of the PS-S2 sample displayed a redshift of 14 cm\(^{-1}\) in its peak stretching frequency. A similar shift was reported by Moilanen, et al. in their study of NAFION\(^{\circledR}\), whereas the hydration number was increased from \(\lambda = 1\) to \(\lambda = 9\), the OD peak was redshifted by 44 cm\(^{-1}\). The high frequency OD stretch was caused by the first few water molecules of hydration being tightly bound to the sulfonate group of the NAFION\(^{\circledR}\) sidechain. It is known that the hydrogen bond between the water and the sulfonate group is longer and therefore weaker than a water-water hydrogen bond, resulting in a shift of the OD stretch to higher wavenumber compared to bulk water. The frequency shift as hydration increased in the poly(styrene)-based polymer was smaller than that measured in NAFION\(^{\circledR}\). This difference in water hydrogen bonding environment with backbone composition could be due to the presence of stronger hydrogen bond acceptors in the backbone of the PS compared to any hydrogen bonding acceptors in NAFION\(^{\circledR}\). There has been extensive work carried out on the \(\pi\)-hydrogen bonding system between water and benzene, which has shown that the interaction is weak, but ubiquitous in aqueous solutions.

Interestingly, as PSU was hydrated, the OD stretch peak did not shift, indicating there was no distinct change in the hydrogen-bonding network of water as the water content of the membrane was raised. The absence of a shift as hydration increased was due to the presence of strong hydrogen bond acceptors in the PSU backbone allowing for the first few water molecules to interact with the sulfonate, ether, or sulfone moieties. PSU is more polar than poly(styrene) because its Hansen solubility parameter (\(\delta = 20.3\) (MPa\(^{1/2}\)) is more similar to water.
(δ = 47.9 MPa^{1/2}), indicating it is more miscible in that solvent compared to poly(styrene) with δ = 18.6 MPa^{1/2}. We can conclude that as the backbone becomes more polar, the less the OD stretch peak shifts due to the presence of additional hydrogen bond acceptors which increase the population of intermediate water.

Figure 4-2. The OD stretch peak of (a) PS-S2 and (b) PSU-S2 at various λ values.

When fully hydrated, both the PS and PSU backbones with the perfluorsulfonate ionic group exhibited an OD stretch peak that was blueshifted compared to the sample with aryl sulfonate sidechains, displayed in Figure 4-3. The blueshift was caused by the water molecules experiencing a weaker hydrogen bond to the perfluorosulfonate group compared to the aryl sulfonate. When the sulfonate moiety is ionized, the negative charge is stabilized by the fluoroalkyl groups, causing the sulfonate to behave as a weak conjugate base. Therefore, the perfluorosulfonate anion forms weaker hydrogen bonds to the surrounding water molecules compared to hydrogen bonds with the aromatic analog, and the OD peak blueshift results. For the aromatic tethered sulfonates, they have higher electron density on the sulfonate group, which increases the hydrogen bond strength with the OD. A similar trend was found when comparing a series of halogen-containing salts. As the electron density of the halogen became more diffuse, as in I, the OH stretch frequency shifted to higher wavenumbers, indicating a weaker hydrogen
bond between water and the anion. First principles studies of the differences in dissociation between hydrated triflic acid and para-toluene sulfonic acid found that the proton of the superacid lies further away from the sulfonate group at hydration numbers from 0-5, allowing it to be more mobile. Interestingly, upon comparing the binding energy of the water molecules to the acid group, it was found that water molecules hydrating the superacid are generally more loosely bound than water hydrating the aromatic sulfonate. Both proton distance away from the sulfonate (or average extent of dissociation) and hydration dynamics in the vicinity of the ions are important to proton transport. When tethered to polymers, superacids provide excellent transport properties because they are highly shielded by water molecules, which allow the proton to more easily participate in transport, and these shielding water molecules are loosely bound to the sulfonate group, allowing them to aid in the transport of protons. The combination of longer proton distance and more loosely bound water makes superacids ideal for ion-containing polymer used for aqueous proton transport applications.

Figure 4-3. The OD stretch peak of PSU-S1 at $\lambda = 8.5$ and PSU-S2 at $\lambda = 11.6$. Hydration was obtained for each membrane by equilibrating at 100% RH.
The hydrated morphology of the PSU and PS samples was similar as observed in SANS measurements Figure 4-4(a) and (b). The interdomain spacing, \(d\), for both hydrated PS-S1 and PS-S2 was 4.2 nm and 4.5 nm, respectively. For hydrated PSU, the interdomain spacings for PSU-S1 and PSU-S2 were 4.2 nm and 4.9 nm, respectively. The interdomain spacings measured with SANS are based on the scattering length density differences between deuterium and hydrogen. Therefore when not hydrated with D\(_2\)O, the membranes did not exhibit any SANS features. SAXS measurements illustrate the dry membrane nanophase segregation based on the electron density difference between polymer and ionic domains. The PSU samples contain a more polar backbone, therefore there is less apparent ionic clustering in both the PSU samples when compared to the PS samples from SAXS measurements, Figure 4-4(c). However, the PSU backbone contains sulfur, which also provides the contrast in the sulfonic acid domains, so there may be differences in contrast between PSU and PS samples. The scattering data reveal that morphology is similar when the samples are hydrated and therefore is not a factor when characterizing water-polymer interactions in these samples.

Figure 4-4. Wet and dry small angle neutron scattering (SANS) results for (a) PS and (b) PSU samples. Wet samples were equilibrated in liquid D\(_2\)O during scattering. Small angle x-ray scattering (SAXS) of dry PS and PSU membranes shown in panel (c).
4.3.2 OD Peak fitting and analysis

The spectra in Figure 4-5 of both PS-S1 and PSU-S2 polymers equilibrated at 30 % and 100% RH were fit with three Gaussian peaks over a range of 2700 cm\(^{-1}\) to 2400 cm\(^{-1}\). The lower frequency peak maximum was set to 2509 cm\(^{-1}\) and a FWHM of 170 cm\(^{-1}\), which is the signature stretching frequency of the OD in HOD participating in hydrogen bonds with other water molecules. The position and FWHM of the intermediate bound water peak was allowed to vary for each sample and accounts for the water that is in an intermediate state between the first and second hydration shells of the sulfonate. This peak appeared at low frequencies, closer to that of bulk water, because perturbations in the hydrogen bonding network are still felt by water molecules not directly interacting with the sulfonate group. There is evidence for this classification of water, usually referred to as loosely bound water.\(^{10,11}\) More recently, ultrafast experiments on small AOT micelles (\(\lambda = 2-10\)) have started to reveal an intermediate state of water that exhibits slower vibrational lifetime than bulk water, but not as slow as interfacial water that is directly interacting with the sulfonate group.\(^{12}\) The headgroup-associated peak represents water interacting with the sulfonic acid group, and the peak position appears at much higher frequencies due to reasons previously discussed. The peak position and FWHM of this third peak were also allowed to vary for each sample. Additional deconvolutions can be found in Figure A-1. The superacid samples could be fit using a three-state model, where the peak position and FWHM for bulk water, intermediate water, and headgroup water were determined by fitting the lowest RH and keeping the peak position and FWHM constant for all other RH spectra. When the same routine was used to fit the aromatic sulfonate samples, the resulting spectral fits were not adequate. We found that by fixing the peak positions, but letting the FWHM of the headgroup water peak and the intermediate water peak vary, much better agreement between the ensemble-summed spectra and the experimental data were obtained. Fitting parameters are given in Table
with addition parameters given in Table A-1. We hypothesize that the acid strength plays a role in distinguishing microenvironments within the polymer, so a weaker acid group yields less distinction between headgroup and intermediate water and the homogeneity of each ensemble can change as a function of hydration. For strong acids, the headgroup water is more distinguishable because the interface is more robust and well-defined, resulting in distinct ensembles of water that are consistently homogenous.

Figure 4-5. The OD stretch deconvolution of PS-S1 at a λ of 1.7 and 7.3, and PSU-S2 at a λ of 2.5 and 11.6. Hydration was obtained for each membrane by introducing the sample to 100% and 30% RH.
The percentage of bound water in each sample as a function of $\lambda$ derived from the spectral deconvolution, Table A-2 and Table A-3, is plotted in Figure 4-6. Poly(styrene)-based membranes consistently have a larger amount of headgroup-associated water when compared to poly(sulfone)-based membranes as a function of $\lambda$ (Table A-4 and Table A-5). A similar result was observed by calculated pair correlation functions of the sulfonate-hydronium pair in the same set of polymers, where the solvation effect was larger in the PS compared to PSU, due to PSU having more locations for the water to associate.\textsuperscript{13,14} The PSU has more locations for the water to associate, resulting in the poly(sulfone)-based polymers having less water bound to the headgroup than their poly(styrene) analogs. The superacid consistently had the highest percentage of water that was associated with the ionic groups compared to the aromatic sidechains. The trend of increased bound water is consistent with previously published pair correlation simulations on these specific polymers, indicating that the perfluorosulfonate moiety attracts more water molecules because of its greater dissociation.\textsuperscript{13} Interestingly, as hydration increases, the amount

<table>
<thead>
<tr>
<th></th>
<th>PS- S1</th>
<th>PSU- S2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda = 1.7$</td>
<td>$\lambda = 7.3$</td>
<td>$\lambda = 2.5$</td>
</tr>
<tr>
<td>intermediate peak (cm$^{-1}$)</td>
<td>2514</td>
<td>2514</td>
</tr>
<tr>
<td>fwhm (cm$^{-1}$)</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>percent intermediate</td>
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<tr>
<td>headgroup peak (cm$^{-1}$)</td>
<td>2592</td>
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</tr>
<tr>
<td>fwhm (cm$^{-1}$)</td>
<td>112</td>
<td>112</td>
</tr>
<tr>
<td>percent headgroup</td>
<td>80</td>
<td>75</td>
</tr>
</tbody>
</table>
of headgroup water decreases for the superacid samples and the opposite trend is observed for the aromatic sulfonate samples. Again, this trend can be explained due to the increased acidity of the superacid, which behaves as a weak base. The total charge of the oxygen atoms of the superacid is less negative than the total charge of the oxygen atoms of the aromatic sulfonate, therefore as more water is introduced into the system the aromatic sulfonate becomes more hydrated than the perfluorinated sulfonate analog. We can conclude that the perfluorosulfonate group interacts with more water molecules than its aryl counterpart, but the hydrogen bond formed is comparatively weaker.

![Figure 4-6](image_url)

Figure 4-6. The percentage of water bound in sulfonated syndiotactic poly(styrene) and sulfonated poly(sulfone) based samples as a function of $\lambda$.

