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Salt Solubility Measurements in Partially Disulfonated Poly(arylene ether sulfone) for
Reverse Osmosis Water Purification Applications

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by

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Thesis

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Dedication

This work is dedicated to my fiancée Jasen Falcon, who encouraged me to pursue my dreams.

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May 2010

Abstract

Salt Solubility Measurements in Partially Disulfonated Poly(arylene ether sulfone) for Reverse Osmosis Water Purification Applications

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The University of Texas at Austin, 2010

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Partially disulfonated poly(arylene ether sulfone) (BPS) membranes have shown great promise as robust, chlorine tolerant alternatives to the current polyamide materials as reverse osmosis desalination membranes for water purification. The random copolymers are synthesized by direct polymerization of a disulfonated monomer (3,3'-disulfonato-4,4'-dichlorodiphenyl sulfone (SDCDPS)) and other monomers (4,4'-dichlorodiphenyl sulfone (DCDPS) and 4,4'-biphenol (BP)). The sulfonation of the materials adds necessary hydrophilic character and adjusting the percent sulfonation of the material changes the water and salt uptake of the material. Additionally, sulfonation causes the membranes to be charged, making them ion exchangers in which anions are partially excluded from the membrane, thus affecting the partitioning of salt in the

membrane. The amount of sodium chloride present in the membrane after equilibration with external soaking solutions of varying concentrations of sodium chloride was measured by measuring the amount of individual ions, i.e., the sodium cation and chloride anion, separately. One area in which this work is unique is that it sought to measure the concentrations of the ions independently of one another. The analysis of sodium and chloride has shown the concentration of sodium in the membrane to be significantly greater than that of chloride, where the uptake of chloride is the limiting factor in the uptake of sodium chloride. The trends in the concentrations as well as in the partition coefficients of the ions are consistent with Donnan Exclusion.

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CHAPTER 1: GENERAL INTRODUCTION

In the last century, medical, scientific and engineering breakthroughs have changed the way we live and have significantly increased the lifespan of much of the world. A result of this is a rapid increase in the global population and a demand for lifestyles that use overwhelming amounts of energy. The use of energy goes hand and hand with the use of water, for cooling and as a source of energy itself, as has an increase in the pollution of our fresh water sources. Additionally, there has been an increase in the population of groups of people living in areas with scarce fresh water sources, including the Middle East, Africa, India and parts of the United States. Desalination is a practical answer to the growing water shortage as a way to purify brackish and seawater for human consumption. As membrane technology has advanced in recent decades, reverse osmosis membranes have become one of the dominant technologies in water purification⁴.

The two primary types of membranes currently used for reverse osmosis desalination are cellulose acetate (CA) and polyamide (PA) membranes (the most widely used desalination membranes)¹³, both with various benefits and drawbacks. A great deal of research, including that which is detailed here, aims to develop membranes that are more robust and efficient and able to withstand repeated exposures to chlorine, which is used for sterilization purposes in water purification¹³. A material with very good chlorine resistance that has shown potential as a reverse osmosis membrane is disulfonated poly(arylene ether sulfone)⁴. The work described in this thesis aims to better understand the partitioning of sodium chloride in these materials through measurements of the concentration of sodium and chloride ions in membranes which have been equilibrated in

solutions of varying sodium chloride concentrations. With better understanding of the mechanisms which govern sodium chloride uptake by the membranes will come a better understanding of their potential as reverse osmosis membranes for the desalination of brackish and seawater as potable water.

CHAPTER 2: BACKGROUND

Reverse Osmosis

Some water purification technologies utilize filtration membranes for the purification of seawater or brackish water in which the undesirable solute is removed from the water feed by the exclusion of molecules by size. Examples of these are microfiltration (MF) and ultrafiltration (UF) membranes which operate by pore-flow⁹. Reverse Osmosis (RO) purification, however involves a diffusive mechanism where separation is dependent on solute concentration, pressure and water flux. Reverse osmosis for water purification is the reverse of the normal osmosis process, which is the movement of solvent from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied. It involves applying a pressure to a salt solution in excess of its osmotic pressure to drive water through the membrane preferentially over the solute, salt⁶. Osmotic pressure can be described by the van't Hoff equation⁸

$$\pi \cong C_s RT \quad (1)$$

for sufficiently dilute solutions where π is the osmotic pressure, C_s is the molar concentration of the solute (for our purposes, sodium chloride), R is the gas constant and T is the temperature in Kelvin.

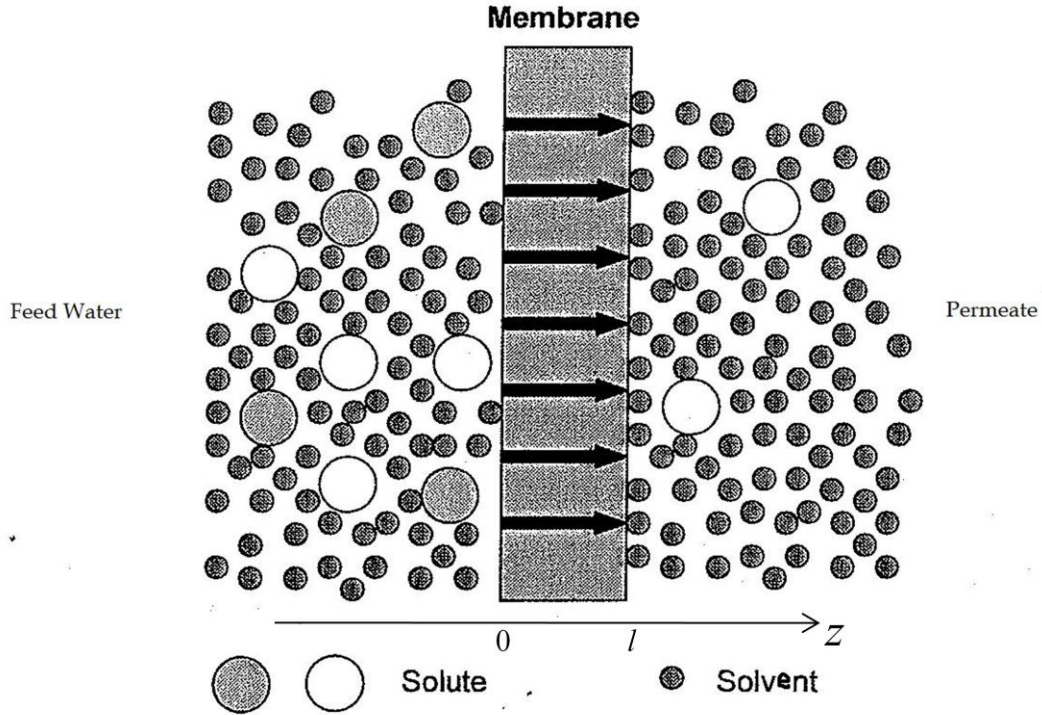


Figure 1. Reverse Osmosis in a solution-diffusion membrane.

The flux of water and of salt in the reverse osmosis process can be described by the following equations²²

$$\text{Water Flux} = \frac{D_{wm} C_w^m V_w}{IRT} [\Delta p - \Delta \pi] \quad (2)$$

$$\text{Salt Flux} = \frac{D_{sm} \Delta C_s^m}{l} \quad (3)$$

where flux is the amount that flows through a unit area per unit time, D_{wm} is the diffusion coefficient for water in the membrane, C_w^m is the concentration of water in the membrane, V_w is the partial molar volume of water, Δp is the hydraulic pressure differential across the membrane, $\Delta \pi$ is the osmotic pressure differential across the

membrane, D_{sm} is the diffusion coefficient for salt in the membrane, ΔC_s^m is the differential of the concentration of salt in the membrane and l is the thickness of the membrane. Equations 2 and 3 show that for a given membrane water flux is proportional to the net driving pressure differential across the membrane, that salt flux is proportional to the salt concentration differential across the membrane and is also independent of applied pressure. Obviously, the flux equations are important in designing RO systems and yield insight into the complexity of balancing the variables which determine the volume of water permeate and salt passage through the membrane. Of particular note is the presence of the diffusion coefficient for water in the membrane indicating the importance of water uptake by the membrane. The chemical and physical nature of the membrane determines its ability to allow for preferential transport of water over sodium and chloride ions as well as its ability to take up water. The distinct characteristics of the membrane of interest will be discussed later.

Transport of small species through polymer films in reverse osmosis is described by the solution-diffusion model in which water transport occurs in three steps, absorption onto the membrane surface at the high pressure feed side of the membrane, diffusion through the thickness of the membrane, and desorption from the permeate surface of the membrane at the lower pressure, permeate side¹¹. For our purposes, this model applies to binary diffusion, where one component is the RO membrane and a penetrant is the other component. The process of diffusion typically follows Fick's law for binary diffusion^{6,8}

$$n_i = w_i(n_i + n_m) - \rho D_{im} \frac{dw_i}{dz} \quad (4)$$

where the subscripts i and m indicate the penetrant and membrane, respectively, n_i is the mass flux of the penetrant, w_i is the mass fraction of the penetrant, ρ is the density of the mixture, and D_{im} is the binary diffusion coefficient. The membrane is considered to be the stationary element, and therefore the flux of the membrane itself is zero. Simplifying the equation for this condition yields

$$n_i = -\frac{\rho D_{im}}{1-w_i} \frac{dw_i}{dz} = -\frac{\rho D_{im}}{w_m} \frac{dw_i}{dz} \quad (5)$$

For the case in which the content of the penetrant is small, further simplifications arise and $w_m \cong 1$. The density of the membrane and ion mixture can be considered relatively constant, so that equation 5 simplifies to

$$n_i = -D_{im} \frac{dC_i}{dz} \quad (6)$$

where C_i is the mass concentration of the penetrant and $\frac{dC_i}{dz}$ is the concentration gradient of the penetrant. By dividing both sides of the equation by the molecular weight of i yields

$$N_i = -D_{im} \frac{dC_i}{dz} \quad (7)$$

where C_i is now the molar concentration of the ion penetrant and N_i is the molar flux. The equation above further demonstrates the importance of the ability of the membrane to take up water and thus the necessity of the presence of hydrophilic groups in the RO membrane, which will be discussed further along with other structural details of the membrane of interest.

