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Sodium chloride diffusion in sulfonated polymers for membrane applications

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ABSTRACT

Sodium chloride permeability and sorption measurements were used to calculate average salt diffusion coefficients for charged, sulfonated polymers of interest for membrane applications. A sulfonated polysulfone random copolymer and two phase-separated, sulfonated styrenic pentablock copolymers were considered, and data for these materials were compared with those for an uncharged cross-linked poly(ethylene glycol diacrylate) hydrogel. The average salt diffusion coefficients reported for the block copolymers are apparent salt diffusion coefficients because the values have not been adjusted for the polymer's phase separated morphology. The sodium chloride permeability of the uncharged hydrogel decreases by about 16% as upstream salt concentration increases from 0.01 to 1 mol L⁻¹. This salt permeability change results from a decrease in the salt diffusion coefficient with increasing salt concentration because the polymer's water content decreases as salt concentration increases (i.e., osmotic de-swelling). This decrease in salt diffusion coefficient is consistent with free volume theory, wherein a decrease in water content leads to a decrease in free volume, thereby decreasing the salt diffusion coefficient and, in turn, salt permeability. In contrast, the sodium chloride permeability of the charged polymers increases by more than an order of magnitude as upstream salt concentration increases from 0.01 to 1 mol L⁻¹. This salt permeability increase is due to increases in both mobile salt sorption and diffusion coefficients with increasing salt concentration, despite the fact that water content (and, therefore, free volume) in the polymer decreases as salt concentration increases. Thus, the increase in salt diffusion coefficient with increasing salt concentration in the charged polymers results from factors (which are currently poorly understood) other than simply water uptake or free volume.

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1. Introduction

Charged polymers, such as sulfonated polymers, are of interest for a variety of membrane applications aimed at addressing water and energy needs [1–7]. These applications include separation-based technologies, such as desalination and reverse osmosis (RO) [8–13], forward osmosis (FO) [14–16], electrodialysis (ED) [9,17–20], membrane-assisted capacitive deionization (CDI) [21–26], and energy production technologies, such as pressure retarded osmosis (PRO) [27–31], reverse electrodialysis (RED) [17–20,30,32–35], and fuel cells [3,35–37]. The ion permeability of membranes used in these applications is a critical property, and the efficiency of many of these technologies relies on controlling ion transport rates.

Introduction of polymer charge through, for example, sulfonation of a polymer backbone or side chains can profoundly influence salt permeability and sorption properties of a polymer in part because these charged groups markedly increase water uptake in such polymers, and water content has a strong impact on both water

and ion transport [10,12,13,38–43]. Additionally, these charged groups can interact with ions that sorb into and diffuse through the polymer [12,44–46]. Previously, we reported the influence of polymer charge on salt sorption in sulfonated polymers and compared the observed behavior with that in an uncharged poly(ethylene glycol) hydrogel [44]. In this study, we compare sodium chloride diffusion properties of sulfonated polymers to those of an uncharged hydrogel to further study the impact of charged groups on salt transport. This study focuses on the transport of mobile salt through polymers due to the importance of such salt transport in applications such as desalination or PRO.

As indicated in Fig. 1, the focus of this study is steady state transport of salt through a thin, nonporous polymer film in contact with two essentially infinite aqueous salt solutions of different salt concentrations. Salt diffuses through the film from the high salt concentration solution contacting one face of the film into the low salt concentration solution contiguous to the other face of the film. The term “mobile salt” refers to cations and anions (e.g., sodium chloride) that diffuse through the swollen polymer matrix from the high concentration solution into the low concentration solution. For each anion that sorbs into an uncharged polymer, a cation also sorbs into the polymer to maintain electro-neutrality, so all cations and

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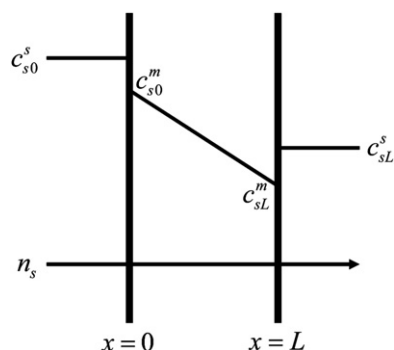