### 4.3.3 Fingerprint analysis

While we have focused on water’s vibrational signatures in this work, the fingerprint region of the FTIR spectra provided information about how polymer tethered functional groups are interacting with water, causing subtle shifts of their vibrational frequency in the range of 1600
to 950 cm\(^{-1}\). However, due to the complexity of these polymers, the majority of the fingerprint region cannot be easily interpreted due to many strong overlapping peaks. We were able to resolve the sulfonate symmetric stretch for each polymer, shown in Figure 4-7, which gives a peak in the range of 1070-1030 cm\(^{-1}\), Table 4-2. It is apparent that the position of the sulfonate symmetric stretch depends on the sidechain structure. When the sulfonate was tethered via a fluoroalkyl sidechain, the sulfonate symmetric stretch was shifted to higher frequency around 1061 cm\(^{-1}\) which is consistent with literature.\(^{15,16,17}\) This shift indicated a strengthening of the S-O bond. Fluorine is the most electronegative atom and therefore, the fluoroalkyl sidechain is very electron withdrawing as evidenced by its interaction with water, as previously described. The electron withdrawing perfluorinated tether caused the electron density to be drawn from the oxygen atoms, and distributed into the S-O bond. A sulfonate group tethered to an aromatic species experiences a weakening of the S-O bond, as indicated by the symmetric stretch of the sulfonate group being shifted to lower wavenumbers around 1042 cm\(^{-1}\). It is reasonable that sulfonates tethered by an aromatic ring experience a weakening of the S-O bonds induced by resonance destabilization, where electron density can either be delocalized in aromatic ring, or on the oxygens bonded to the sulfonate.

Table 4-2. Symmetric sulfonate stretch peak position. Measurements taken at 0% RH.

<table>
<thead>
<tr>
<th>sample</th>
<th>symmetric SO(_3) stretch position (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU-S1</td>
<td>1063</td>
</tr>
<tr>
<td>PS-S1</td>
<td>1061</td>
</tr>
<tr>
<td>PSU-S2</td>
<td>1043</td>
</tr>
<tr>
<td>PS-S2</td>
<td>1042</td>
</tr>
</tbody>
</table>
4.4 Conclusions

We used FTIR spectroscopy to better understand the hydrogen-bonding network of water sorbed into polymer membranes with varying backbone composition and sulfonate group character. We found that polymers with more polar backbones experienced a smaller change in the hydrogen-bonding network as hydration was increased due to the presence of more hydrogen bond acceptors in the backbone, leading to an increased amount of intermediate water. Upon comparing sulfonate groups with different tethers, it was found that perfluorosulfonate sidechains interacted with water more readily due to facile formation of solvent-separated ion pairs between the sulfonate group and sodium counterion, but the hydrogen bonds formed were weaker compared to the aryl sulfonate sidechains. This insight is important for the development of membranes for proton transport, as tethered superacids facilitate transport more readily than their aromatic analogs because of the weaker headgroup hydrogen bond to water molecules. Both the
proton and the water molecules are less tightly bound to the perfluorinated sulfonate headgroup, allowing the water molecules to more easily participate in proton transport compared to sulfonate groups with lower acidity that bind water more strongly. The sulfonate symmetric stretch peak was dependent on the chemical structure of the tether. Sulfonate groups attached to perfluoroalkyl sidechains will experience a strengthening of the sulfur-oxygen bond, resulting in the peak shifting to higher wavenumbers.
4.5 References


(13) Chang, Y.; Brunello, G. F.; Fuller, J.; Hawley, M.; Kim, Y. S.; Disabb-Miller, M.; Hickner, M. A.; Jang, S. S.; Bae, C. Aromatic Ionomers with Highly Acidic Sulfonate


Chapter 5

Spectroscopic Characterization of Sulfonate Charge Density in Ion-Containing Polymers

5.1 Introduction

Early studies of the vibrational spectra of electrolyte solutions revealed that the hydrogen bonding network of water was disrupted when ionized species were introduced to solution and there must be a new type of hydrogen bond, one between water and the anion.\textsuperscript{1,2} By studying the vibrational frequency (OD) of isotopically dilute HOD, researchers were able to determine trends for various anions based on their size, charge and electronegativity. Those intrinsic characteristics correlated to physical quantities which are commonly used to characterize hydrogen bonds, such as the frequency (OD) and hydrogen bond distance measured by neutron or X-ray diffraction.\textsuperscript{3,4} These studies concluded that there is a correlation between the OD frequency in dilute HOD and the distance of the O-D···X- hydrogen bond. Recently this has again been confirmed in work by Kropman and Bakker, who used both linear and nonlinear vibrational techniques to describe the differences in the hydrogen bond strength in a series of halide salts, and found that as the electronegativity of the anion decreases the OD frequency was more shifted into the blue.\textsuperscript{5} Where NaI produced the largest blueshift of the series compared to bulk water. This trend can also be described in terms of acidity, where the I- anion is considered the weakest conjugate base founded on its low electronegativity and that HI is an extremely strong acid with an estimated pK\textsubscript{a} of 10 in water.\textsuperscript{6}

The anions in ion-containing polymers, such as NAFION\textsuperscript{®} have also been studied using vibrational spectroscopy to understand how water hydrogen bonding to an anion influences the mechanism of cation transport through the membrane.\textsuperscript{7-9} When NAFION\textsuperscript{®} is sufficiently hydrated with H\textsubscript{2}O containing dilute HOD, which has a characteristic peak frequency of 2509 cm\textsuperscript{-1}, the peak
is significantly blueshifted to ~2588 cm\(^{-1}\) indicating that the hydrogen bonding network is perturbed and that the bond between water and the anion is weak.\(^7\) The sulfonate anion in NAFION\(^\text{®}\) is special in that it is considered a superacid by definition that its pK\(_a\) value is more negative than that of pure sulfuric acid.\(^10\) The increased acidity is caused by the perfluorinated tether of the sulfonate group; the fluorine atoms are highly electronegative and inductively withdraw excess electron density away from the sulfonate group decreasing its overall charge density. Moilanen, et al. were also able to characterize the water-polymer interactions by implementing a peak-fitting routine to extract hydrogen bonding population data from the OD peak. They were able to determine percentages of the total membrane sorbed water that were experiencing hydrogen bonds to other water molecules (bulk water) or hydrogen bonds to the sulfonate anion.

Computational studies by Paddison revealed the differences between two different types of anions, \textit{para}-toluenesulfonic acid and triflic acid, and how the two moieties interacted with water. Paddison calculated the total charge on the oxygen atoms of each sulfonate group as it was exposed to an increased number of water molecules and found that triflic acid had an overall lower charge and as a results experienced a longer and therefore weaker bond to water.\(^11\) The fluorine atoms of the triflic acid can better stabilize the excess negative charge than the aromatic ring of \textit{para}-toluene sulfonic acid. We were able to confirm these results using FTIR, and found that when a two sulfonated poly(styrene) films were hydrated with HOD, the one containing a perfluorosulfonate displayed an OD peak frequency that was blueshifted by ~40 cm\(^{-1}\) compared to its aromatic sulfonate analog.\(^12\)

In this study, we were interested in investigating novel sulfonate tether structures to better understand the water-polymer interactions in ion-containing polymer materials by using both FTIR and first principal computations.
5.2 Materials and Experimental Methods

Thin films of sulfonated poly(sulfone), shown in Figure 5-1, in sodium form were cast from dimethyl sulfoxide onto CaF$_2$ windows, dried at 50°C for 4 h, then at 80°C for 6 h and placed in an FTIR transmission flow cell (Model 64100-F, New Era Enterprises, Vineland, NJ). Humid air containing 5 mol % D$_2$O was flowed (20 std. cm$^3$ s$^{-1}$) through the cell while spectra were recorded using a Bruker (Billerica, MA) VERTEX 70 spectrometer with a nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Humidification of the flowing air through the FTIR cell was achieved by dew-point mixing of fully-humidified and dry air streams. Air at dewpoint was produced by a water sparging system, and was then mixed with a dry air stream at controlled mass flow ratios to yield a range of relative humidities. The relative humidity of the mixed stream was measured using an RH probe (Omega HX15-W, Omega Engineering, Inc., Stamford, CT) before being introduced to the measurement cell at the same temperature as the system. Each RH corresponded to a different hydration number ($\lambda$ = mole of water/mole of sulfonate group) depending on the polymer sample. Hydration numbers were measured using a TA Instruments Q5000SA water vapor sorption analyzer and reported as a function of RH. Each spectrum was recorded at 2 cm$^{-1}$ resolution and 100 scans. The hydrated spectra were obtained by using the dry polymer as a reference. Spectra were extracted from 2700 cm$^{-1}$ and 2400 cm$^{-1}$ and baselined by setting the absorbance equal to 0 at those two points (two-point linear baseline).
Figure 5-1. Repeat unit of the poly(sulfone) (PSU) backbone where R represents various tether structures.

5.3 Results and Discussion

5.3.1 OD peak deconvolution

The deconvolution of the OD stretch peak of the four samples is shown in Figure 5-2. Curve fitting was performed using Origin 8.0 (OriginLabs, Northampton, MA) data analysis software. The curve-fitting routine employed a three-state weighted-sum model where we consider water to be present in three different microenvironments within the polymer membrane. The first of which is a bulk-like state, where water is hydrogen bonded to other water molecules. The vibrational parameters for this microenvironment are known; with a peak position of 2509 cm$^{-1}$ and fwhm of 170 that can be approximated as Gaussian (the experimentally-measured line
shape is not perfectly Gaussian). The second microenvironment is intermediate water, which encompasses water that is not directly interacting with the charged headgroup, but is still affected by its electric field. This lineshape is not known and is difficult to measure experimentally since there are likely a distribution of continuum states in this population. Lastly, there is water directly interacting with the charged headgroup, referred to as headgroup-associated water. Water in this microenvironment will have unique vibrational properties depending on how the headgroup behaves as a conjugate base, here characterized by the charge density of the sodium salt form of the sulfonate. The fitting parameters (peak position and fwhm) of the intermediate and headgroup-associated water are determined by fitting the OD stretch peak at the lowest hydration (30% RH). The population peak parameters are then held constant for fitting of the higher hydration samples. Deconvolution of the broad OD peak allows us to extract the populations of water in these three different microenvironments to understand how the chemical structure of the tether is affecting the hydrogen bonding network. However, for the population distributions to be accurate, the area of the peaks must be correcting for the strong non-Condon effects in water.
(a) PSU-S1
\( \lambda = 3.09 \)

(b) PSU-S1
\( \lambda = 6.77 \)

(e) PSU-S5
\( \lambda = 2.59 \)

(c) PSU-S4
\( \lambda = 3.11 \)
Figure 5-2. The OD stretch deconvolution of the four samples shown at both 10 and 20 wt% water uptake.

The OD peak positions for all samples hydrated at both 10 and 20 wt% water are given in Table 5-1. When hydrated with 20 wt% water, S6 gave an OD peak stretch position of 2572 cm\(^{-1}\) indicating that it is the most acidic due to its unique sidechain architecture that includes two perfluorosulfonate groups. The S4 sidechain contains a sulfur linkage yields and OD peak stretching frequency at 2552 cm\(^{-1}\) signifying it is slightly more acidic than S1 which contains an oxygen linkage and gave an OD peak stretching frequency at 2549 cm\(^{-1}\). This subtle difference causes these two sidechains to behave differently when hydrated. When the two are hydrated with
only 10 wt% water, the peak position of OD stretch for S4 is blueshifted significantly compared to S1, indicating that the sulfonate groups are forming, longer and weaker bonds with the surrounding water molecules. Interestingly, S5 yields the lowest OD peak position at 2540 cm\(^{-1}\) showing that removing one of the -CF\(_2\) units affects the acidity. This decrease in acidity has been demonstrated computationally by first principle studies of the electron affinity sulfonate groups with various amounts of fluorination.\(^{15}\) As the amount of fluorination increased, the proton affinity decreased. The fluorine units are extremely electron withdrawing, allowing the proton of the sulfuric acid to be easily removed. Additionally, once the proton is removed, the fluorines aid in stabilizing the resulting negative charge, allowing the sulfonate group to behave as a weak conjugate base.