The rate of transport of a penetrant through the polymer membrane can be described by permeability, defined in terms of the flux of the penetrant, the membrane

thickness and the driving force of transport which was defined earlier as the pressure differential across the membrane.

$$P_i = \frac{(N_i)(l)}{(p_0 - p_1)} \quad (9)$$

When the penetrant concentration and pressure at downstream are negligible compared to the upstream conditions, permeability can instead be defined as⁶

$$P_i = K_i D_{im} \quad (10)$$

where K_i is the penetrant partition coefficient; detailed derivation of the equation is found elsewhere⁶.

The purpose of the RO membrane of interest is to separate solvent and solute, preferentially passing water though both will pass through the membrane. The quantity of salt removed from the feedwater stream as a percentage is known as rejection and is a commonly used measure of the effectiveness of the membrane¹² Salt rejection is a result of the differing mass transfer rates of salt and water through the membrane²²

$$R \equiv \left[1 - \frac{C_{sl}^s}{C_{s0}^s} \right] \times 100\% = \left[1 + \frac{D_{sm} K_s RT C_{wl}^s}{D_{wm} C_w^m V_w (\Delta p - \Delta \pi)} \right] \quad (11)$$

where K_s is the partition coefficient for salt between the solution and membrane phases, C_{wl}^s is the concentration of water in the permeate solution, C_{sl}^s is the salt concentration in the permeate and C_{s0}^s is the salt concentration in the feed. The salt partition coefficient is equal to the chloride partition coefficient, as will be explained in more detail later^{1,22}

$$K_{NaCl} = K_{Cl^-} = \frac{C_s^m}{C_s^s} = \frac{\text{mmol } i / \text{cm}^3 \text{ hydrated membrane}}{\text{mmol NaCl} / \text{cm}^3 \text{ soaking solution}} \quad (12)$$

where C_s^s is the concentration of salt in the external soaking solution in which the membrane has been equilibrated and the values for C_s^m were obtained empirically using the procedure given later and are seen in Table 3.

The major types of reverse osmosis membranes currently used for water purification are cellulose acetate (CA) and aromatic polyamide (PA)⁴ membranes. A significant amount of the work currently underway at The University of Texas at Austin on reverse osmosis membranes aims to overcome the drawbacks of these two types of materials. CA membranes are susceptible to microbiological attack, undergo compaction at higher temperatures and pressures, and are limited to a relatively narrow pH range. PA membranes, which are currently the most widely used desalination membranes, exhibit better transport properties at a given applied pressure and are more stable over a wider range of pH values than CA membranes¹³. However, one of the major issues is the chlorine instability of PA membranes. PA membranes suffer from poor resistance to continual exposure to oxidizing agents such as chlorine, leading to irreversible performance loss over time¹³. Membrane failure is due to certain structural changes within the polymer structure in response to chlorine exposure. These changes in PA membranes result from chlorine attack on an amide nitrogen and the aromatic rings in the polymer's backbone. The exact chemical mechanism of the chlorine and polymer reaction and the following increase in salt permeability is not yet clearly understood¹⁴. While the exact mechanisms for degradation of the PA membranes by chlorine are not precisely known, it is thought that two different types of reactions occur, aromatic substitution at low pH and chain scission at high pH. Both of these mechanisms decrease

the salt rejection of the membrane; chain scission by reducing molecular weight, thereby creating openings in the polymer structure which allow for greater passage of salt^{15,25}.

A promising alternative to the PA and CA membranes is the bi-phenyl based, partially sulfonated poly(arylene ether sulfone) (BPS) material which lacks the amide bond that is susceptible to chlorine attack, and research on the materials has shown it to have high chlorine tolerance for a wide range of pHs¹³. Additionally, the polymer has shown good anti-fouling behavior¹³. The polymer is based on polysulfone, a family of thermoplastic polymers known for their toughness. They contain the subunit aryl-SO₂-aryl, with the sulfone group being the defining feature⁴. The random copolymers are synthesized by direct polymerization of a disulfonated monomer (3,3'-disulfonato-4,4'-dichlorodiphenyl sulfone (SDCDPS)) and other monomers (4,4'-dichlorodiphenyl sulfone (DCDPS) and 4,4'-biphenol (BP))^{13,26}. The structure of these monomers and the structure of the BPS repeat unit are seen in Figure 3. The nomenclature used to describe the BPS materials is BPSY-XX, where XX is the molar percentage of hydrophilic sulfone groups, i.e. SDCDPS, in the polymer and Y is H or N. If Y is H the membrane is said to be in the acid form, if Y is N the membrane is in the sodium salt form. Other cations can be present, such as potassium, due, for example, to conditions during synthesis, but for our purposes the membrane is generally used in either the acid or sodium salt form.

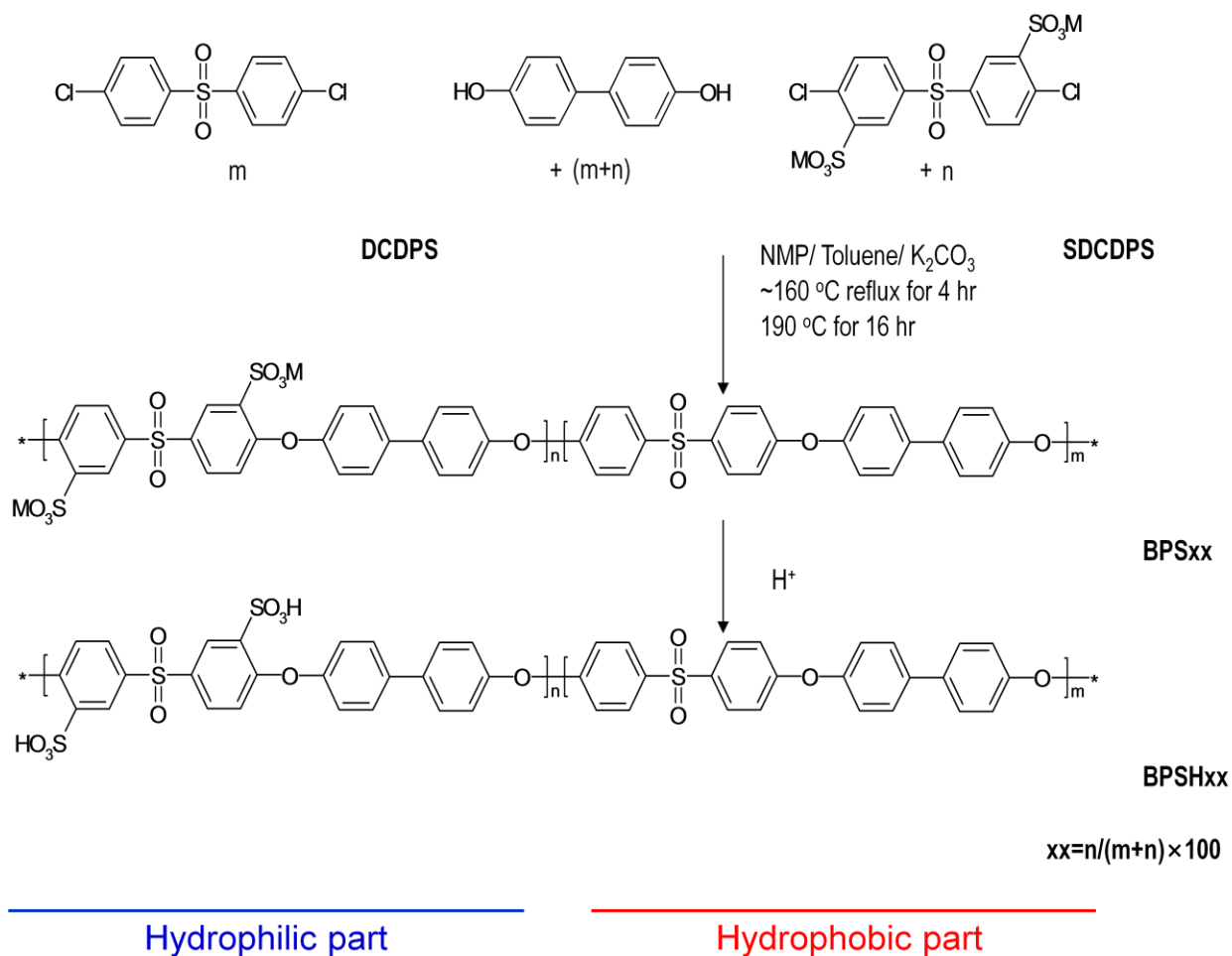


Figure 2. Chemical structure of random disulfonated biphenol-based poly(arylene ether sulfone) (BPSY-X)²⁶. X=mol% of disulfonated monomer; Y= H (acid form), N (sodium salt form), or K (potassium salt form); M=H⁺, Na⁺ or K⁺.

Sulfonation of the monomer before polymerization leads to greater control of the degree of sulfonation present in the polymer, and thus in the RO membrane¹³. Control of

sulfonation leads to control of the level of hydrophilicity of the membrane which affects characteristics of the membrane such as water flux and salt permeability¹³.

For water purification, reverse osmosis membranes should have high water permeability and low salt permeability. Most polymers with a backbone resistant to chlorine attack, like polysulfones, are hydrophobic and do not sorb water to an extent needed to achieve a high water permeability⁸. Sulfonation of these materials increases the equilibrium uptake of water and, therefore, water permeability. Increased water flux can be beneficial, however the higher water uptake increases swelling of the membrane, which increases salt permeability. As mentioned, the degree of sulfonation of the materials can be controlled and the preference of one degree of sulfonation over another depends on the applications of the membrane and the desired characteristics.