Fig. 1. Steady-state salt flux and mobile salt concentration profile in a dense, nonporous polymer film.

anions contribute to mobile salt [44]. In contrast, a polymer bearing fixed charges contains an excess of counter-ions (i.e., ions of opposite charge to the fixed charge on the polymer backbone or side chain) compared to co-ions to maintain electro-neutrality in the polymer. Thus, a cation exchange material, such as the sulfonated polymers considered in this study, would have more cations (e.g., sodium ions) sorbed in it than anions (e.g., chloride ions) because some of the sorbed cations associate with the negatively charged groups within the polymer to form electrically neutral cation/anion pairs with those groups [44,47,48]. In addition to cations that sorb into the polymer and are associated with a fixed negative charge on the polymer, additional cations can sorb into the polymer without being associated with a fixed negative charge on the polymer. These cations sorb with an equivalent number of anions from solution to maintain electro-neutrality in the polymer, and these cations and anions are mobile and may diffuse into, through, and out of the polymer. Therefore, the mobile salt in a cation exchange material is composed of anions (i.e., co-ions) and the cations required to maintain electro-neutrality with those anions [12,45,47–51]. In many cases of practical interest, the vast majority of the cations are associated with the polymer's sulfonate groups and do not, therefore, contribute to the mobile salt concentration [12,45,47–51].

Salt transport through dense, nonporous polymers occurs via a solution-diffusion process whereby mobile ions sorb into the polymer matrix at the upstream face of the polymer, diffuse down a concentration (i.e., chemical potential) gradient, and desorb at the downstream face of the polymer [52–54]. Fig. 1 illustrates the steady-state salt flux, n_s , and the simplest possible mobile salt concentration profile (i.e., linear) in a dense, nonporous polymer film of thickness L . In this figure, c_{s0}^s and c_{sL}^s are the concentrations of salt in the external bulk solutions contiguous to the upstream and downstream faces of the film, respectively. c_{s0}^m and c_{sL}^m are the concentrations of mobile salt sorbed in the polymer (or membrane) phase at the upstream and downstream sides of the film, respectively. Thermodynamic equilibrium exists at each membrane–solution interface, and a mobile salt sorption (or partition) coefficient, K_s , describes the relationship between the mobile salt concentration in the polymer and that in the contiguous external solution [44,45,47,48,55].

At steady state, Fick's law can be applied to the polymer to describe the diffusive salt flux, and the salt flux can be written as [53,56]

$$n_s = D_s \frac{c_{s0}^m - c_{sL}^m}{L} \quad (1)$$

where D_s is the concentration averaged salt diffusion coefficient:

$$D_s \equiv \frac{1}{c_{s0}^m - c_{sL}^m} \int_{c_{s0}^m}^{c_{sL}^m} D_{sp} dc_s^m \quad (2)$$

where D_{sp} is the mutual diffusion coefficient of mobile salt through the polymer. Salt permeability is defined as [57]

$$P_s \equiv \frac{n_s L}{c_{s0}^s - c_{sL}^s} \quad (3)$$

In these studies, the upstream salt concentrations in both the external solution (superscript s), c_{s0}^s , and the polymer matrix in contact with that solution, c_{s0}^m , are typically much greater than the downstream salt concentrations in the external solution, c_{sL}^s , and in the polymer matrix in contact with that solution, c_{sL}^m . That is, $c_{s0}^s \gg c_{sL}^s$ and $c_{s0}^m \gg c_{sL}^m$. In this limit, Eqs. (1) and (3) can be combined and simplified to relate the salt permeability to the salt diffusion and sorption coefficients [52,53]:

$$P_s = D_s \frac{c_{s0}^m}{c_{s0}^s} = D_s K_s \quad (4)$$

Thus, if one measures the equilibrium mobile salt sorption coefficient in a polymer and the steady state permeability under conditions where the downstream salt concentration is negligible relative to the upstream salt concentration, Eq. (4) can be used to calculate the average (i.e., effective) salt diffusion coefficient, D_s .