<table>
<thead>
<tr>
<th>Sidechain</th>
<th>peak position at 10 wt% H(_2)O (cm(^{-1}))</th>
<th>peak position at 20 wt% H(_2)O (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2547</td>
<td>2549</td>
</tr>
<tr>
<td>S4</td>
<td>2560</td>
<td>2552</td>
</tr>
<tr>
<td>S5</td>
<td>2548</td>
<td>2540</td>
</tr>
<tr>
<td>S6</td>
<td>2566</td>
<td>2572</td>
</tr>
</tbody>
</table>
5.3.2 Relating OD peak position to charge density determined by DFT calculations

The charge density of the sulfonate headgroup can be characterized by the vibrational frequency of water that is directly hydrogen-bound to the oxygen atoms, in this case, the peak frequency of the headgroup-associated water. Table 5-2 shows the peak frequency for each polymer sample. The samples are listed in order of increasing charge density according to the peak frequency, where the S4 sidechain has the lowest charge density and the S5 sidechain has the highest charge density. A higher peak frequency indicates water experiencing a weaker hydrogen bond. The S4 and S1 sidechains have the lower charge density because of their perfluorinated character. Paddison has shown that the fluorine groups are able to stabilize the negative charge of the sulfonate group better than an aromatic ring, causing the sulfonate group to have a decreased electron density and therefore behave as a weak conjugate base.\textsuperscript{11} The difference in charge density between S4 and S1 can be explained based on the differences between thioether and ether linkages. It is has been shown that sulfur’s ability to expand its octet can increase the acidity of an α-hydrogen compared to when an oxygen takes on the same position.\textsuperscript{16,17} This effect can be observed in the fact that S4 displays a slightly greater headgroup-associated peak frequency than S1, due to the ability of sulfur expand its octet and therefore more readily except additional electron density compared to oxygen.

Table 5-2. Headgroup peak position determined by FTIR and the total charge of the oxygen atoms on the sulfonate headgroup determined computationally.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured headgroup-associated peak frequency (cm\textsuperscript{-1})</th>
<th>$\lambda$</th>
<th>Calculated total charge on oxygen atoms at $\lambda = 1$</th>
<th>$\lambda$</th>
<th>Calculated total charge on oxygen atoms at $\lambda = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU-S4</td>
<td>2621</td>
<td>1</td>
<td>-1.411</td>
<td>5</td>
<td>-1.305</td>
</tr>
<tr>
<td>PSU-S1</td>
<td>2617</td>
<td>1</td>
<td>-1.509</td>
<td>5</td>
<td>-1.505</td>
</tr>
</tbody>
</table>
The trend of charge density is confirmed by computing the partial charge of the sulfonate group using DMol³ DFT calculations. Full geometry optimizations were performed using the general gradient approximation (GGA) with a PBE functional set. Electrostatic potential derived atomic charges were obtained by using the B3LYP method with a DNP basis set. Table 5.2 lists the calculated total charge on the oxygen atoms (of the sulfonate) of each tether at both high and low hydrations. The charge density is directly related to the conjugate base character of the sulfonate group. When the charge is most concentrated on the oxygen atoms, a proton will interact more strongly therefore causing the sulfonate to behave as a strong conjugate base. However, if the charge is less localized on the headgroup, the sulfonate will behave a weak conjugate base and consequently a stronger acid. At low hydrations, S5 is the only tether that does not follow the charge density trend found from the experimental measurements, however at high hydrations all calculations correlate to the charge density determined by FTIR. Interestingly, the fluorinated S5 tether does not display the same superacid characteristics as S1 and S4. This effect of a single perfluoromethylene tether compared to the addition of two or more perfluorinated carbons has been shown previously in calculation of the proton affinity of sulfonates with varying amounts of fluorination. It was found that perfluoroalkyl sulfonates experienced a large increase in proton affinity upon removal of a -CF₂ group.

\[\text{Table 5.2 lists the calculated total charge on the oxygen atoms (of the sulfonate) of each tether at both high and low hydrations.}\]

<table>
<thead>
<tr>
<th></th>
<th>2601</th>
<th>1</th>
<th>-1.558*</th>
<th>5</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU-S6</td>
<td>2580</td>
<td>1</td>
<td>-1.526</td>
<td>5</td>
<td>-1.698</td>
</tr>
</tbody>
</table>

*Average of both sulfonate headgroups*
### 5.3.3 Water population analysis correlates to predicted geometry of the sidechain

Table 5-3 displays the population distributions of water in each of the three different microenvironments at both high and low hydrations. Population distributions give insight into how the hydrogen bonding network is changing within the membrane as it is hydrated. We have previously shown that a strong acid will have a higher population of headgroup-associate water because of greater dissociation and stronger ionic character.\(^{12,20,21}\) In this set of membranes, we observe a similar trend, but S4 and S6 have a very small population of water interacting with the headgroup at both high and low hydrations. We believe this effect can be explained based on the conformations of the tethers obtained from DFT calculations. The thioether bond in S4 causes the tether to take on a bent conformation where the sulfonate group is forced to be closer to the aromatic ring and therefore closer to the polymer backbone, displayed in Figure 3c and d. This bent conformation causes the sulfonate to be crowded and therefore water is not as able to interact with the oxygen atoms as readily.

---

**Table 5-3.** Deconvoluted peak positions and percentages of water in different microenvironments at low hydration and high hydrations

<table>
<thead>
<tr>
<th>sample</th>
<th>(\lambda)</th>
<th>headgroup (%)</th>
<th>intermediate (%)</th>
<th>Bulk (%)</th>
</tr>
</thead>
</table>

---

\(^{12,20,21}\)
The S1 tether takes on a conformation that is linear, allowing the sulfonate to interact with water molecules from all directions. The dihedral angle in dimethyl sulfide (98.5°)\textsuperscript{22} is smaller compared to dimethyl ether (112.2°)\textsuperscript{23} which can be explained due to the increased size of the 3p orbitals on the sulfur atom compared to the 2p orbitals of the oxygen atom. The difference in bond angles causes the drastic differences in water binding between S1 and S4 tethers. S4 can take on both cis and trans conformations, however, the energies for the two states calculated are equivalent.
Figure 5-3. Fully optimized minimum energy structures of (A) S1 and (C) S4 with benzene in the plane and (B) S1 and (D) S4 with benzene out of the plane to show kinked structure of the tether. The differences in confirmation lead to differences in the amount of water than can associated with the sulfonate headgroup.

In the *cis* position, Figure 5-3c and d, the shortest distance from the ring to an oxygen atom of the head group is 4.855 Å, whereas in the *trans* position, Figure S2, this distance is 5.612 Å. The S1 tether prefers a *trans* conformation but, the fluorine groups will either orient perpendicular (Figure 4A and B) or parallel (Figure S3) to the aromatic ring. In the parallel conformation, the shortest distance to an oxygen atom from the ring is 5.558 Å and in the perpendicular conformation this distance is 5.498 Å. The *cis* conformation in S4 causes the headgroup to be much closer to the backbone of the polymer, resulting in the headgroup being more shielded from water molecules and therefore reducing the population of headgroup-associated water determined from OD peak deconvolutuion. A similar argument can be made for the S6 tether, which has two sulfonate moieties in close proximity, shown in Figure 5-4. In one tether, there are two aromatic rings containing two perfluorosulfonate headgroups. Paddison investigated how the distance between two side chains
in short-side-chain perfluorosulfonic acid membrane affected their conformation and proton-transfer and found that as the distance (number of tetrafluoroethylene units in the backbone) increased so did the zero point energy of the system.\textsuperscript{24} It was also noted that \textit{cis} conformation (sidechains on the same side of the backbone) was preferred to the \textit{trans} conformation. Both results suggest that there is a source of long-range stabilization between the sulfonic acid groups that is lost as distance between the headgroups increases.\textsuperscript{24} At sufficiently short tetrafluorethylene segments, two conformations were obtained, where the sulfonate groups are separated by 11 Å and one where the sulfonates are at distance of 4.2 Å and have formed two hydrogen bonds between the acid proton and the oxygen atoms of the adjacent headgroup.\textsuperscript{25} In our optimization of the S6 tether, we observe that the sulfur-sulfur bond distance is 6.448 Å, but there are no acidic protons in our model so there are no hydrogen bonds between the two sulfonate groups. When hydrated, one water molecule bridges the two sulfonates. Paddison reported similar results at short distances between sulfonates.\textsuperscript{24,25} We hypothesize that the small population of headgroup-associated water found experimentally is due to the short distance between the sulfonate groups which promote the sharing of water molecules and does not allow water to full access to the sulfonate group due to the distance between the headgroups and bulkiness of the aromatic groups.
Figure 5-4. Fully optimized minimum energy structure of the S6 tether. Two sulfonates per tether causes crowding and fewer water molecules can associate with the sulfonate headgroup.

5.4 Conclusion

In conclusion, we have examined five different ion-containing polymer membranes that contain various sulfonate tethers structures both experimentally, using FTIR of dilute HOD in H2O, and computationally to determine how the chemical structure of the tether affects the acidity of the sulfonate headgroup. Our findings suggest that a perfluorosulfonate containing a thioether linkage produces the most acidic sulfonate based on the peak position of the headgroup-associated HOD peak and the overall charge density of the oxygen atoms of the headgroup that was calculated using DMol3 DFT modeling. Although the thioether S4 is the most acidic sulfonate, our population distribution calculations determined from peak fitting analysis showed that S4 did not display a large population of water interacting with the headgroup. We attributed the low hydration of S4 to the unique cis conformation that the thioether tether preferred, causing the sulfonate headgroup to
be more shielded from the water molecules by the backbone. A similar result was determined for the S6 tether, due to the close proximity of the sulfonates to one another and the overall bulkiness of the group, water molecules were not able to interact with the headgroup as readily.
5.5 References


(15) Yeh, K.-Y.; Restaino, N. a.; Esopi, M. R.; Maranas, J. K.; Janik, M. J. The Adsorption of
Bisulfate and Sulfate Anions over a Pt(111) Electrode: A First Principle Study of
Adsorption Configurations, Vibrational Frequencies and Linear Sweep Voltammogram

(16) Brehm, W. J.; Levenson, T. The Relative Acidifying Influence of Oxygen and Sulfur


(18) Delley, B. An All-Electron Numerical Method for Solving the Local Density Functional

**2000**, *113*, 7756.

(20) Chang, Y.; Brunello, G. F.; Fuller, J.; Disabb-Miller, M. L.; Hawley, M. E.; Kim, Y. S.;
Hickner, M. A.; Jang, S. S.; Bae, C. Polymer Electrolyte Membranes Based on

(21) Chang, Y.; Brunello, G. F.; Fuller, J.; Hawley, M.; Kim, Y. S.; Disabb-Miller, M.;
Hickner, M. A.; Jang, S. S.; Bae, C. Aromatic Ionomers with Highly Acidic Sulfonate
8469.