Ion Exchange and Exclusion

Another result of sulfonation is a negatively charged polymer membrane in which the ionic groups can repel negative ions (here chloride) in solution^{1,23}. Therefore, salt rejection with charged membranes can depend on charge effects in addition to the water uptake by the membrane. The BPS materials act as ion exchange membranes, allowing them to separate solute from solvent through the preferential sorption of cations²⁴. The membrane interior may be viewed as a solution containing bound fixed charges, mobile counter-ions and electrolyte and water from the external soaking solution⁶. The fixed charges are anions ($-\text{SO}_3^-$) and the counter-ions are cations (H^+ and Na^+). The membrane

has a distinct number of fixed ion sites that set the maximum quantity of exchanges that can take place for a given amount of membrane; this is known as the membrane's Ion Exchange Capacity (IEC), typically expressed as milliequivalents per gram of dry polymer. As the membrane takes up water, i.e., is swollen during diffusion, IEC can be expressed in terms of swollen polymer, milliequivalents per unit of swollen membrane volume⁶, C_A^m

$$C_A^m = \rho_m \text{ IEC} = w_m \rho \text{ IEC} \quad (13)$$

where ρ_m is the mass concentration of polymer in the swollen membrane, i.e., the mass of the dry membrane divided by the volume of the swollen membrane, w_m is the mass fraction of polymer in the swollen membrane equal to the mass of the dry membrane divided by the mass of the hydrated sample and ρ is the density of the water swollen membrane. Values for C_A^m are seen in Table 5. In this reaction, the proton of the sulfate group is exchanged for the sodium ion of the sodium chloride molecule. The degree the reaction proceeds to the right will depend on the relative concentrations of the two ions inside and outside the membrane phase and the ion exchanger's preference or selectivity for one ion over another^{1,23}. BPS exchanges protons for sodium at ambient temperature, though the acidification process, during which the membrane exchanges sodium for protons, occurs if the membrane is immersed in boiling sulfuric acid.

Ion exchange and the significance of the charged sulfonate groups in the BPS membrane are important concepts in understanding these membranes. The effect of the charge of sulfonate groups in the membrane (in addition to providing a hydrophilic nature to the membrane) is primarily to change the partitioning of salt in the membrane. Ion

exchange involves the interchange of the counterion (here, the positively charged ions H^+ and Na^+) associated with the fixed charge site on an insoluble material and ions of the same charge (here, the negatively charged ion Cl^-) in the external solution. Ion exchange reactions are stoichiometric and generally reversible, and in that way they are similar to other solution phase reactions¹. For example:



This leads to a significant reduction, or exclusion, in the concentration of chloride in the membrane in equilibrium with the electrolyte solution, the result is a concentration of chloride in the membrane which is much less than in the external soaking solution. This reduction is known as Donnan Exclusion^{1,6,8}. In this case, the moles of chloride that are present in the membrane will be equal to the moles of sodium chloride in the membrane and the moles of sodium will be equal to the sum of the moles of fixed charge sites and of chloride in the membrane at equilibrium with the external soaking solution.

If Donnan Exclusion is significant in a polymer membrane, the relationship between the concentration of sodium chloride present in the membrane and in soaking solution at equilibrium can be expressed as⁶

$$C_s^m = \left[\frac{1}{4} (C_A^m)^2 + (C_s^s)^2 \left(\frac{\gamma_{\pm}^s}{\gamma_{\pm}^m} \right)^2 \right]^{1/2} - \frac{1}{2} C_A^m \quad (15)$$

where γ_{\pm} are the mean activities of the ions in the solution or membrane and C_s^s is the concentration of salt in the soaking solution. Alternatively, equation 14 can be expressed in terms of the salt partition coefficient⁶

$$K_s \equiv \frac{C_s^m}{C_s^s} = \left[\frac{1}{4} \left(\frac{C_A^m}{C_s^s} \right)^2 + \left(\frac{\gamma_{\pm}^s}{\gamma_{\pm}^m} \right)^2 \right]^{1/2} - \frac{1}{2} \frac{C_A^m}{C_s^s} \quad (16)$$

where at the limit of very high salt concentrations, equation 15 becomes

$$K_s \rightarrow K_{\infty} = \frac{\gamma_{\pm}^s}{\gamma_{\pm}^m} \quad \text{when} \quad C_s^s \gg C_A^m \quad (17)$$

where K_{∞} is the salt partition coefficient that would be observed for a non-charged polymer that takes up an equal amount of water as the charged polymer of interest⁶. The significance of these equations in terms of the BPS polymer materials will be discussed further later.

Research Objective

The primary objective of this work was to measure the amount of sodium chloride present in the membrane after equilibration with external soaking solutions of varying concentrations of sodium chloride by measuring the amount of individual ions, i.e., the sodium cation and chloride anion, separately. One area in which this work is unique is that it sought to measure the concentrations of the ions independently of one another. Additionally, the ashing technique for making cation concentration measurements had not been previously used for these materials. The technique of ashing can be used on other membrane materials to measure concentrations of other cations which may be of significance to future work, such as magnesium and calcium. The significance of developing these techniques lie in understanding sodium chloride transport in reverse

osmosis membranes, here, specifically to understand how the sulfonation of polysulfones affects the transport of sodium chloride in the charged sulfonated polysulfone membrane. In addition, it is helpful to further understand how salt transport is linked to water sorption in these membranes. By developing techniques to measure ion sorption (and thus sodium chloride sorption) in any of the BPS materials, one can compare water uptake and sodium chloride uptake in materials of varying IECs to see what relationships exists among percent sulfonation, water uptake and ion uptake.

CHAPTER 3: EXPERIMENTAL

Membrane Preparation

Experiments were conducted using BPSH-32 polymer membranes produced from polymers synthesized by Dr. Chang Hyun Lee in the laboratory of Dr. James E. McGrath at Virginia Polytechnic Institute and State University (*Virginia Tech*). The material was determined by Dr. Lee to have an Ion Exchange Capacity (IEC) of approximately 1.19 meq per gram of dry polymer by using ^1H NMR. Additionally, the IEC value was determined here by immersing the acid form of the BPS membrane in 100 milliliters of aqueous Na_2SO_4 solution, prepared using an amount of Na_2SO_4 five times the weight of dry polymer, to convert to the membrane to the sodium salt form. Using Na_2SO_4 as the solute allowed the introduction of sodium into the solution (as it dissociates) using an easily obtainable material, without the introduction of other ions of interest, particularly chloride. The Na_2SO_4 solution containing the immersed membrane was stirred for twelve hours after which it was titrated with standardized 0.01 N NaOH. The IEC was calculated using the following equation

$$\text{IEC (meq/g of dry polymer)} = \frac{\text{vol of NaOH} * \text{strength (N) of NaOH}}{\text{g of dry polymer}} \quad (18)$$

The polymer membrane is prepared using a 10 wt % BPS 32N solution which was prepared by dissolution of BPSN-32 polymer pellets in N, N-dimethyl acetamide. The polymer and solvent are mixed until a transparent homogeneous solution was obtained. An appropriate amount of solution based on mold dimensions and desired membrane

thickness was poured into a glass mold, which had been leveled to ensure consistent membrane thickness, and then heated at 80°C in an oven for 24 hours to evaporate solvent. Following this, it was placed under vacuum for 24 hours to remove residual solvent. Conversion of the membrane from salt (BPSN-32) to acid (BPSH-32) form was performed by boiling the membrane in 0.5M H₂SO₄ for three hours, during which ion exchange as described previously occurred, after which it was boiled in water for two hours to remove excess sulfuric acid. The membrane was then placed under vacuum with heat at a temperature of 110°C for 24 hours for removal of water. The membrane separates from the glass plate during drying. The membranes were used in the acid form with thickness of approximately 250µm for all experiments.

Ion and Sodium Chloride Concentration Measurements

Techniques were developed to measure the concentrations of the chloride anions and the cations separately. Developing appropriate procedures for measuring ion solubility in BPSH-32 was initially approached as choosing from techniques that either did or did not require the extraction of the ion from the membrane before measuring the amount of the ion. Techniques that did not require extraction were considered preferable over those that did. This was in part due to the interaction of the sodium cation with the sulfonate groups in the membrane during ion exchange.

Experiments were performed at ambient temperature using the prepared BPSH-32 membrane. A disk was cut from the prepared acid form membrane which was accurately weighed and the thickness and volume measured. Enough quantity of membrane per sample was needed to ensure enough ions were present in the sample to allow for accurate measurements with the available instruments. More about the detection limits of the instruments used in the experiments will be discussed later. A range of external soaking solution sodium chloride concentrations was needed to provide enough data to make isotherms from which trends in ion concentration and ion partition coefficient vs. external soaking solution sodium chloride concentration could be seen. The concentrations of sodium chloride in the external soaking solution used for the sodium ion concentration measurements were 0.01, 0.1, 0.25, 0.5, 0.75, 1.00 and 1.50 molar. For chloride ion concentration measurements the same concentrations of sodium chloride were used, excluding the 0.01M NaCl solution. Chloride ion concentration measurements were made using the 0.01M NaCl external soaking solution, but the amount of chloride in the samples was so low as to be below the instrument detection limit. It was not determined how close to zero concentration the value actually was and it was therefore not included in the data summary for this work.

For these experiments, approximately 0.25 grams of membrane were used per sample, except for the measurement of chloride at the external sodium chloride soaking solution concentration of 0.1M NaCl, for which approximately 0.5 grams of sample were used. The increased sample size was due to the very low concentration of chloride present in the sample, so low as to be below the instrument's detection limit for chloride

for a sample size of only 0.25 grams. Six samples were used for each experiment, five unknowns in order to diminish fluctuations due to membrane inhomogeneities and one blank (a water-equilibrated BPSH 32 membrane sample). A blank was used to account for any sodium or chloride ions that may be present in the sample before equilibrating in sodium chloride solution. For all experiments, the amount of sodium and chloride found in the blank sample was below the instrument detection limit.

To remove ion impurities before experimental use, all samples were soaked in four successive solutions of 100ml of pure water for a minimum of 12 hours, 48 hours total. The amount of time needed to wash the membrane is based on the assumption that any ions which may affect the NaCl solubility in the membrane are desorbed at times much greater than that for diffusion of NaCl in the membrane⁸

$$t \gg \frac{x^2}{2D} \quad (19)$$

where x is one half the thickness of the membrane and D is the diffusion coefficient of NaCl equal to approximately $3.2 \times 10^{-7} \text{ cm}^2/\text{sec}$. The soaking times used throughout the experiments are based on the same concept. The water equilibrated membrane was thoroughly wiped using a laboratory wipe to remove surface water.