This study uses salt permeability and mobile salt sorption coefficient measurements to determine sodium chloride diffusion coefficients, D_s , for a sulfonated polysulfone random copolymer and two sulfonated styrenic pentablock copolymers. While the reported salt diffusion coefficients are averaged values (cf., Eq. (2)), the D_s values reported for the block copolymers are also apparent salt diffusion coefficients because D_s has not been adjusted to account for the phase separated nature of the polymer. Currently, there is insufficient detailed information regarding the morphology of these materials to permit an unambiguous calculation of the average salt diffusion coefficient in the hydrophilic micro-domains of these polymers, which are presumed to be the locus of essentially all of the salt sorption and transport in the polymer. The D_s values from the sulfonated (i.e., charged) polymers are compared with those from an uncharged cross-linked poly(ethylene glycol diacrylate) hydrogel to explore the influence of polymer charge on mobile salt diffusion properties. Salt diffusion coefficients are reported as a function of upstream external solution salt concentration, and the data are compared to predictions from free volume theory. According to free volume theory, changes in a polymer's water content as external solution salt concentration is varied will influence the salt diffusion coefficient in the polymer [40,41,58].

2. Materials and methods

2.1. Polymers

Polymers considered in this study include a cross-linked poly(ethylene glycol diacrylate) hydrogel (XLPEGDA), whose structure is shown in Fig. 2A [59], a sulfonated polysulfone random copolymer (BPSH), whose structure is shown in Fig. 2B [39,60–63], and a sulfonated styrenic pentablock copolymer (SPBC), whose structure is shown in Fig. 2C [10,11,13,44,64–66]. The XLPEGDA and BPSH polymers are microscopically homogeneous, but the sulfonated styrenic pentablock copolymer micro-phase separates into hydrophilic and hydrophobic micro-domains [13,64,67].

The XLPEGDA hydrogel was prepared by mixing poly(ethylene glycol diacrylate) (average $M_n = 700 \text{ g mol}^{-1}$, catalog number 455008, Sigma-Aldrich, St. Louis, MO) with 0.1 wt% 1-hydroxycyclohexyl phenyl ketone (HCPK) and 45 wt% de-ionized (DI) water. HCPK is a UV-sensitive free-radical initiator [59]. The reaction mixture was cured under 312 nm UV radiation

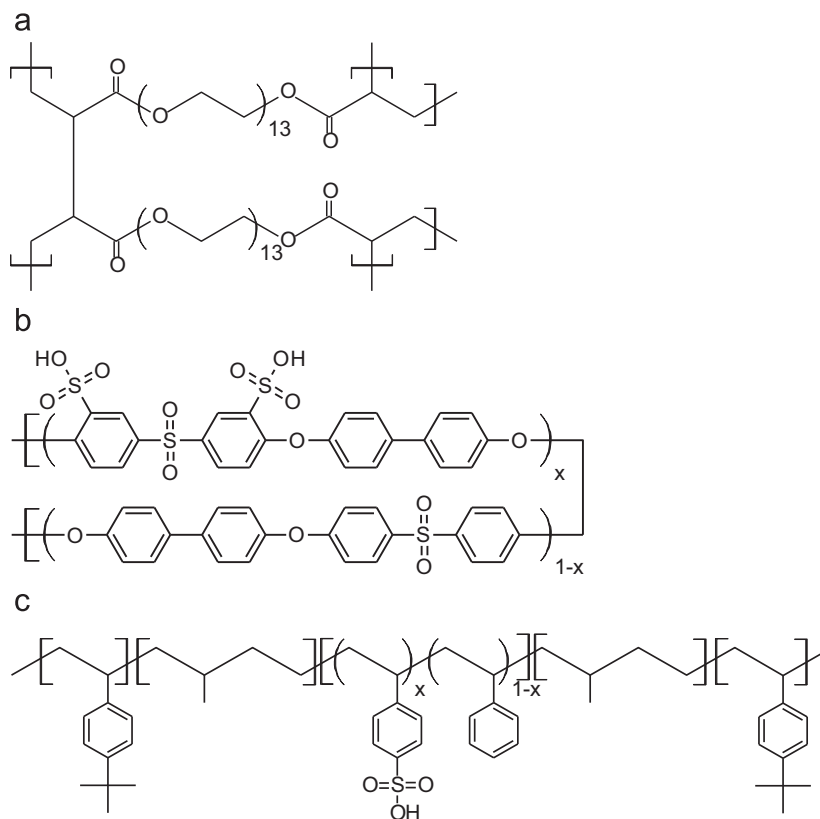


Fig. 2. Structures of the polymers considered in this study: (a) cross-linked poly(ethylene glycol diacrylate) (XLPEGDA), (b) acid-form sulfonated poly(arylene ether sulfone) random copolymer (BPSH), and (c) acid-form sulfonated styrenic pentablock copolymer (sPBC).

for 90 s at 3.0 mW cm^{-2} to produce solid, transparent, cross-linked polymer films [59].