(22) Westerman, W.; Atlinger, N. L.; Hickey, M. J. Conformational Analysis, CVIII. The
Calculation of the Structures and Energies of Alkanethiols and Thiaalkanes by the

(23) Jones, P. M.; Tang, H.; Yan, X.; Stirniman, M.; Li, L.; Hsia, Y.-T. Torsional Energy
Barriers in Dimethyl Ether and Perfluoro-Dimethyl Ether: Electronic Structure

(24) Paddison, S. J.; Elliott, J. A Molecular Modeling of the Short-Side-Chain Perfluorosulfonic

(25) Paddison, S. J. Proton Conduction Mechanisms At Low Degrees of Hydration in Sulfonic
Chapter 6
Backbone chemistry effects on sulfonate acidity

6.1 Introduction

The search for an alternative electrolyte materials for proton exchange membrane fuel cells (PEMFC) has been an area of much research for many years. Currently, perfluorosulfonic acid (PFSA) polymers, such as NAFION®, are used in commercial cells because they can withstand the harsh conditions in an operating fuel cell. However, PFSAs suffer from low proton conductivity and poor mechanical stability at temperatures above 80 °C and low water content.1 PSFA membranes are also expensive to produce and for PEMFCs to be a viable source of alternative energy, the cost must be comparable to combustion based energy sources.2 The poly(arylene ether) family of polymers are considered a viable alternative to PFSA based membranes because of their oxidative and hydrolytic stability under the harsh operating conditions in a fuel cell. Poly(arylene ether)s include materials such as poly(arylene ether ether ketone) (PEEK), poly(arylene ether sulfone) and many other derivatives due to their simple synthesis and ease for modifications and sulfonation.3,4 Recently, researchers have synthesized a poly(arylene ether sulfone) polymer that contains a NAFION®-like sidechain, the resulting membrane yielded conductivity properties similar to that of the PFSA membrane.5

The acidic group in sulfonated poly(ether ether ketone) or sulfonated poly(sulfone) are directly connected to the backbone aromatic rings, whereas in NAFION® the sulfonate groups is tethered via a perfluoroalkyl tether. Both types of moieties behave as strong acids, however, the electron-withdrawing perfluoralkyl tether in NAFION® causes the sulfonate group to behave as a
superacid. The greater acidity of the perfluorakly group is thought to be the key to PSFA membranes increased conductivity at low relative humidity. First principle studies by Paddison comparing para-toluenesulfonic acid and triflic acid indicated that differences in acidity of the sulfonate moiety affect the proton mobility and conductivity. The excess electron density is stabilized more readily by the -CF₃ group of triflic acid due to the strong electron-withdrawing properties of fluorine. The sulfonate group of triflic acid had calculated charge density of -1.438, compared to the aromatic ring of para-toluenesulfonic acid, which has a charge density of -1.602. The additional inductive stabilization causes the triflic acid to behave as a weak conjugate base, resulting a longer distance between the sulfonate anion and the hydrated proton in triflic acid than in para-toluenesulfonic acid. However, the push to use non-fluorinated materials has resulted in researchers searching for alternative materials that combine sulfonate groups with increased acidity and increased backbone stability. Recently, Schuster, et al. have developed a new type of highly sulfonated poly(arylene sulfone) membrane which yielded proton conductivities greater than NAFION®. The researchers hypothesize that the sulfonate, although directly tethered to the aromatic backbone, will have an increased acidity due to the additional electron withdrawing sulfone groups between each aromatic rings.

The vibrational frequency of the adsorbed water can be studied to learn more about the charge density of the sulfonate group as well as the population distribution of water in various microenvironments. The vibrational signature of dilute HOD in H₂O has been used in both electrolyte solutions and membranes alike to better character the charge density of the various anions. In the work by Kropman and Bakker, the hydrogen bonding strength of a series of halides salts was studied and the researchers found that the less electronegative the anion, the more the OD peak was blueshifted. A solution containing NaI, was blueshifted the most compared to bulk water, where a solution of NaF was actually redshifted, indicating that the hydrogen bond between water and the fluorine anions was strong that bulk-like water. These results have direct
implications on the charge density and acidity of the anions as well. The halides are known to form very strong acids, except for fluorine because of its high charge density. Iodine, for example, forms a very strong acid ($\text{pK}_a = -10$) because of its very low charge density. Similar results have been shown for tethered anions in PEMs. When two poly (arylene sulfone) based PEMs, one functionalized with a perfluoroalkyl sulfonate and one with an aromatic sulfonate, are hydrated with 5% HOD in H$_2$O the membrane containing the more acidic (lower charge density) perfluoroalkyl sulfonate has an OD peak position that is blueshifted by 40 cm$^{-1}$ compared to the membrane with the aromatic sulfonate. The OD peak can also be deconvoluted, because it is the signature of a single vibrational mode, and the deconvoluted peak positions can give more insight into charge density/acidity differences, while the area of the peaks yields information about the population. A three state model has been developed for deconvoluting the OD peak of water adsorbed into sulfonated membranes. Bulk-like water refers to water that is interacting with itself and has a distinct vibrational signature that is unchanged. Intermediate water refers to water that is not directly hydrogen bonding to the sulfonate group, but its dynamics are still affected by the electric field on the sulfonate group. Finally, water can be directly hydrogen bonded to the sulfonate group, this type of water is termed bound water.

In this work we aim to better understand how the backbone chemistry of three sulfonated poly(arylene sulfone)s affects the acidity of the sulfonate moiety by using linear FTIR to study the OD stretch of dilute HOD in H$_2$O and first principle computations to accurately calculate the charge densities. The OD peak was deconvoluted to extract subtle differences between the three samples and was also used to better understand the amount of water in each microenvironment and how that influences the membrane properties. To further understand the results, conductivity and water uptake experiments were also carried out on the three samples. FTIR results correlated with both first principle studies, conductivity and water uptake measurements to fine-tune subtle structure-property relationships in sulfonated poly(arylene sulfone)s.
6.2 Materials and Methods

Thin films of sulfonated polymer, shown in Figure 6-1, were cast from dimethyl sulfoxide or dimethylacetamide, depending on the solubility, onto CaF$_2$ windows. Samples were dried at 50°C for 24 hr. Samples were placed in an FTIR transmission flow cell (Model 64100-F, New Era Enterprises, Vineland, NJ). Humid air containing 5 mol % D$_2$O was flowed (20 std. cm$^3$ s$^{-1}$) through the cell while spectra were recorded using a Bruker (Billerica, MA) VERTEX 70 spectrometer with a nitrogen-cooled mercury-cadmium-telluride (MCT) detector. The relative humidity of the mixed stream was measured using an RH probe (Omega HX15-W, Omega Engineering, Inc., Stamford, CT) before being introduced to the measurement cell at the same temperature as the system. The hydrated spectra were obtained by using the dry polymer as a reference. Spectra were extracted from 2700 cm$^{-1}$ and 2400 cm$^{-1}$ and baselined by setting the absorbance equal to 0 at those two points. Curve fitting was performed using Origin 8.0 (OriginLabs, Northhampton, MA) data analysis software. The curve-fitting routine employed a three-state weighted-sum model where we consider water to be present in three different microenvironments within the polymer membrane, and has been described in detail previously.$^{10,11}$ Table 6-1 gives the IEC values for each membrane. Each membrane was selected based on its IEC values such that it would not affect the water uptake and conductivity measurements. Previous FTIR experiments have shown that the IEC does not affect the OD peak position.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion exchange capacity (IEC) (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-360</td>
<td>2.62</td>
</tr>
<tr>
<td>SES0106</td>
<td>2.42</td>
</tr>
<tr>
<td>sPS-V</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Figure 6-1. Repeat units of sulfonated (a) poly(arylene ether sulfone), (b) poly(phenylene sulfone) and (c) poly(phenylsulfone) where R and R’ are a sulfonate group or H.

Water uptake was measured using a TA Instruments Q5000SA water vapor sorption microbalance at 30°C between relative humidity 20% and 98%. The hydration number (λ) was calculated from:

$$
\lambda = \left( \frac{m_{RH} - m_0}{m_0} \right) \times \left( \frac{1000}{M_{H_2O} \cdot IEC} \right)
$$

where, $m_{RH}$ is the sample mass at a given RH, $m_0$ is the mass of the dry samples, $M_{H_2O}$ is the molar mass of water, 18.02g, and IEC is the ion exchange capacity with units of milliequivalents of ions per gram of polymer.
Conductivity was measured using electrochemical impedance spectroscopy (EIS) with a Solartron 1260A impedance/gain-phase analyzer. The conductivity of the free-standing membranes was obtained using a two-probe, in-plane geometry cell, at frequencies between 1MHz and 100 Hz (scanning from high to low frequencies\textsuperscript{15,16}. Proton conductivity ($\sigma_+$) was calculated using:

$$\sigma_+ = \frac{L}{R A}$$  \hspace{1cm} (6.2)

where L is the length between the electrodes, R is the resistance (real impedance extrapolated to x-axis) and A is the cross sectional area of the membrane available for ionic current. The hydrated membranes were equilibrated at 30°C between relative humidity ranging between 30% and 95% in an Espec SH-241 humidity chamber.

Charge densities were calculated using Materials Studio to run DMol\textsuperscript{3} DFT calculations.\textsuperscript{17,18} Full geometry optimizations were performed using the general gradient approximation (GGA) with a PBE functional set. Electrostatic potential derived atomic charges were obtained by using the B3LYP method with a DNP basis set approximation (GGA) with a PBE functional set.

6.3 Results and Discussion

6.3.1 OD peak fitting and charge density calculations

The OD stretch peaks were deconvoluted in order to better understand the characteristics and populations of the three microenvironments of water in each membrane. Each dataset was fit using the same three-population model described previously, where the peak position and fwhm of bulk water is known to be 2509 cm\textsuperscript{-1} and 170, respectively.\textsuperscript{10,11} The peak position and fwhm of
the intermediate and bound water peaks were held constant for all samples, only the area of the peaks changed. The fits for sPS-360 at both 30% and 100% relative humidity are shown in Figure 6-2. The fits for SES0106 and sPS-V show in Figure A-4 and Figure A-5, respectively. We were able to achieve excellent fits for all three samples at various levels of hydration.