The water hydrated membrane sample was put into successive solutions of 100ml of NaCl solution of known concentration and pH where the pH measurements were taken using a Fisher Scientific accumet Excel XL25 pH/ion meter and a Mettler Toledo InLab Basics pH electrode. The NaCl solution was equilibrated with the atmosphere so that later pH changes were not due to H_2CO_3 from atmospheric carbon dioxide. During

equilibration with the external sodium chloride soaking solution, the membrane was removed from the solution and placed into a new solution after each soaking in order to maintain a constant sodium chloride concentration. As ion exchange takes place and sodium ions are taken up by the membrane, the external sodium concentration decreases. Another reason for changing the soaking solution is to simulate an infinite volume of external solution, providing a quantity of sodium cations much greater than protons and increasing the likelihood of complete ion exchange. The membrane remained in the sodium chloride solution for a minimum of four hours after which the pH of the solution was measured. This was done repeatedly until no significant change in pH was detected, after which the membrane remained in the soaking solution for an additional 24 hours to ensure complete equilibration. The pH of the soaking solution was found to decrease by more than two pH units, up to three, during the first four hours of soaking. During the second four hours the pH decreased by approximately one pH unit and after the third soaking the pH was about 0.5 pH points less than the control sodium chloride solution pH. After the fourth four hour soaking the pH was approximately equal to the control NaCl solution indicating that ion exchange was complete. This trend applied to all concentrations of sodium chloride solutions for 0.25 grams of sample. Thus, the membranes were in the sodium chloride soaking solution for a minimum of 40 hours. The pH change of the soaking solution occurs due to the release of H^+ into the solution during ion exchange in the membrane occurring as sodium is introduced into the membrane. The sodium chloride equilibrated sample was thoroughly wiped to remove surface NaCl.

Desorption of the sodium cation from the membrane was not preferred due to the interaction of the cation with the negatively fixed charged groups in the membrane. Investigation into a technique to measure the amount of sodium cation directly from the membrane was performed. The organic nature of BPS made dry ashing a first choice. Dry ashing is usually defined as the incineration of a sample at temperatures greater than 525°C so that the organic material in the sample is destroyed. Using this technique, extraction of the cation from the membrane is not necessary, making this a desirable method. Another reason contributing to the desirability of the ashing method is a decrease in the amount of time required by the analyst compared to desorption. More time is required from the analyst for desorption experiments because the desorption solution must be changed regularly and the pH must be recorded for each changed solution. Once the membrane has been equilibrated in the external soaking solution, a sample ready for sodium analysis can be prepared in as little as approximately seven hours using the instrument parameters given below.

In the dry ashing process the NaCl equilibrated membrane was heated in a muffle furnace in air to destroy the combustible material of the membrane leaving behind ash, which contains the sodium that entered the membrane during equilibration in the sodium chloride solution. A Carbolite 1200°C horizontal split tube furnace, model HZS/TVS, was used to ash the membranes. Though a tube furnace was used in these experiments, there are numerous other types of furnaces that are suitable. The membrane was heated in a porcelain crucible at a rate of 5°C per minute to 700°C, dwelling at 700°C for one hour after which it was allowed to cool to ambient temperature. This results in the ability

to have a sample prepared in as little as three and half hours plus the time for the furnace to cool after membrane equilibration. The ash remaining after combustion of the sample is white and holds the shape of the pre-ashed membrane whereas relatively little or no residue remains after ashing the blank sample. The ash is rinsed from the crucible into a 100ml volumetric flask with 2% HNO₃ using a funnel. This solution is submitted for sodium ion analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)⁵ performed by Dr. Nathan Miller in the Department of Geosciences at The University of Texas at Austin using an Agilent 7500ce Quadrupole ICP-MS. 2% HNO₃ was chosen as the sample matrix as requested by the analyst. Of note is the rapid dissolution of the ash in pure water as well as in the acid solvent, allowing for a range of future experimental possibilities using the ashing technique.

For this technique the choice of ashing vessel, the crucible, is important as factors such as heat resistance and contaminants from the crucible material must be considered. If the wrong material is chosen, there can be loss of analyte due to adhesion to the crucible as well as contamination from the breaking down of the crucible material due to high temperatures or reaction with solvent. Porcelain crucibles were chosen from a range of options for this experiment because of their versatility and low cost. They can withstand temperatures of 1150°C without cracking or reacting with the compounds in BPSH 32¹⁸. They are resistant to acids but will crack with too-rapid heating or cooling.

It is fairly common in the literature to find examples of procedures in which the sample is charred prior to ashing in a furnace in order to speed the decomposition process²⁰. Charring is usually performed by holding a crucible containing the sample

with tongs and heating it with a propane torch or Bunsen burner flame in a fume hood, after which the sample may be wetted with sulfuric acid as an ashing aid. Magnesium nitrate is commonly used during ashing as an ashing aid and also to produce ash with a greater density that is less likely to be lost due to air currents²⁰. After manipulating the experimental procedure it was determined that these steps are unnecessary for ashing the BPS materials for sodium analysis. Additionally, such steps make the method less safe by introducing an open flame and corrosive acids as well as producing toxic and corrosive fumes (in the case of adding acid as an ashing aid) during ashing.

Adjustments to the procedure to lower the dwelling temperature were attempted without success. At lower temperatures, up to 650°C, with one hour dwell time black carbon residue was present in the ash, which is evidence of incomplete combustion.

Pintauro² developed a method for desorption of chloride from Nafion, a technique considered and ultimately chosen for the measurement of chloride in the membrane. Investigation into other methods was performed to find an alternative method which did not require extraction of the ion from the membrane. This included dissolution of the membrane in concentrated acids and combustion of the membrane in a closed system using a type of oxygen combustion bomb (Parr Bombs and Schöniger flasks were considered), after which the chloride remaining in the residue could be analyzed. The closed system combustion techniques are useful for materials in which chloride takes part in chemical bonds with the sample but are unnecessary for our purposes. Dry ashing in an open system was not used for chloride analysis because it was found that chloride was lost during the ashing process, most likely as HCl vapor.

Additionally, it was attempted to measure chloride by performing the desorption experiment and reacting the desorbed chloride with excess AgNO_3 . Silver chloride precipitates out of solution while the excess silver is present in the ionic form in water and can be analyzed by ICP-MS, which has a lower detection limit than IC. More steps were needed in this process, including the filtration of the solution so that a sample containing particulates was not sent to the ICP-MS lab, which could be detrimental to the instrument. As the amount of chloride in the solution was so low, it was important to avoid incorporating more possibilities for error. This would otherwise have been useful to measure the concentration of chloride in a membrane equilibrated in 0.01M NaCl. As mentioned previously, the concentration of chloride in a membrane equilibrated in 0.01M NaCl was below the IC detection limits. Potentiometric titration of Cl^- in the desorption solution was also considered, but ultimately analysis of Cl^- by IC was the chosen method.

Pintauro's method was used for chloride ion desorption from the membrane. The chloride desorption experiment was begun by submerging the sodium chloride equilibrated membrane in 100ml of pure water for 12 hours after which a qualitative measurement of chloride was performed using a Fisher Scientific accumet combination chloride selective electrode and the dual channel pH/ion meter mentioned previously. Successive soakings were repeated until no chloride was detected. The soaking solutions were combined in an Erlenmeyer flask and the solution was analyzed for chloride by ion chromatography (IC) using a Metrohm ion chromatograph composed of the 732 Detector, 762 Interface, 709 Pump and 752 Pump Unit and a Metrosep A Supp5 150/4.0mm column. The amount of chloride in the first 100ml of soaking solution was significantly

greater than that of successive soakings, the degree depending on the concentration of the external soaking solution. The number of desorption soakings is inversely related to the time the membrane is in the desorption solution so that the longer the membrane soaks in the solution the less volume the final solution will have, and therefore more concentrated it will be. A more concentrated final solution is preferable due to the low amount of chloride in the membrane and detection limits of the IC. Due to the lower concentration of chloride, increasing the chloride desorption solution concentration is beneficial so as to minimize effects of experimental error. The concentration of chloride in the membrane was shown to be significantly less than the sodium concentration.

The analytical instruments mentioned thus far for sodium and chloride analysis, ICP-MS and IC, were chosen over other instruments due their greater suitability to the needs of the author based on multiple factors, including detection limit, precision, ease of access and cost. The detection limits unique to the instruments available to the author on The University of Texas at Austin campus are summarized below, where detection limit is generally defined by the EPA under federal guidelines to be the minimum concentration of an analyte that can be determined with 99% confidence that the true concentration of said analyte is greater than zero¹⁰. The detection limit for the ICP-MS and ICP-OES were determined by Dr. Nathan Miller and Dr. Chia-Chen Chen at the Center for Research in Water Resources, Cockrell School of Engineering at The University of Texas at Austin, respectively. The value for the IC was determined by the author. All values were obtained using the procedure outlined by the EPA in 40 CFR 136¹⁰. According to this procedure, a solution of the analyte of concentration one to five

times the estimated detection limit is prepared and analyzed at least seven times. The standard deviation and Student's t-distribution of the measurements are calculated from which the detection limit is calculated as equal to the product of the two values.

Table 1. Summary of the detection limits and precision values of the instruments considered for the ion concentration measurements.

| Instrument | Analyte | Detection Limit* | Precision (%RSD)* |
|--|-----------------|----------------------|-------------------|
| Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) | Na ⁺ | < 13ppb ⁵ | <4 |
| Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) | Na ⁺ | ~ 50ppb ⁹ | <4 |
| Ion Chromatography (IC) | Cl ⁻ | ~10ppb | <5 |

*Varies with analyte concentration.