![Figure 6-2](image_url)

**Figure 6-2. OD peak deconvolution of sPS-360 at 30% and 100% relative humidity.**

From the deconvolution, the intermediate and the headgroup-associated peak positions can be compared to better understand the acidity differences of the sulfonate group caused by the backbone chemistry. Table 6-2 gives the peak positions of the intermediate and headgroup-associated peaks for the three sulfonated polymers. The intermediate water peak position of sPS-360 is blueshifted by 10 cm⁻¹ compared to SES0106 and 16 cm⁻¹ compared to sPS-V. A high frequency shift indicates the water is experiencing a weaker hydrogen bonding environment.¹⁹ In the past we have compared the headgroup-associated peak position to better understand the effect the sidechain chemistry had on acidity of the sulfonate group. However, because the sulfonate group is directly attached to the backbone and each backbone contains two or more electron-rich sulfone moieties, we hypothesize that the head-group associated water peak is convoluted by water that is interacting with the sulfone groups on the backbone. The calculated atomic charges indicate the average charge of the oxygen of a sulfonate group in sPS-360 is -0.545, while the
average charge of the oxygen of a sulfone moiety is -0.4505. The lower negative charge of the sulfone oxygen results in a weaker hydrogen bond to water, yielding a peak that is blueshifted. We hypothesize that these excess sulfone groups are convoluting the head-group associated peak position and instead used the intermediate water peak position to characterize the sulfonate acidity. It has been shown that the hydrogen bonding of water in an intermediate state (not directly bound to the sulfonate, but not in the bulk-like liquid state) is directly affected by the charge density of the hydrogen bonding moiety.\textsuperscript{14}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bound peak position (cm(^{-1}))</th>
<th>Intermediate peak position (cm(^{-1}))</th>
<th>Average charge* on -SO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-360</td>
<td>2636</td>
<td>2568</td>
<td>-1.636</td>
</tr>
<tr>
<td>SES0106</td>
<td>2632</td>
<td>2558</td>
<td>-1.703</td>
</tr>
<tr>
<td>sPS-V</td>
<td>2636</td>
<td>2552</td>
<td>-1.702</td>
</tr>
</tbody>
</table>

\* Value represents the average total charge of the oxygen atoms of each sulfonate moiety.
\* One sulfone per repeat unit.

Based on the intermediate water peak position, sPS-360 contains sulfonate groups with the lowest charge density, while SES0106 and sPS-V are more similar. The trend of charge density is confirmed by computing the partial charge of the sulfonate group using DMol\(^3\) DFT calculations and the structures shown in Figure 6-3.\textsuperscript{17,18} The average charge of the sulfonate group for each polymer is listed in Table 6-2 and scales with the intermediate water peak position. Moieties with lower charge densities will behave as weak conjugate bases and form a weaker hydrogen bond to water, resulting in blueshifted peak.\textsuperscript{10,11,19,20} The charge density of the sulfonate on sPS-360 is lower because of the additional electron withdrawing sulfone groups on the
backbone. Figure 6-3 shows that in sPS-360, each aromatic ring that contains a sulfonate group is flanked by two additional sulfone moieties, connecting it to the next aromatic ring. The electron withdrawing properties of the sulfone group provides additional stability for the negative charge of the sulfonate groups, allowing them to behave as weak conjugate based. Similar effects have been seen with the addition of fluorine atoms to an aromatic ring containing a tethered sulfonate; additional fluorination lowered the proton affinity (charge density) of the sulfonate group significantly.\(^{21}\)

![Chemical structures](image)

**Figure 6-3.** Schematic and 3-D model representations of segments used for DFT calculations.

SES0106 and sPS-V have the same backbone chemistry, but the placement of the sulfonate group is different depending the sulfonation method.\(^{2}\) SES0106 was synthesized using a copolymerization method and contains two sulfonate moieties attached to the two deactivated rings. Whereas sPS-V was sulfonated via a post polymerization method and contains one or two sulfonates on the activated rings. Copolymerization is the preferred method because it yields materials that are more hydrolytically stable because the sulfonate groups are attached at the meta position of the deactivating sulfone group.\(^{22}\) It was also hypothesized that the placement of the
sulfonate groups on the deactivated rings increased their acidity; however, our charge density calculations in Table 6-2 suggest that the acidity is unchanged based on the sulfonate position, as long as both activated rings are sulfonated, which is not always the case. Postsulfonation methods are not easily controlled and results in one sulfonic acid group that is randomly bonded at the ortho position of the electron-donating aromatic ether. The charge density of sPS-V was calculated when only one of the rings was sulfonated and was found to increase to -1.737 from -1.702 when both rings are functionalized. FTIR results (peak position of intermediate water) indicate that the sulfonate groups in SES0106 are slight more acidic than sPS-V and the DFT calculations support this result when both possible charge densities of sPS-V are considered. The additional sulfone group between the two deactivated was previously thought to stabilize the excess charge of the sulfonate groups, like it does for sPS-360. However, our experimental and theoretical results show that having both rings sulfonated, activated or deceived, provides similar stability to the excess negative charge from the sulfonate moiety. We can also hypothesize that the stability that is gained by the additional sulfone group is equivalent to the stability achieved by resonance between two conjugated sulfonated aromatic rings.

6.3.2 Conductivity and water uptake

The difference in charge density of the sulfonate groups in these three polymer systems also affects the membranes conductivity. The measured conductivity for sPS-V and SES0106 are shown in Figure 6-4, along with the literature reported value for sPS-260.¹ sPS-V and SES0106 have similar conductivities values at low water content, but as SES0106 absorbed more water, the conductivity increased. As expected based on the charge density calculations, the literature value for the sPS-360 polymer is greater than both SES0106 and sPS-V. The differences in conductivity between SES0106 and sPS-V can be attributed to the slight increased acidity of the sulfonate
moieties of the SES0106 membrane versus the sPS-V as shown by FTIR and DFT calculations previously.

![Graph showing conductivity versus hydration number](image)

Figure 6-4. Measured conductivity values versus hydration number of SES0106 (×) and sPS-V (●) and literature reported value for sPS-360 (▲).

The water uptake and hydration number as a function of relative humidity for each polymer are shown in Figure 6-5. Water uptake properties have a strong influence on the proton conductivity. The trend of water uptake and hydration number increasing with greater acidity has been seen many times when comparing sulfonated aromatic based membranes to membranes containing a fluorinated sulfonate groups, like that found in NAFION®. A more acidic sulfonate group has been shown to be more ionic and therefore more readily hydrated. The IEC of the three samples is similar and therefore is not a factor in the water uptake and hydration number measurements.
6.3.3 Water population analysis

To better understand how the water content absorbed into the polymer membrane affects the conductivity, the OD peak can be deconvoluted and the populations of water in various microenvironments can be calculated.\textsuperscript{10,11} Figure 6-6 shows the amount of water in the bulk-like state versus the total amount of water in each polymer system. The amount of bulk-like water in the system correlates the conductivity of the system. For example, sPS-360 contains the highest amount of bulk-like water compared to the other two systems, while also having higher conductivity. Previous work has shown a similar relationship; where polymer systems that have water self-diffusion coefficient that are closer to that of bulk-like water have higher conductivity.\textsuperscript{23,27,28} The reason for this correlation between water diffusion and ion conductivity is because the dynamics of water molecules that are interacting with the polymer membrane are slowed, however the degree to which they are slowed depends on the acidity of the sulfonate headgroup. In cases where the water self-diffusion coefficient is higher, like in NAFION\textsuperscript{®}, the sulfonate acidity is also greatly increased. Here, we can attribute the higher bulk-like water content in sPS-360 to the increased acidity of the sulfonate group due to the unique backbone
chemistry, which was supported by DFT charge density calculations. The differences in acidity between SES0106 and sPS-V were very subtle; however the effect of having both rings functionalized has drastic effects on the conductivity and the water binding populations.

![Figure 6-6](image)

Figure 6-6. Calculated λ value of bulk-like water versus the total amount of water (λ_{total}) in each polymer system, SES0106 (×) and sPS-V (●) and sPS360 (▲).

6.4 Conclusions

Our findings show that the acidity of a sulfonate moiety that is directly tethered to an aromatic polymer backbone can be altered by changing the backbone chemistry. Both FTIR and charge density calculations show that by placing a sulfone group between the two sulfonated aromatics rings, the acidity of the sulfonate group will increase due to the additional electron withdrawing capabilities of the sulfone group. It was hypothesized that the additional stability from the sulfone groups is equal to having both aromatic sulfonate simultaneously, as is the case for both sPS-360 and SES0106. The charge density calculations suggested that when only one
ring is sulfonated, the total negative charge of the sulfonate groups is increased, but is reduced when both rings are sulfonated. Transport and water-binding properties also correlated to the acidity findings. Because sPS-V was synthesized using a postsulfonation method, both rings are not always functionalized and therefore the acidity is decreased and the conductivity and water-binding measurements suffered. SES0106 yielded much better conductivity than sPS-V, even though they have the same backbone chemistry, but was synthesized using a copolymerization method. sPS-360 contained the sulfonate group with the lowest charge density due to the addition of multiple sulfone groups. The increased acidity led to a polymer with a higher conductivity and higher amount of bulk-like water. Therefore, we can conclude that the addition of sulfone groups between sulfonated aromatic rings will result in a material with increased sulfonate acidity and conductivity.
6.5 References


Chapter 7

FTIR analysis of poly(amide) reverse osmosis membranes

7.1 Introduction

Fully aromatic polyamide is a common polymer found in the active layer of many commercial thin film composite RO membranes for water desalination applications. Thin film composite membranes consist of three discrete layers. A thick woven polyester layer provides mechanical strength and support, an asymmetric poly(sulfone) film sits atop the polyester adding additional support and acts as the surface for formation of the polyamide layer. Typically, the polyamide layer is formed via interfacial polymerization between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) monomers; the resulting layer is dense and about 100 nm thick. The two monomers can react forming linear chains. The two remaining unreacted acyl chlorides of the TMC monomer can either undergo hydrolysis and form carboxylic acid or can react with addition MPD monomers and form a highly cross-linked structure. Studies have shown that about 4-9% of the total acyl chloride content in the active layer have been converted to carboxylic acid moieties.\textsuperscript{1} The dense, highly cross-linked polyamide layer is highly selective while also having high flux, making it attractive for RO membranes. Membrane performance is controlled by the interaction of water with the polyamide active layer, therefore it is important to deeply understand the relationship between the active layer chemistry and the resulting transport properties.\textsuperscript{2,3}

The polyamide layer is difficult to isolate, causing limited characterization of the active layer which is crucial to the understanding of the structure-property relations and how the
physicochemical properties affect transport properties. The surface of the active layer has been well characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM) and tunnel electron microscopy (TEM) to better understand the cross sectional structure and the surface roughness. The inner region of only a few RO membranes have been studied using positron annihilation lifetime spectroscopy (PALS) and X-ray photoelectron spectroscopy (XPS) to characterize the pore size distribution and elemental composition. PALS has shown two types of pores present in the active layer, a smaller network pore formed within a chain and a large aggregate pore formed between polymers chains. Rutherford back scattering (RBS) provides information about the volume-averaged properties of the inner membrane elemental composition of both charged and uncharged species. When compared to XPS elemental results of the same RO membranes, there were major differences, indicating the bulk properties differ from the surface properties. RBS is a powerful technique because it can be used quantify the ratio of carboxylic acid groups (R-COOH) to ionized groups (R-COO⁻) by neutralizing the charged species with Ag⁺ ions and analyzing the resulting RBS spectra for the Ag⁺. This technique has provided vital information about the functional group concentrations in RO membranes and has been correlated to the bimodal pore distribution discussed above.

Studies of commercial active layer when hydrated are limited. Little research has analyzed how the functional groups in the active layer interact with the adsorbed molecules and how these water-polymer interactions can be used to develop structure-property relationships and correlate them to transport properties. The hydrogen bonding of water can be examined by linear FTIR spectroscopy, using dilute HOD in H₂O as an easily interpretable probe of the water behavior and hydrogen bonding environment in the material. The frequency of the OD stretch is indicative of the strength of the hydrogen bond between water absorbed into the sample and its surroundings. For example, when HOD is in the solid state, exhibiting strong hydrogen bonds, the OD stretch is centered around 2440 cm⁻¹. Whereas in the liquid water state, where the hydrogen
bonding environment is not as strong, the OD stretch frequency is blueshifted to 2509 cm\(^{-1}\).\(^{14}\) Waters associated with acidic or other functional groups have weaker hydrogen bonds than water-water hydrogen bonds and the OD shift is located at frequencies higher than 2509 cm\(^{-1}\), depending on the hydration number and chemical structure of the material.\(^{16-18}\) We attempted to use the OD peak to analyze how the hydrogen bonding network is changing in the polymer as a function of hydration or relative humidity and how water is associating with the different functional groups on the polymer. However, the N-H moiety of the amide bond readily exchanges to N-D why exposed to HOD. The details of this phenomenon are discussed in depth.

The aim of this study was to analyze commercially produced RO membranes provided by the Dow Chemical Company. We were interested in understanding how water uptake values, transport measurements and water-polymer interaction measurements relate to one another. Samples were exposed to humid air as FTIR spectra were collected. Water uptake values were measured using RH-TGA. Transport measurements include flux and salt passage and were measured by Dow. To measure the water-polymer interaction, the FTIR derivative peak obtained by referencing the fully hydrated sample to the dry sample. The magnitude of the peak yields information about how much water is interacting with that specific polymer peak.

7.2 Materials and Experimental Methods

7.2.1 Materials and FTIR sample prep

Samples were provided by the Dow Chemical Company and were delaminated by removing the nonwoven fabric support such that only the poly(sulfone) and polyamide layer remained. The remaining two-layered membrane was placed in a funnel lined with filter paper and washed with sufficient dimethylformamide (DMF) to remove the poly(sulfone) layer. To
remove the DMF, the remaining polyamide layer was washed with water and then methanol. The polyamide fibers were placed onto a calcium fluoride crystal and allowed to dry at 50 °C under vacuum for 20 h. Samples were then placed in an FTIR transmission flow cell (Model 64100-F, New Era Enterprises, Vineland, NJ). Humid air containing 5 mol % D₂O was flowed (20 std. cm³ s⁻¹) through the cell while spectra were recorded using a Bruker (Billerica, MA) VERTEX 70 spectrometer with a nitrogen-cooled mercury-cadmium-telluride (MCT) detector. The relative humidity of the mixed stream was measured using an RH probe (Omega HX15-W, Omega Engineering, Inc., Stamford, CT) before being introduced to the measurement cell at the same temperature as the system. All flux measurements were conducted on behalf of the Dow Chemical Company.

![Repeat units of highly crosslinked polyamide. Both a linear and crosslinked structures are shown for clarity.](image)

**Figure 7-1** Repeat units of highly crosslinked polyamide. Both a linear and crosslinked structures are shown for clarity.

### 7.2.3 Water uptake

Water uptake (WU) was measured using a TA instruments Q5000SA water vapor sorption microbalance at 30 °C between relative humidity of 30% and 95%. Samples were allowed to equilibrate at each RH for 20 min. Water uptake percentages were measured using the following equation,
\[ w_u \, \% = \left( \frac{m_{RH} - m_0}{m_0} \right) \]

where, \( m_{RH} \) is the sample mass at a given RH, \( m_0 \) is the mass of the dry sample.

7.3 Results and Discussion

7.3.1 OD and ND peak analysis of aromatic polyamide

The delaminated polyamide layers for two commercial available high and low flux RO membranes were hydrated at various relative humidity with a 5 mol % HOD. The resulting OD frequency peak is shown in Figure 7-2. The low flux sample has a peak centered at 2507 cm\(^{-1}\) which is very close to the frequency of bulk-like water (2509 cm\(^{-1}\)) and the peak position does not shift as the hydration is increased. The lack of a shift with increasing hydration indicates that the hydrogen bonding network does not depend on the hydration level in the polymer.\(^{19}\) In the case of the high flux sample, the OD peak position is blueshifted from the peak position of bulk-like water at low hydrations. As the polymer uptakes more water, the OD peak redshifts back to 2511 cm\(^{-1}\). Previous studies of the OD peak in ion-containing membranes attribute the redshift with increasing hydration to an increase in the population of bulk-like water.\(^{12,19}\) The initial blueshift of the OD peak is caused by the water molecules experiencing a weaker hydrogen bonding environment than that of a water-water hydrogen bond, for example, the interaction of a water molecule with an amide moiety. Therefore, the hydrogen bonding network of water adsorbed into the high flux sample changes as a function of hydration. As the first few water molecules are absorbed, they hydrogen bond with the amide moieties, but as the hydration increases and the amide moieties are hydrated, the water molecules begin to interacting with one another, increasing the amount of bulk-like water in the system.
Figure 7-2. OD peak frequency of a low flux membrane (a) and high flux membrane (b) as the relative humidity is increased from 30% to 100%. Peak position does not shift in the low flux membrane, but does shift in the high flux membrane.

The low frequency shoulder at 2400 cm$^{-1}$ is caused by an H$\rightarrow$D exchange of the amide NH moiety. This exchange results in two bands near 2480 and 2420 cm$^{-1}$, which are convoluted in this case because the sample contains only 5% deuterated and the bands are hidden under the strong OD vibrational mode. These bands arise from Fermi resonance between the ND stretch fundamental and a combination between the deuto-equivalent of the amide II and amide III modes.\textsuperscript{20–22} The ND modes are very sensitive to changes in the hydrogen bonding strength and geometry and have been used extensively to study the differences in water adsorption into the crystallinity and amorphous regions in various polyamides, like Nylon-6.\textsuperscript{22,23} Aliphatic polyamides undergo the exchange when exposed to 100% D$_2$O vapor at room temperature and can be exchanged back to the proton form depending on whether the structure crystalized upon adsorption of D$_2$O vapors.\textsuperscript{23} Amide protons readily exchange in the presence of D$_2$O because the N-H proton is labile, a phenomenon that has been used extensively to study protein tertiary structure.\textsuperscript{24–26}

The FTIR spectrum of a dried commercial polyamide reverse osmosis membrane before and after it has been exposed to 100% D$_2$O vapor is shown in Figure 7-3. The peak at 3305 cm$^{-1}$
corresponds to the N-H stretching mode, indicating the exchange does not go to completion. The two ND combination bands appear at 2391 cm\(^{-1}\) and 2452 cm\(^{-1}\) which is redshifted from the peaks generated from aliphatic polyamide samples. We believe this is due to differences in the amide II and III modes in aliphatic and aromatic polyamides.\(^{23}\) These peaks are also not as sharp as those characterizing nylon, which can be highly crystalline. The ratio of the two peaks has been used to correlate bond lengths determined by scattering data to hydrogen bond strength.\(^{22}\) The ND combination bands convolute the OD region the spectrum and make peak fitting analysis difficult; however, the fingerprint region can be used to better understand water-polymer interactions in polyamide membranes.

![FTIR spectrum of dry polyamide membrane before and after exposure to 100% RH D\(_2\)O.](image)

**Figure 7-3.** FTIR spectrum of dry polyamide membrane before and after exposure to 100% RH D\(_2\)O.

### 7.3.2 Fingerprint analysis of aromatic polyamides

The fingerprint region of the FTIR spectra can be used to better understand how changes within the polymer structure are affecting the water-binding and transport properties. The peak
assignments for aromatic polyamides are well documented in the literature\textsuperscript{27,28} and are given in Table 7-1. The fingerprint region consists of signatures from the aromatic rings and combinations bands from the various amide moieties. The peak at 1725 cm\textsuperscript{-1} is attributed purely to the vibrations of a carboxylic acid carbonyl and is not present in all polyamide membranes. This peak will appear when unreacted trimesoyl chloride monomer undergoes nucleophilic addition in the presence of water forming a carboxylic acid, yielding a membrane with appreciable acidic character. Increased carboxylic acid content is also characteristic of membranes that contain more linear chains and less crosslinked chains, depicted in Figure 7-1.

<table>
<thead>
<tr>
<th>Wavenumber (cm\textsuperscript{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1725</td>
<td>C=O stretching of carboxylic acid</td>
</tr>
<tr>
<td>1661</td>
<td>Amide I, C=O stretching</td>
</tr>
<tr>
<td>1608</td>
<td>Aromatic ring breathing</td>
</tr>
<tr>
<td>1537-1415</td>
<td>Amide II, N-H bend and C-N stretching</td>
</tr>
</tbody>
</table>

The fingerprint spectra for five different aromatic polyamide membranes are shown in Figure 7-4a. The spectra were normalized to the benzene breathing mode at 1608 cm\textsuperscript{-1} to account for differences in thickness. The amide II peak was not chosen because the intensity of the peak depends on both the thickness and the crosslinking density of the samples. As the sample number increases, the shoulder at 1725 cm\textsuperscript{-1} increases in intensity indicating the presence of more free carboxylic acids. The peak at 1661 cm\textsuperscript{-1}, which corresponds to amide I region (composed mostly of the amide carbonyl vibration), also broadens as the acid content increases. Broader peaks are
indicative of a more heterogeneous environment, therefore as the carboxylic acid content increases; the vibrational frequency of the amide carbonyl (which could be attached to same benzene ring) becomes more varied. Figure 7-4b shows the relationship between sample number and the absorbance of the peak at 1725 cm$^{-1}$. The sample number correlates nicely with the increasing acid content in the membrane.

![Figure 7-4](image)

Figure 7-4. The fingerprint region of five different polyamide membranes (a). A plot of the absorbance of the peak at 17225 cm$^{-1}$ versus the sample number (b). As the samples number increase, the carboxylic acid content also increases.

Amides contain two functional groups that can hydrogen bond with water molecules. The carbonyl of the amide is electron dense and therefore will act as a hydrogen bond acceptor. The amide N-H group is deprived of electron density and therefore behaves as a proton donor. When water molecules interact with the amide moieties, the vibrational frequency corresponding to those functional groups will shift compared to the dry spectra. The change in peak frequency is usually a few wavenumbers (2-4 cm$^{-1}$), shown in Figure 7-5a, making it difficult to quantify. The two peaks that shift the most are the peaks at 1661 cm$^{-1}$ and 1536 cm$^{-1}$, corresponding to the amide I (mostly carbonyl) and amide II (combination of C-N stretching and N-H bending).