CHAPTER 4: RESULTS AND DISCUSSION

Ion Exchange Desorption

The plot in Figure 3 shows the change in pH that occurs in the membrane over time as it comes to equilibrium in an external soaking solution of sodium chloride. The pH was monitored after placing the approximately 0.25 gram sample of polymer membrane in 100ml of sodium chloride soaking solution, which was replaced after the four hour soaking, i.e., after each point. The pH and change in pH at the end of each serial soak is seen in the plot. The decrease in pH is evidence of an increase in the concentration of H^+ in the soaking solution and release of H^+ from the membrane. This release of protons from the membrane is the result of ion exchange, occurring as the membrane sorbs sodium cations resulting in the release of protons from the sulfonate groups. The leveling off of the pH and change in pH seen on the plot is evidence of ion exchange coming to completion. The membrane is then back in the sodium salt form once the protons have been released from the sulfonate groups and sodium cations have taken their place. This same trend was witnessed for all soaking solutions used (from 0.01M NaCl through 1.5M NaCl) in the experiments for membranes left in the solutions for a full four hours. The fact that this is so is evidence for a binding constant between the sulfonate groups and sodium cations that is greater than that of the sulfonate groups and protons under these conditions. Even at low external soaking solution sodium chloride concentrations equilibrium will be reached in which the salt form of the membrane is achieved.

As the conversion from acid form to salt form takes place in a relatively short time period, it can be understood that over the lifetime of experiments conducted (primarily by others in this research group) on this material for properties such as salt and water permeability, that the term “acid form” can be misleading as the experimental data are for experiments on a membrane in the salt form even though it may have initially been in the acid form. This raises questions as to what conformation changes may be occurring in the membrane during the transformation from the salt form, in which the polymer is originally synthesized and thus the form in which the membrane originally is in, to the acid form and perhaps as it changes back to the salt form during ion exchange occurring during experimentation.

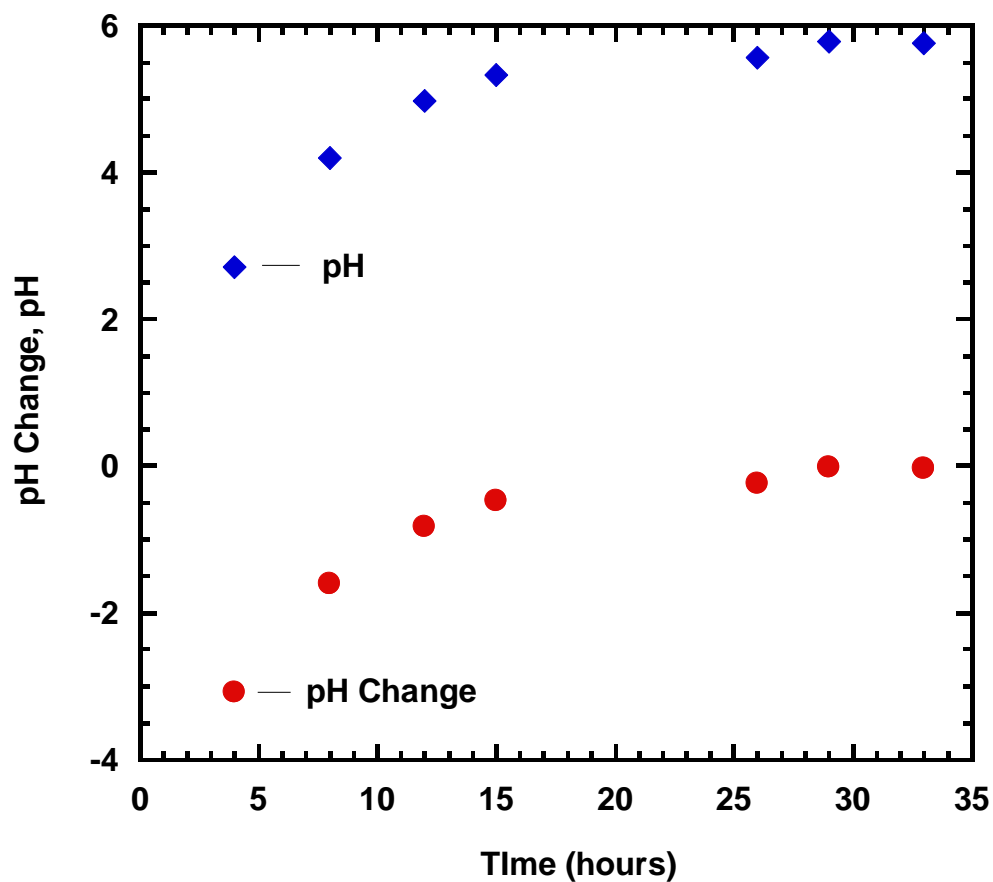


Figure 3. Plot of pH and pH change vs. time.

Ion and Sodium Chloride Concentration Measurements

Table 2 summarizes the amount of sodium sorbed per gram of dry membrane for varying external sodium chloride soaking solution concentrations. The values were obtained by the ashing experiment detailed previously. The error in the sodium measurements was based on the detection limit for the ICP-MS for the particular sample

run, as determined by the analyst, Dr. Nathan Miller. It can be seen that even in dilute solutions of sodium chloride the concentration of sodium in the membrane at equilibrium with the soaking solution remains fairly constant and is approximately equal to the IEC value of 1.19. The fact that the concentration of the ion is generally above the IEC value is also consistent with the theory that the total sodium in the membrane will be equal to the amount present due to ion exchange, i.e., interacting with the sulfonate groups, plus the sodium present with chloride as sodium chloride. It can be concluded that the concentration of sodium in the membrane is independent of the soaking solution sodium chloride concentration and dependent on the material IEC. This is further evidence of what was concluded from the pH experiments, that ion exchange is indeed taking place and that the membrane is converting to the sodium salt form while immersed in a sodium chloride solution, even in dilute solutions.

Table 2. a) Concentration of sodium cation in the BPSH-32 membrane for external soaking solution concentrations of 0.01, 0.10, 0.25 and 0.50M NaCl and b) concentration of sodium cation in the BPSH-32 membrane for external soaking solution concentrations of 0.75, 1.00 and 1.50M NaCl.

a)

| External Soaking Solution NaCl Concentration (M) | 0.01 | 0.10 | 0.25 | 0.50 |
|--|-------------|-------------|-------------|-------------|
| Concentration of Na ⁺ (meq Na ⁺ /g dry membrane) | 1.127±0.000 | 1.193±0.000 | 1.253±0.000 | 1.259±0.000 |
| | 1.325±0.000 | 1.203±0.000 | 1.227±0.000 | 1.254±0.000 |
| | 1.200±0.000 | 1.215±0.000 | 1.234±0.000 | 1.260±0.000 |
| | 1.129±0.000 | 1.153±0.000 | 1.219±0.000 | 1.337±0.000 |
| | 1.243±0.000 | 1.160±0.000 | 1.212±0.000 | 1.302±0.000 |
| Average | 1.205 | 1.185 | 1.229 | 1.282 |
| Standard Deviation | 0.083 | 0.027 | 0.016 | 0.036 |

b)

| External Soaking Solution NaCl Concentration (M) | 0.75 | 1.00 | 1.50 |
|--|-------------|-------------|-------------|
| Concentration of Na ⁺ (meq Na ⁺ /g dry membrane) | 1.204±0.000 | 1.196±0.000 | 1.225±0.000 |
| | 1.193±0.000 | 1.191±0.000 | 1.271±0.000 |
| | 1.176±0.000 | 1.373±0.000 | 1.188±0.000 |
| | 1.185±0.000 | 1.209±0.000 | 1.223±0.000 |
| | 1.214±0.000 | 1.221±0.000 | 1.261±0.000 |
| Average | 1.194 | 1.238 | 1.234 |
| Standard Deviation | 0.015 | 0.076 | 0.033 |

As the existence of sodium chloride in the membrane depends on the presence of both sodium and chloride ions, the amount of the salt – as well as the transport of NaCl across the membrane – will be controlled by the ion of lesser concentration. It can be seen in a comparison of Tables 2 and 3 that this ion is chloride, and thus the concentration of sodium chloride in the membrane is equal to the concentration of chloride in the membrane (assuming the amount of chloride present with any other cation in the membrane is insignificant). It can also be seen in Table 3 that the chloride ion content is significantly lower than the sodium content and increases with the NaCl concentration of the soaking solution. When the amount of chloride in the membrane expressed as millimoles is subtracted from the total amount of sodium in the membrane, the remaining value for sodium is approximately the IEC of the material. As will be discussed in more detail later, this is evidence that ion exclusion appears to be significant.

Table 3. Concentration of chloride anion in BPSH-32 membrane.

| External Soaking Solution NaCl Concentration (M) | 0.10 | 0.25 | 0.50 | 0.75 | 1.00 | 1.50 |
|---|-------------|-------------|-------------|-------------|-------------|-------------|
| Concentration of Cl ⁻ (meq Cl ⁻ / g dry membrane) | 0.002±0.000 | 0.041±0.002 | 0.032±0.002 | 0.071±0.002 | 0.100±0.002 | 0.202±0.002 |
| | 0.002±0.000 | 0.034±0.002 | 0.035±0.002 | 0.086±0.002 | 0.105±0.002 | 0.192±0.002 |
| | 0.002±0.000 | 0.039±0.002 | 0.035±0.002 | 0.080±0.002 | 0.095±0.002 | 0.171±0.003 |
| | 0.002±0.000 | 0.045±0.002 | 0.033±0.002 | 0.083±0.002 | 0.101±0.002 | 0.193±0.003 |
| | 0.002±0.000 | 0.047±0.002 | 0.039±0.002 | 0.072±0.002 | 0.152±0.002 | 0.208±0.002 |
| Average | 0.002 | 0.040 | 0.035 | 0.078 | 0.111 | 0.270 |
| Standard Deviation | 0.000 | 0.005 | 0.003 | 0.007 | 0.023 | 0.012 |

The data in Tables 2 and 3 are summarized in Figures 4, 5 and 6 in plots of the concentration values of the sodium and chloride ions in the membrane vs. the concentration of sodium chloride in the external soaking solution. Shown for comparison to the sodium value is the IEC of the material. The trends mentioned in the immediately preceding paragraphs are also seen here. In a comparison of Figures 5 and 6 it can be seen that changing the scale of the y-axis from a linear to a logarithmic scale allows the trend in the data for the concentration of chloride in the membrane to be observed. The

concentration of the co-ion (and sodium chloride) sorbed by the membrane is expected to decrease with the square of its concentration in the external soaking solution¹. Evidence of ion exclusion is seen in the significant difference between the concentrations of sodium and chloride in the membrane as well as in the fact that there are differing trends seen in the concentrations of the sodium and chloride ions as the sodium chloride concentration in the external soaking solution is increased.