Because the frequency shifts are so small, the difference peak is used to analyze and quantify how
the center of mass of the peak changes when the sample is hydrated. The magnitude of the difference peak provides a direct and clear demonstration of the population change in different vibration energy states. A difference spectrum is obtained by subtracting (referencing) the dry state spectra from the spectrum of the hydrated polymer, therefore only the peaks that change between the two states will have a nonzero signature. The difference maximum corresponds to the increasing interaction and the minimum to the decreasing noninteracting amide groups, thus the magnitude of the difference peak is an indicator of the increased interaction between water and the amide groups upon hydration. Figure 7-5b gives an example of a difference spectrum resulting from subtracting a spectrum of a polyamide in the dry state (0 % RH) from a spectrum of the hydrated state (100 % RH). The difference of the peak at 1661 cm\(^{-1}\) was analyzed to better understand how the carbonyl moieties were interacting with water molecules. The magnitude of the difference peak (maximum to minimum) was obtained by normalizing the difference magnitude by the absorbance intensity of the OD stretch peak to account for water uptake differences in each sample.

Figure 7-5. FTIR spectra of aromatic polyamide when dry (black) and when hydrated (blue) and 100% relative humidity. When the sample is hydrated the peaks corresponding the amide I and amide II vibrational modes at 1661 cm\(^{-1}\) and 1537 cm\(^{-1}\), respectively.
The normalized difference peak magnitude versus membrane water uptake is displayed in Figure 7-6. Samples 5 and 7 display small difference magnitudes, which indicates a smaller amount of the carbonyl moieties are hydrogen bonding to water molecules. These two samples also display a high water uptake percentage. The combination of low water-polymer interactions and high water uptake suggests the presence of large water filled cavities or pores in the polymer matrix. Samples 3 and 4 display the opposite trend, with lower water uptake and more water-polymer interactions, indicating the presence of small water filled pores. These small pores will have a greater water/carbonyl ratio therefore increasing the amount of water-polymer hydrogen bonds. Positron annihilation lifetime spectroscopy (PALS) has been used to measure the void space in commercial RO membranes and researchers have found two types of pores in the radius ranges of 1.0 to 3.0 Å and 3.0 to 6.0 Å.\textsuperscript{12} The findings are further supported by statistical mechanics calculations pertaining to the interstitial-void model.\textsuperscript{29} A schematic representation of the morphology RO membranes is shown in Figure 7-7. Where the black spheres indicate water interacting with the polymer (light grey) and the dark grey interiors indicate free or bulk-like water. According to the difference analysis, samples 5 and 7 would have greater populations of the large pores, while samples 3 and 4 would have a great number of the smaller pores.
Figure 7-6. Normalized difference peak magnitude versus water uptake (%) for commercial polyamide membranes. A large difference magnitude and low water uptake corresponds to the abundance of small pores, while a smaller difference magnitude and higher water uptake correspond to the presence of larger pores.

Figure 7-7. Schematic representation of the various pore sizes found in commercial RO membranes. The light grey background presents the polymer matrix, the black spheres represent water that is
interacting with the polymer backbone and the grey spheres are representative of water that is interacting with its self or bulk-like water.

Because these samples are commercial membranes, the transport properties could be measured and plotted as a function of the normalized magnitude of the difference peak, found in Figure 7-8. Sample 7 has the higher flux and also has the smallest difference peak magnitude, suggesting that having larger water filled cavities leads to an increase in the flux. Samples 3 and 4 have a lower flux, but a large difference peak magnitude, this result suggest that having a large population of small pores will cause the membrane to have an overall lower flux. The size of a water molecules is about 2.5-3.0 Å, which could be too large to fit through some of the small pores, resulting in reduced flux.

![Figure 7-8. RO flux performance versus normalized magnitude difference peak of polyamide membranes. Samples with larger difference magnitude have low flux, while samples with smaller difference magnitude have a higher flux.](Image)

The abundance of the larger pores and increased flux is caused by the increase in the carboxylic acid content that was determined by FTIR in Figure 7-4b. The additional carboxylic
acid groups lead to larger pores because the membrane is not highly crosslinked and instead a more linear structure is formed. The linear structure gives way to larger pores and therefore a higher flux. The higher carboxylic acid content also leads to the membrane having greater hydrophobicity, which has also been shown to lead to a higher flux.\textsuperscript{33,34}

7.4 Conclusions

Two sets of commercial RO membranes were provided by The Dow Chemical Company and the polyamide active layer was studied using linear FTIR as a function of hydration in order to determine how structure-property relationship correlated to transport properties of the membrane. When the polyamide active layer was hydrated with HOD, it was discovered that aromatic polyamide bond will readily undergo N-D exchange, a phenomena that has been extensively studied in protein and various other aliphatic polyamides but never in an aromatic polyamide. The N-D exchange causes the deconvolution of the OD peak to be extremely difficult, but does not affect the fingerprint region of the FTIR spectra. The fingerprint region revealed a shoulder at 1725 cm\textsuperscript{-1} corresponding to the presence of carboxylic acids in samples 3-7 that increased in intensity with increasing sample number. The difference peak was calculated by subtracting a wet spectrum from a dry state spectrum, elucidating which functional groups were interacting with water the strongest. The amide II (mostly C=O stretching) peak at 1661 cm\textsuperscript{-1} and the amide II peak at 1537 cm\textsuperscript{-1} gave constantly large difference peaks, indicating those moieties were hydrogen bonding with water. Samples 3 and 4 had the largest difference magnitude while also having the lowest water uptake, which indicated the presence of small water filled pores. Samples 5 and 7 had the smallest difference magnitude and the highest water uptake, which indicated the presence of large water filled pores. Pore size distribution correlated to the carboxylic acid content determined by FTIR, a higher amount of carboxylic acid present in the
membranes yielded a larger average pore size. These structure-property relationships correlated with the measured flux, where samples with higher carboxylic acid content and larger pore size also had the highest flux. Samples with lower carboxylic acid content and smaller pore sizes had a lower flux comparatively.
7.5 References


Chapter 8
Summary of Findings and Directions for Future Research

8.1 Conclusions

8.1.1 Water Hydrogen Bonding in Sulfonated Polymers

The OD stretch of dilute HOD in H₂O in a series of sulfonated syndiotactic poly(styrene) and poly(sulfone) polymer membranes was studied using FTIR spectroscopy. This spectroscopic technique was used to measure how the acidity of the sulfonate group and backbone polarity influenced the water-polymer interactions. The results yielded information about the ratio amount of absorbed water participating in hydrogen bonds with the polymer-tethered alkyl, aromatic, or perfluoroalkyl sulfonate groups or with other polymer-bound functional groups versus the amount of water hydrogen bonded with other water molecules in the hydrophilic domains of the membranes. This information was extracted by employing a three-state model that designated one population of water with a peak stretching frequency at 2509 cm⁻¹ and FWHM of 170, the same as bulk water, and another population whose peak stretching frequency varied with the strength of the water-polymer interaction. Analyzing the OD stretch also gave insight to the strength of the hydrogen bonds formed between water and the sulfonate groups. The electron withdrawing capabilities of the fluoralkyl sidechain causes the superacid to behave as a weak conjugate base, resulting in a weaker hydrogen bond to water than an aryl or alkyl sulfonate. The superacid displayed an OD stretch peak position that is was blueshifted by 39 cm⁻¹ compared to the aryl and alkyl OD stretching frequencies that were located at 2547 cm⁻¹.
The polarity of the backbone also affected the OD region of the FTIR spectrum. The poly(styrene) based samples displayed a redshift of the OD stretch frequency from 2566 cm\(^{-1}\) to 2553 cm\(^{-1}\) as hydration increased, however the poly(sulfone) samples displayed no such shift with increasing hydration and the peak OD stretch frequency remained at 2553 cm\(^{-1}\) for all hydration levels. This result is attributed to the more polar backbones experiencing no change in interfacial hydrogen-bonding with increased hydration due to the presence of additional hydrogen bond acceptor groups on the polymer backbone. The symmetric stretch of the sulfonate anion was observed to vary depending on the chemical structure of the tether with the perfluoroalkyl tether causing the sulfur oxygen bond to be shorter and thus blueshifted compared to the other acidic moieties.

**8.1.2 Spectroscopic Characterization of Sulfonate Charge Density in Ion-Containing Polymers**

We continued our investigation of how acidity of the sulfonate group affects the hydrogen bonding network of water in a polymer membrane by studying polymers with subtle differences in the perfluorosulfonate sidechain. In addition to the vibrational spectroscopy measurements using HOD as a probe, the partial charges of the sulfonate groups were computed using DMol3 DFT calculations. The calculations and the experimentally determined peak position of the OD stretch correlated to give us a ranking of acidity for the various sidechains. The findings showed that having a thioether linkage instead of an ether linkage (typical linkage for perfluorosulfonates) increased the acidity of the sulfonate group due to the capability of sulfur to expand its octet and more readily accept additional electron density. Through our DFT geometry optimization, that the thioether linkage prefers a kinked configuration while the ether linkage gives a more linear sidechain structure. This structural artifact correlated to my
experimental findings that more water interacts with the sulfonate group containing the ether linkage than the thioether linkage due to the sulfonate group being more easily accessible, even though the thioether sidechain is more acidic.

8.1.3 Backbone chemistry effects on sulfonate acidity

The effect of the placement of the sulfonate moiety on three different polymer backbones was studying using both FTIR and first principle DFT calculations. Increasing the number of sulfone groups in the backbone chemistry will decrease the charge density of the sulfonate moiety, due to the additional electron withdrawing properties of the sulfone groups. Having a lower charge density allows the sulfonate to behave as a strong acid and therefore increased conductivity at low relative humidity. Additionally, using a post-sulfonation method that does not fully functionalize the two aromatic rings of the backbone led to a decrease in measured charge density and the conductivity and water uptake values suffered. To better understand how the acidity affects the populations of water in the hydrated membranes, the OD peak was deconvoluted. The sPS-360 sample that has the most sulfone groups in the backbone and therefore the lowest charge density (highest conductivity) showed the highest percentage of bulk-like water. Having a high population of bulk water allows the protons to be transported faster because the dynamics of the water are not slowed.

8.1.4 Vibrational analysis of polyamide membranes for water treatment membranes

In this project we were interested in understanding how the water uptake values, transport measurements and water-polymer interaction measures relate to one another. Transport measurements include flux measurements that were performed by the Dow Chemical Company.
Initial measurements using an HOD probe revealed a shoulder at ~2410 cm\(^{-1}\) in the OD region, which is a result of the deuterium atoms in HOD exchanging with the NH of the amide to form ND. To measure the water-polymer interacting, the magnitude of the difference peak at 1661 cm\(^{-1}\) yielded information about how much water is interacting with the carbonyl groups on the backbone. There was a clear trend that the more water the polymer absorbs, the less water is interacting with the functional groups on the backbone. This result is an indication of the formation of hydration pockets in the higher water uptake materials and points to heterogeneity between backbone regions and hydrated regions. This type of behavior is indicative of the existence of water filled cavities instead of water hydrating the functional groups. The samples that displayed the largest cavities also had the higher number of free carbonyl groups, as determined by the intensity of the 1725 cm\(^{-1}\) peak. These samples also had higher flux, indicating that a greater number of free carboxylic acid groups will lead to larger pores and higher flux. These findings have increased our understanding of how the water-polymer interactions affect transport properties in the polyamide active layer.