The detection limit for the ion chromatograph used for these experiments for chloride concentration measurement is approximately 0.01ppm (or mg/L). This is reflected in the chloride data by the use of error bars. Error bars are also used to reflect the error for the sodium data. The error was based on the detection limit for the ICP-MS for the particular sample run, as determined by the analyst, Dr. Nathan Miller. Though the error bars are too small to be seen on the plot, the values can be seen in the appropriate tables.

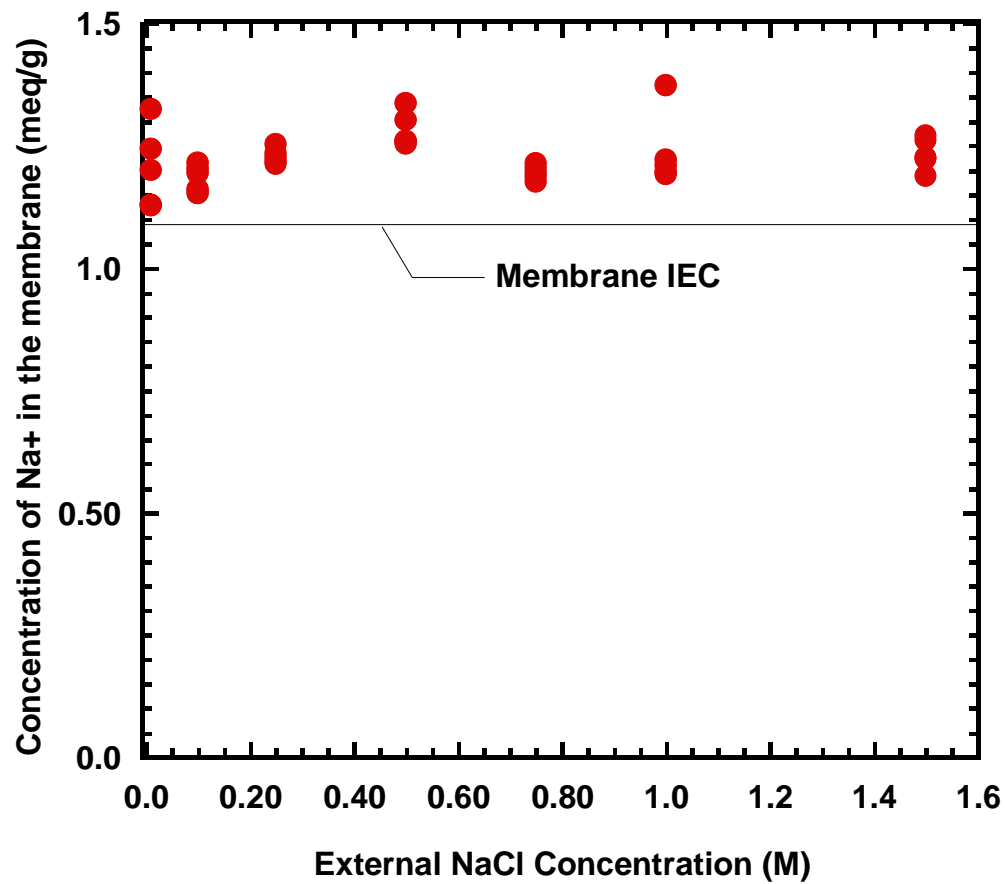


Figure 4. Plot of concentration of sodium ion in the membrane at equilibrium with an external soaking solution vs. the concentration of NaCl in the external soaking solution. Shown for comparison is the IEC of the material.

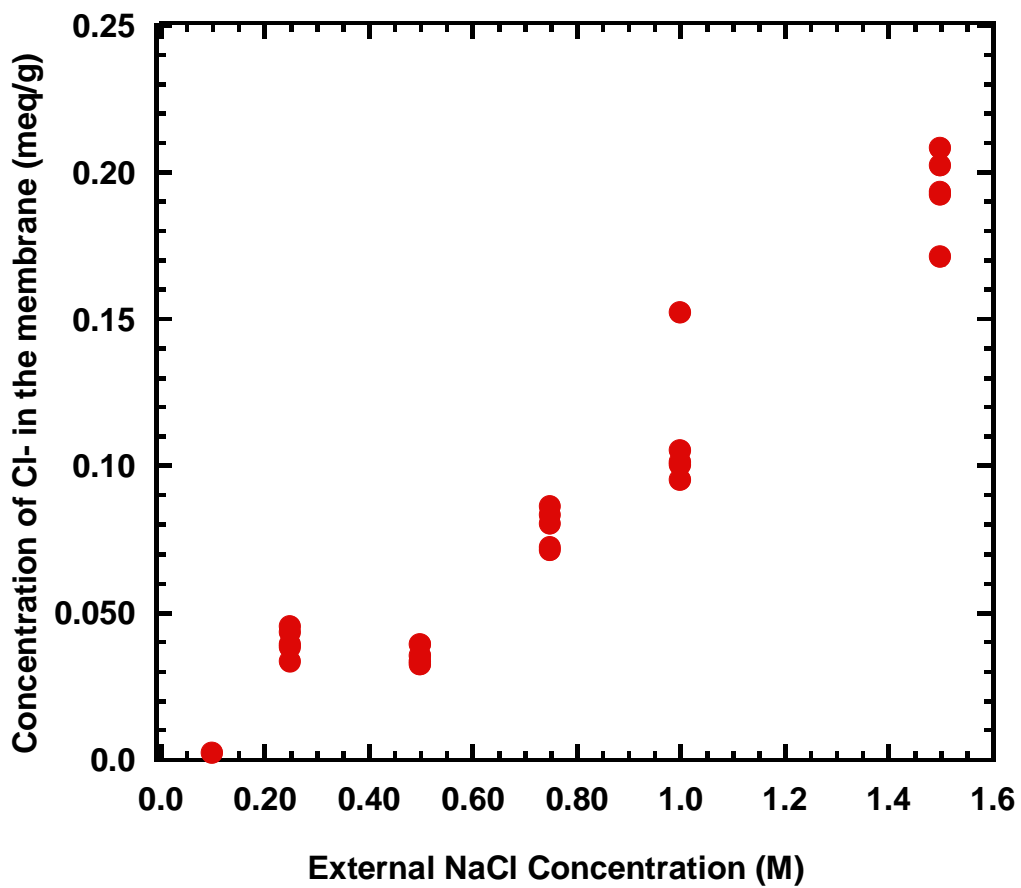


Figure 5. Plot of concentration of chloride ion in the membrane at equilibrium with an external soaking solution vs. the concentration of NaCl in the external soaking solution.

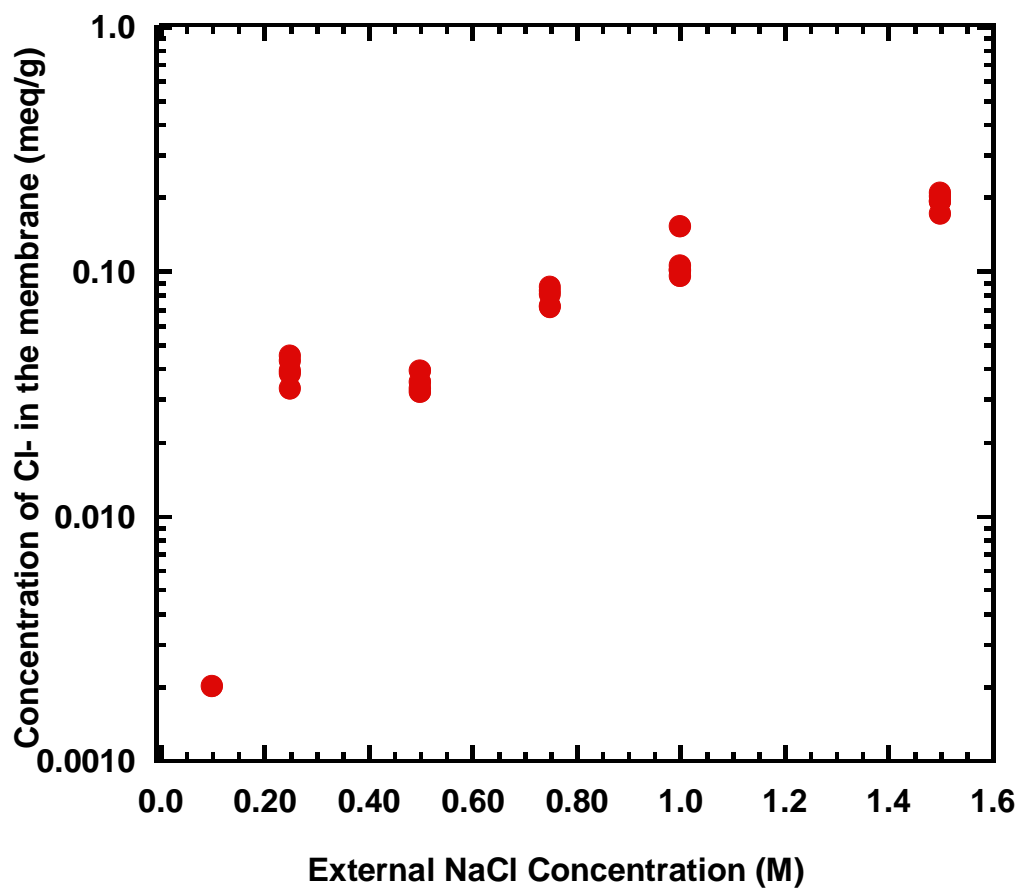


Figure 6. Plot of concentration of chloride ion in the membrane at equilibrium with an external soaking solution vs. the concentration of NaCl in the external soaking solution using a logarithmic scale for the y-axis.

Ion and Sodium Chloride Partition Coefficients

It was desired to measure the partition coefficient of sodium chloride in the membrane, K_{NaCl} , as defined in equation 12. Table 4 summarizes the values for K_{NaCl} at varying concentrations of sodium chloride in the external soaking solution. These values were calculated using the experimentally determined values for the amount of chloride in the membrane and the measured value of the volume of the hydrated membrane to get the C_s^m values. The volume of the hydrated polymer used to calculate C_s^m was equal to 0.509 cm^3 except for the membranes equilibrated in 0.1M NaCl, for which a larger sample size was used and the volume of the hydrated polymer was equal to 4.44 cm^3 . The polymer samples of the same diameter have the same volume because the same die was used to cut the samples and the same mold was used to make the membranes. The concentration of chloride in the membrane at equilibrium with external soaking solutions of increasing sodium chloride concentrations leads to the increase of the partition coefficient as external soaking solution concentration increases.

Table 4. Sodium chloride partition coefficient, K_{NaCl} .

| External Soaking Solution NaCl Concentration (M) | 0.10 | 0.25 | 0.50 | 0.75 | 1.00 | 1.50 |
|--|-------------|-------------|-------------|-------------|-------------|-------------|
| K_{NaCl} | 0.024±0.001 | 0.117±0.004 | 0.112±0.005 | 0.166±0.004 | 0.175±0.003 | 0.252±0.003 |
| | 0.021±0.001 | 0.091±0.004 | 0.122±0.005 | 0.198±0.004 | 0.181±0.003 | 0.242±0.003 |
| | 0.022±0.001 | 0.102±0.004 | 0.114±0.005 | 0.175±0.004 | 0.156±0.003 | 0.185±0.003 |
| | 0.020±0.001 | 0.100±0.004 | 0.104±0.005 | 0.177±0.004 | 0.161±0.003 | 0.227±0.003 |
| | 0.022±0.001 | 0.118±0.004 | 0.108±0.005 | 0.177±0.004 | 0.210±0.003 | 0.251±0.003 |
| Average | 0.022 | 0.106 | 0.112 | 0.178 | 0.177 | 0.232 |
| Standard Deviation | 0.002 | 0.012 | 0.007 | 0.012 | 0.021 | 0.028 |

The values in Table 4 are plotted in Figure 7, including error bars calculated using the upper and lower error limits for the IC, though they are too small to see. According to Helfferich¹, it is expected to see positive curvature in a plot of the co-ion partition coefficient versus concentration of the external soaking solution if Donnan Exclusion is significant. Also seen in Figure 7 are curves for K_s , the partition coefficient for sodium chloride in the membrane as calculated using the right hand side of equation 16. The volume of the hydrated polymer used to calculate ρ_m seen equation 13 was equal to 0.509 cm³ except for the membranes equilibrated in 0.1M NaCl, for which a larger sample size

was used and the volume of the hydrated polymer was equal to 4.44 cm^3 . As mentioned previously, ρ_m is the mass of the dry membrane divided by the volume of the swollen membrane. The IEC value used in the calculation of C_A^m was 1.19. For the curve, the value of $\frac{\gamma_{\pm}^s}{\gamma_{\pm}^m}$ has been approximated as K_{∞} as seen in equation 17. Here, the K_{∞} value is the value for K_{NaCl} for an external soaking solution of 1.5M NaCl. The two curves for K_s seen in the plot were determined using the upper and lower values of K_{∞} to solve the right hand side of equation 16 for K_s . Additionally, if Donnan Exclusion is significant the data for K_{NaCl} as determined using equation 12 is expected to approximately follow the trend seen for K_s as determined using equation 16⁶. This is seen in Figure 7.

Table 5. Values of C_A^m calculated using equation 13 and the values for C_s^s and the mass of the dry polymer.

| C_s^s (M) | 0.1 | 0.25 | 0.5 | 0.75 | 1 | 1.5 |
|---|--------|--------|--------|--------|--------|--------|
| Mass of Dry Polymer (g) | 0.5440 | 0.0561 | 0.0561 | 0.0561 | 0.0561 | 0.0598 |
| | 0.4986 | 0.0524 | 0.0550 | 0.0550 | 0.0550 | 0.0605 |
| | 0.5130 | 0.0510 | 0.0524 | 0.0524 | 0.0524 | 0.0551 |
| | 0.5666 | 0.0442 | 0.0510 | 0.0510 | 0.0510 | 0.0564 |
| | 0.4778 | 0.0492 | 0.0442 | 0.0592 | 0.0442 | 0.0580 |
| C_A^m (meq/cm ³ hydrated Membrane) | 0.15 | 0.13 | 0.13 | 0.13 | 0.13 | 0.14 |
| | 0.13 | 0.12 | 0.13 | 0.13 | 0.13 | 0.14 |
| | 0.14 | 0.12 | 0.12 | 0.12 | 0.12 | 0.13 |
| | 0.15 | 0.10 | 0.12 | 0.12 | 0.12 | 0.13 |
| | 0.13 | 0.12 | 0.10 | 0.14 | 0.10 | 0.14 |

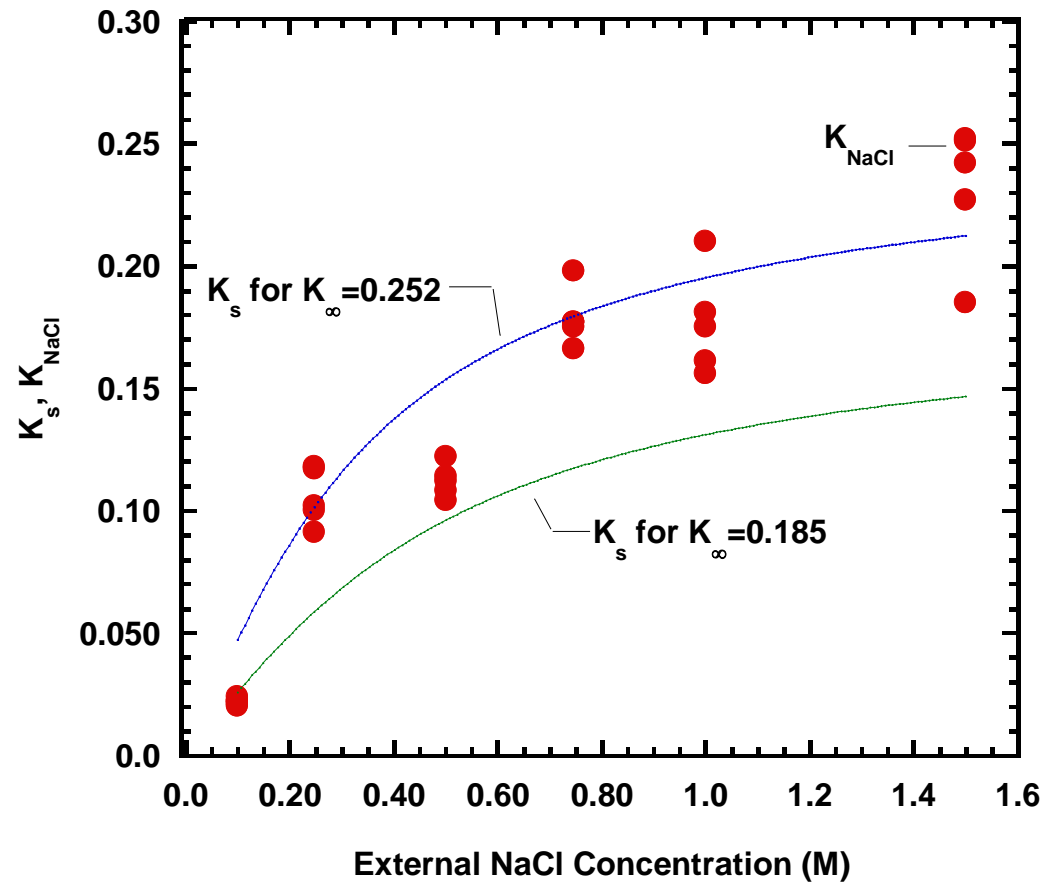


Figure 7. Range of sodium chloride partition coefficient, K_{NaCl} , values as determined by equation 12, and the K_s values as determined using equation 16 vs. the concentration of sodium chloride in the external soaking solution. Shown are two sets of K_s , in which the upper and lower values of K_∞ were used.

The same experiments performed on the BPSH-32 material to determine ion concentration and the sodium chloride partition coefficient were also conducted on membrane samples made from material that is not an ion exchanger, cross-linked polyethylene glycol (PEG) with 43.1% water weight. The membrane was made by Hao Ju, Ph.D. candidate in the Dr. Benny Freeman laboratory at The University of Texas at Austin. The experiments were performed using 0.5M NaCl as the external soaking solution. The data in Table 6 show that the amount of sodium in the membrane was approximately equal to the amount of chloride present, which is expected for a material that does not act as an ion exchanger. It should also be noted that there was no change in the pH of the external soaking solution during equilibration of the membrane with the solution.

Table 6. Ion concentration and salt partition coefficient values for cross-linked PEG.

| | Na ⁺ Concentration (meq/g hydrated membrane) | Cl ⁻ Concentration (meq/g hydrated membrane) | K _{NaCl} (g NaCl/cm ³ film) / (g NaCl/cm ³ solution) |
|-----------------------------|---|---|---|
| | 0.066±0.000 | 0.061±0.002 | 0.148±0.004 |
| | 0.067±0.000 | 0.062±0.002 | 0.176±0.004 |
| | 0.063±0.000 | 0.061±0.002 | 0.146±0.004 |
| | 0.075±0.000 | 0.061±0.002 | 0.152±0.004 |
| | 0.062±0.000 | 0.061±0.002 | 0.162±0.004 |
| Average | 0.067 | 0.061 | 0.157 |
| Standard Deviation | 0.005 | 0.000 | 0.012 |
| Values determined by Hao Ju | -- | -- | 0.169 |

In addition to the experiments described above, ¹H, ²³Na, and ³⁵Cl solid-state NMR (SSNMR) analysis was also performed on BPSH-32 membrane samples for further insight into not only the amounts of sodium, chloride and proton ions relative to one another in the membrane, but also the interactions occurring between the membrane and the ions. The analysis was performed by Dr. Tim Bastow and his colleagues at CSIRO Materials Science and Engineering in Clayton, Victoria, Australia. The membrane samples were equilibrated in 0.5M NaCl using the procedure described above. The results of the analysis show that there is at least some sodium mobility in the sample as well as that some of the sodium in the membrane is highly immobile or tightly bound.