8.2 Future Work

8.2.1 Analyzing the hydrogen bonding network in hydrogels

Binary mixtures of hyperbranched-fluroropolymer (HBFP) and polyethylene glycol (PEG) are used in anti-icing applications that prevent the formation of ice instead of generating a superhydrophobic surface and in antifouling coating.\(^1\)-\(^3\) In both applications, it is critical to understand how the ratio of HBFP:PEG affect the hydrogen bonding network of water in these amphiphilic membranes. DSC experiments of these hydrogels have shown that there are two different states of water in the mixture; water with a \(T_m\) of -25°C is water in a bound state and
water with $T_m0{\degree}C$ is bulk-like water. As the ratios of the hydrogels shifted to larger wt % of PEG, the $T_m$ of the bound water increased, which suggests that the water is becoming less-confined and more bulk-like.4

The interaction between water and the binary system was explored further using Fourier transform infrared (FTIR) spectroscopy. The shifts of the water OD stretch absorbance signals for two samples were studied, relative to the absorbance for neat deuterated water; one with relatively high PEG content (2:5), one with relatively low content (5:2). The relative humidity was adjusted by flowing a 5 mol % D$_2$O solution through the cell. The samples experienced a blueshift in comparison to bulk water (2509 cm$^{-1}$) as a function of hydration. The hypothesis is that this shift is due to water molecules being confined by the polymer matrix, e.g. the hydrophilic PEG domains are sequestering water as previously observed.5,6 The OD peak was deconvoluted to extract the populations of water in the two different microenvironments, bulk and bound, using a method that has discussed previously (Figure 8-1). The percentages correspond with the DSC measures, as the amount of PEG in the sample increased, so does the amount of bulk water. The 5:2 sample contains 12.3% bulk water while the 2:5 samples contains 30.5%. Our preliminary work on these hydrogels can be extended into similar systems to better understand how the populations of the water is changing and what affect the hydrogen bonding network has on the preformation properties (such as fouling or anti-icing) of the membranes. Also a more robust peak fitting routine should be development to better characterize the two types of water. PEG readily uptakes water and therefore obtaining a spectra of hydrated pure PEG would be beneficial for accurate peak fitting.
Figure 8-1. Deconvolution of OD peak stretch vibration of 5:2 HBFP(III)-PEG (A) and 2:5 HBFP(III)-PEG (B) used to extract percentages of water in either the free or bound state.

8.2.2 Azides as an alternate probe for HOD: Cavity Size

Using HOD as probe for studying the hydrogen bonding network is advantageous, however, it has been proposed that the OD vibration is also sensitive to confinement. When reverse micelles of Igepal (a surfactant with an alcohol headgroup tethered by a polyether chain to a nonpolar chain tail) were studying using HOD as a probe, the OD peak positions was slightly blueshifted compared to bulk-like water. The OD vibrational lifetime of the OD stretch was also similar behavior to the AOT reverse micelles and has a biexpodential fit, indicating a two-state water environment.\(^7\) The polyamide and the HBFP:PEG samples in this thesis have also shown and OD peak position that is blueshifted from bulk-like water, likely due to confinement of the water-filled cavities. Measuring the pore sizes in these materials is difficult, but future work using azides (\(\text{N}_3\)) as a probe would measure the cavity size easily.

Azides have been used to probe the hydrated region of reverse micelles. It is an attractive probe because it is small and has a strong and narrow vibrational absorption at \(~2000\ \text{cm}^{-1}\) which is very sensitive to the local environment.\(^8\) The gas phase antisymmetric stretching band appears at 1986.5 cm\(^{-1}\) while the hydrated azide band appears at 2048 cm\(^{-1}\). The azide anion is sensitive to
the hydrogen bonding environment, when exposed to various volume fractions of a H$_2$O-DMSO mixture, the peak position shifted from 2048 cm$^{-1}$, in the pure water environment, to ~2000 cm$^{-1}$ in the pure DMSO environment.\(^9\) Therefore, azides can be used to probe changes in the hydrogen bonding network of water in reverse micelles as an alternative to HOD. Three types of surfactants, anionic, cationic and neutral, were used to create reverse micelles that were studied using an azide probe. AOT has a sulfonate headgroup and was used to create the anionic micelle, cetyltrimethylammonium bromide (CTAB) has a quaternary ammonium headgroup and was used in the cationic micelle, and Igepal was used to create the neutral or nonionic micelle. The FTIR peak positions of the azide probe as a function of $\omega$ (water/ headgroup) for all three samples is shown in Figure 8-2. In the AOT micelle, the peak position is blueshifted from bulk-like water (just like in HOD), but in the Igepal and CTAB micelles, the peak is redshifted by ~16 cm$^{-1}$ and 36 cm$^{-1}$ respectively. The shift correlates with the charge of the headgroup, as the charge of the headgroup becomes more positive the frequency is redshifted. In all three cases, as $\omega$ increases the azide peak position shifts closer to the bulk peak position of 2048 cm$^{-1}$ because as the micelle grows larger, there is more bulk-like water present, a similar phenomenon to what was described using HOD in thesis work. However, this work by Zhong, et al could be used to better characterize the size of the water filled cavities in the neutral membranes mentioned previously. Igepal has similar chemistry to the hydrophilic PEG component of the HBFP:PEG samples and there many few surfactants that closely mimic the polyamide chemistry, such as ALE, SLN and LSA.\(^{10}\) The sizes (in angstroms) of many reverse micelles have been studied extensively; simply extrapolating the method to membranes would be extremely beneficial.
Figure 8-2. The antisymmetric stretching mode of the azide ion as a function of \( \omega \) in reverse micelles formed using (a) AOT (b) Igepal and (c) CTAB surfactants. The dashed line is the frequency of an azide in bulk water.\(^8\)

### 8.2.3 Azides as an alternate probe for HOD: Anionic Exchange Membranes

Recently, the development of alkaline membrane fuel cells (AMFC) that operate at high pH, have received extensive research attention because they do not require the use of precious metal catalysts. AMFC rely on anion exchange membranes (AEMs) to efficiently transport anions, such as hydroxide, from the cathode to the anode.\(^{11,12}\) Analogous work to the reverse AOT micelles, which contain a sulfonate head-group, have been carried out on (CTAB) micelles, which contain a quaternary ammonium head-group, to understand how the hydrogen bonding network changes when the head-group has a positive charge. Dokter, et al. used FTIR to study the OH stretch of dilute H\(_2\)O in D\(_2\)O contained inside CTAB micelles of various sizes and found that there was very little shift in peak position from bulk-like water.\(^{13}\) Water in these reverse micelles...
is mostly interacting with the bromide counter ion at the micelle/water interface. The hydrogen bond formed between the bromide and the water molecules has a lower directionality than the hydrogen bond between oxygen of the sulfonate group to water due to bromide having a larger, more polarizable electron cloud. Low directionality allows for higher orientation mobility of the hydrogen bond that is formed which allows for greater mobility of the water molecules while keeping the hydrogen bond intact.\textsuperscript{13} Therefore, water in a cationic micelle has higher orientation mobility than water in an anionic micelle.

To understand how the charge of the ionic species affects the hydrogen-bonding network in a polymer film, the OD stretch of HOD in dilute H\textsubscript{2}O has been analyzed. The method has been described previously and the material was a sample of poly(styrene) with a benzyl quaternary ammonium group tethered via the aromatic rings with chloride as the counter ion. The hydrated polymer displayed a peak that was very similar to that of bulk water, with only a very slight blueshift, shown in Figure 8-3. The slight blueshift is due to the water hydrogen bonding to the chloride anion. Interestingly, it has been shown that the self-diffusion coefficients in AEMs is higher than in the PEM analog, but lower than in NAFION\textsuperscript{®}.\textsuperscript{14} The reason for NAFION\textsuperscript{®}-s high self-diffusion has been discussed previously, but the difference in self-diffusion of AEMs and PEMs hints at water being less bound within AEMs than in PEMs due to the difference in charge of the ionic species. Using an azide anion as probe in AEMs would give greater insight into the water-polymer interactions and how those affect the hydrogen bonding network. As shown in Figure 8-2 and discussed in the previous section, the azide peak frequency is sensitive to the headgroup charge and the decreases as the charge becomes more positive, making azides an excellent probe for AEMs.
Figure 8-3. The normalized OD stretch peak of quaternary ammonium functionalized poly(styrene) at various hydrations levels. Dotted line indicates the signature from bulk HOD.
8.3 References


Appendices
Appendix A: Water Hydrogen Bonding in Sulfonate Polymers

A.1 Supplementary data

Additional plots and tables discussed in Chapter 3.

Figure A-1. The OD stretch deconvolution of PSU-S1 at a λ of 2.0 and 8.5, PS-S2 at a λ of 1.7 and 7.9. Hydration numbers were obtained by introducing the samples to 100% and 30% RH, respectively.
Table A-1. Deconvoluted peak positions and percentages of water in different microenvironments at low hydration and high hydrations

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<th></th>
<th>PSU-S1</th>
<th>PS-S2</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda=2.0$</td>
<td>$\lambda=8.5$</td>
</tr>
<tr>
<td>intermediate peak (cm$^{-1}$)</td>
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<td>fwhm (cm$^{-1}$)</td>
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<tr>
<td>headgroup peak (cm$^{-1}$)</td>
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<td>90</td>
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<td>percent headgroup</td>
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Table A-2. Peak area values for superacid containing polymers as a result of peak deconvolution and transition dipole wavenumber correction. Peak position and FWHM held constant for all conditions per Table 4-1.

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<th>Area headgroup-associated</th>
<th>Area Bulk</th>
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Table A-3. Peak area values for aromatic sulfonate containing polymers as a result of peak deconvolution and transition dipole wavenumber correction. Peak position for each ensemble of water held constant according to Table 4-1 and Table A-2, FWHM of intermediate and headgroup associated water ensembles were allowed to vary with hydration.

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Table A-4. Hydration numbers for superacid containing polymers.

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Table A-5. Hydration numbers for aromatic sulfonate containing polymers.

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*When applicable.
Appendix B: Characterization of Sulfonate Acidity in Ion-Containing Polymers

A.2 Supplementary data

Figure A-2. Fully optimized minimum energy structures of (a) S4 with benzene ring in the plane and (b) S4 with benzene out of the plane showing the trans conformation of the S4 tether.

Figure A-3. Fully optimized minimum energy structures of (a) S1 with benzene ring in the plane and (b) S1 with benzene out of the plane showing the alternative trans conformation of the S1 tether.
Appendix C: Backbone chemistry effects on sulfonate acidity

A.3. Supplementary data

Figure A-4. The OD stretch deconvolution of SES0106 at 30% and 100% RH.

Figure A-5. The OD stretch deconvolution of sPS-V at 30% and 100% RH.
Sarah Black Smedley

Sarah Smedley (née Black), was born and raised in Crozet, Virginia a suburb of Charlottesville, and attended Western Albemarle High School where she graduated with honors in 2007. Sarah continued her education at the Virginia Polytechnic Institute and State University (Virginia Tech), where she pursued Chemistry. She graduated in 2011, receiving a Bachelor of Science in Chemistry with latin honors. She began graduate school in August of 2011 at The Penn State University, and began working under the tutelage of Dr. Michael A. Hickner in October of 2011. After completing her doctorate, Sarah will begin working for the Center for Naval Analyses, located in Arlington, Virginia, as a Research Analyst.