Additionally, it was difficult to detect the presence of chloride in the membrane. These conclusions are consistent with the data presented here and provide qualitative evidence that the concentration of sodium in the membrane is much greater than that of chloride. Also supported is the conclusion that sodium exists in two environments, as there would be sodium present in the membrane from ion exchange and associated with the sulfonate groups as well as mobile sodium which entered the membrane with chloride. The results of the analysis contribute to the evidence that Donnan Exclusion is significant in the BPSH-32 membrane.

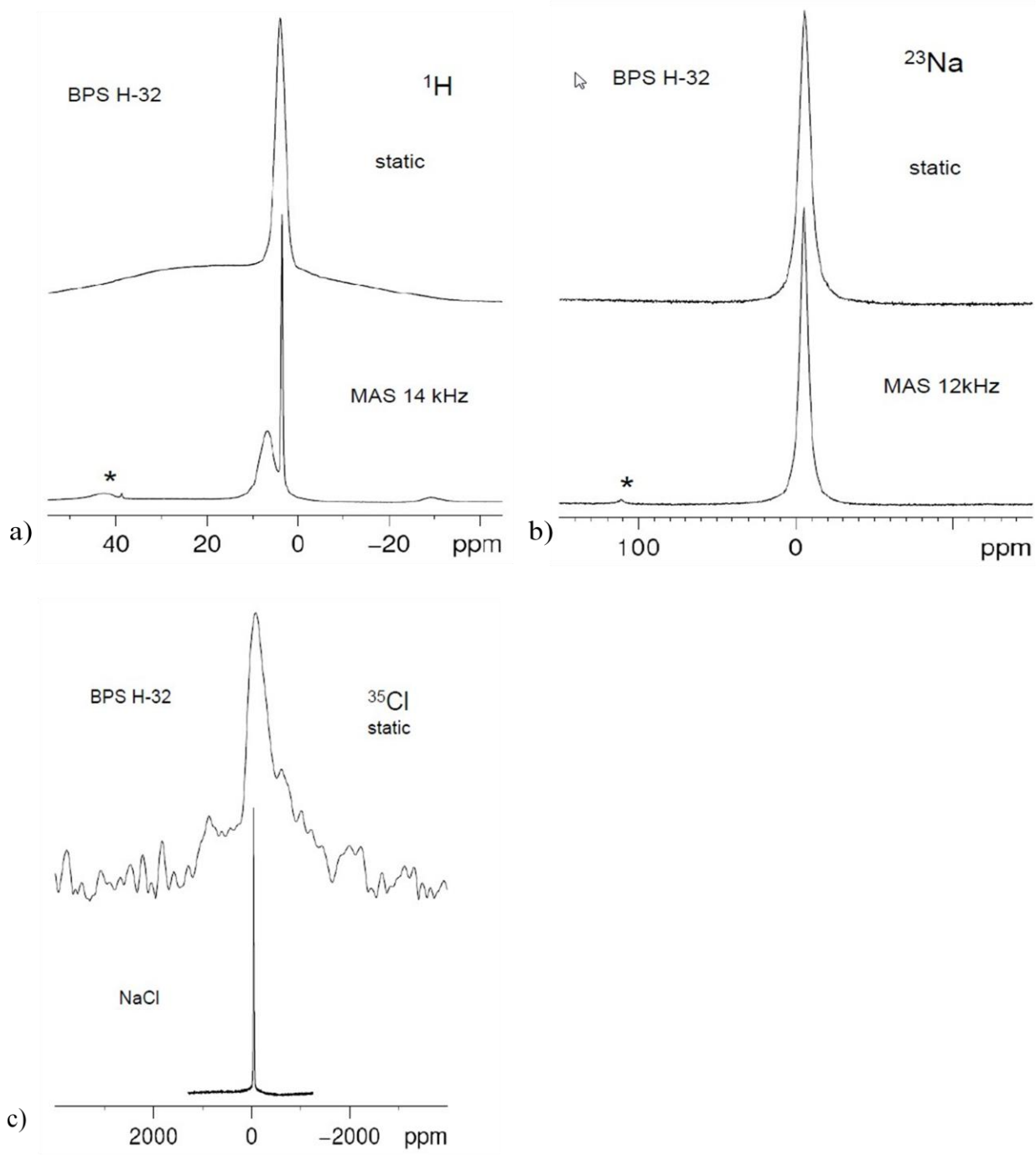


Figure 8. a) ^1H SSNMR spectra b) ^{23}Na SSNMR spectra and c) ^{35}Cl SSNMR spectra of BPSH-32 equilibrated in 0.5M NaCl.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

Using the ashing and desorption techniques for the analysis of sodium and chloride, respectively, have shown the concentration of sodium in the membrane to be significantly greater than that of chloride. Additionally, the difference between the two is approximately the IEC. The trends in the concentrations as well as in the partition coefficients are consistent with Donnan Exclusion as explained by Helfferich and Geise, et al.

Experiments were initially begun with BPSH-40 for which initial data showed the same trend of a greater concentration of sodium than chloride in the membrane. Later, the material of choice for this work was changed to BPSH-32 because a more consistent supply was readily available. For the BPS materials, it would at first glance be expected that a higher fixed charge density, i.e., higher percent sulfonation, would result in decreased salt permeability due to increased exclusion of chloride. As seen in other work, this is not necessarily the case⁴. Sulfonation of the polysulfone material is performed to increase water uptake by the membrane, causing an increase of copolymer swelling pressure. The resulting electrostatic repulsion effects can eventually cause the material to become more ineffective at rejecting salts. Future work on BPS materials of varying IEC as well as ion exchanged materials using the above procedures could be performed.

References

1. Helfferich, F. Ion Exchange; Dover Publications, Inc.: New York, 1995
2. Pintauro, P. N.; Bennion, D. N. Industrial & Engineering Chemistry Fundamentals., 1984, 23(2), 234-243
3. United Nations. UN Booklet: Water for Life Decade 2005-2010; <http://www.un.org/waterforlifedecade/pdf/waterforlifebklt-e.pdf> . 2009
4. Paul, M.; Park, H. B.; Freeman, B. D.; Roy, A.; McGrath, J.E.; Riffle, J.S. Polymer. Volume 49, Issue 9.
5. Department of Geosciences, The University of Texas at Austin. ICP-MS Lab Research Page; <https://webpace.utexas.edu/wg3486/geo-web-folders/miller/QuadICPMSlab/ICP-MS/Home.html>
6. Geise, G.M., H.-S. Lee, D.J. Miller, B.D. Freeman, J.E. McGrath, and D.R. Paul, "Water Purification by Membranes: The Role of Polymer Science," Journal of Polymer Science: Part B. Polymer Physics, in press
7. Duer, Melinda J. (Ed.). Solid-State NMR Spectroscopy Principles and Applications; Blackwell Science, Ltd.: Malden, MA, 2002.
8. Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. Transport Phenomena, 2nd Ed.; Wiley: New York, 2002.
9. Millipore Corporation. Types of Filtration; http://www.millipore.com/membrane/mrc3/filtration_types. 2009.

10. National Archives and Records Administration Code of Federal Regulations. 40 CFR 136 Guidelines Establishing Test Procedures for the Analysis of Pollutants; http://www.gpo.gov/nara/cfr/waisidx_98/40cfr136_98.html
11. Lonsdale, H.K.; Merten, U.; Riley, R. L. Journal of Applied Polymer Science 1965, 9, 1341-1362.
12. Baker, R.W. Membrane Technology and Applications, 2nd Ed.; John Wiley: New York, 2004.
13. Park, H. B.; Freeman, B. D.; Zhang, Z.; Sankir, M.; McGrath, J. E. Angewandte Chemie 2008, 120, 6108-6113
14. Glater, J.; Hong, S.K. Hong; Elimelech, M. Desalination, 1994. 95: p. 325-345.
15. Avlonitis, S.; Hanbury, W.T.; Hidekiss, T. Chlorine Degradation of Aromatic Polyamides. Desalination, 1992. 85: p. 321-334.
16. Lonsdale, H. K.; Merten, U.; Riley, R. L. Journal of Applied Polymer Science, 9 (1965) 1341-1362.
17. IBM Corporation. Water: A Global Innovation Outlook Report. http://www.ibm.com/ibm/gio/media/pdf/ibm_gio_water_report.pdf. 2009.
18. Fisher Scientific. Product specifications; http://www.fishersci.com/wps/portal/PRODUCTDETAIL?prodcutdetail='prod'&productId=795231&catalogId=29104&matchedCatNo=07955H||07955E||07955J||07955A||07955F||07955D||07955B||07955G&pos=1&catCode=RE_SC&endecaSearchQuery=%23store%3DScientific%23N%3D0%23rpp%3D15&fromCat=yes&keepSessionSea

[rchOutPut=true&fromSearch=Y&searchKey=crucibles||porcelain||crucible&highlightProductsItemsFlag=Y](#). 2009.

19. Morel, F. M. Hering, J. G. Principles and Applications of Aquatic Chemistry; John Wiley & Sons, Inc.: New York, 1993.
20. Harris, D. C. Quantitative Chemical Analysis; W. H. Freeman and Co., 2007. 7th ed.
21. Mason, E. A. Journal of Membrane Science 1991, 60, 125-145.
22. Paul, D. R. Journal of Membrane Science 2004, 241, 371-386.
23. Pusch, W. Desalination 1986, 59, 105-198.
24. Glueckauf, E.; Watts, R. E. Proceedings of the Royal Society of London, Series A, Mathematical, Physical and Engineering Sciences 1962, 268, 339-349.
25. Greenlee, L. F.; Lawler, D. F.; Freeman, B. D.; Marrot, B.; Moulin, P. Water Research 2009, 43, 2317-2348.
26. Wang, F.; Hicknew, Y. S.; Xawodzinski, T. A.; McGrath, J. E. Journal of Membrane Science. 2002, 197, 231-242.

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