The sulfonated poly(arylene ether sulfone) was prepared from 32 mol% (i.e., $x=0.32$ in Fig. 2B) sulfonated potassium-form polymer purchased from Akron Polymer Systems (Akron, OH) [60]. The as-received polymer was cast onto an isopropyl alcohol-treated glass plate from a 5 wt% polymer in *N,N*-dimethylacetamide solution that had been filtered through a $0.45 \mu\text{m}$ glass microfiber syringe filter (WhatmanTM GD/X) as described previously [44]. This film was then boiled sequentially in 0.5 M H_2SO_4 for 2 h and DI water for 2 h to produce the final acid-form BPSH-32 polymer [44,68]. The acid-form ion exchange capacity (IEC) of BPSH-32 has been reported to be approximately $1.23\text{--}1.34 \text{ meq g}^{-1}$ (dry polymer) [44].

Two sulfonated pentablock copolymers were considered, and these acid-form polymer films were prepared and kindly provided by Kraton Performance Polymers, Inc. (Houston, TX) [65,69,70]. The films were cast from a ~ 10 wt% micellar suspension of polymer in 72:28 (by mass) heptane:cyclohexane [64,71]. Solvent was removed by exposing the suspension, cast on a silane treated glass plate, to ambient temperature in a $\sim 50\%$ relative humidity nitrogen purge [10,13,66]. The sPBC-1.5 polymer had an acid-form IEC of 1.5 meq g^{-1} (dry polymer) and a degree of sulfonation (i.e., “x” in Fig. 2C) of 0.39, and the sPBC-2.0 polymer had an acid-form IEC of 2.0 meq g^{-1} (dry polymer) and a degree of sulfonation (i.e., “x” in Fig. 2C) of 0.52.

All polymer films were rinsed and soaked in DI water for at least 24 h to remove residual solvent and/or reaction byproducts from the films before performing further experiments [10,59,68]. Additionally, this step ensured that the polymer films were fully hydrated before measuring their properties. Finally, the films were cut into circular disks before use. The approximate thickness of the XLPEGDA films was $100 \mu\text{m}$, and the thicknesses of the

sPBC and BPSH films were in the range of $25\text{--}55 \mu\text{m}$. For a given sample, the variation in film thickness was typically $< 10\%$.

2.2. Water uptake measurement

Water uptake was measured gravimetrically. Film samples were equilibrated in either DI water or salt solutions of known concentration. After reaching equilibrium, the wet mass of the sample, m_{wet} , was measured after carefully removing surface water from the film. The films were placed in covered petri dishes and dried at room temperature under vacuum. Once the polymer's mass stabilized, the dry mass of the sample, m_{dry} , was measured. Water uptake, w_u , was calculated as

$$w_u = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (5)$$

The experimental uncertainty in the water uptake measurements, determined as the standard deviation of water uptake values measured for at least three samples, was less than 5% of the average water uptake value. The volume fraction of water in the polymer can be estimated, assuming volume additivity of water and polymer, which is an appropriate assumption for these polymers [13], as [39]

$$\phi_w^m = \frac{w_u}{w_u + \rho_w / \rho_p} \quad (6)$$

where ρ_w is the density of water, and ρ_p is the dry polymer density. For the polymers considered in this study, the dry polymer densities were: 1.186 g cm^{-3} (XLPEGDA) [58], 1.351 g cm^{-3} (BPSH-32) [68], 1.03 g cm^{-3} (sPBC-1.5) [44], and 1.05 g cm^{-3} (sPBC-2.0) [44]. The density of water was set equal to 1.0 g cm^{-3} [72].

The water sorption coefficient, K_w , was determined from the volume fraction of water in the polymer, ϕ_w^m . The relationship

between K_w and ϕ_w^m is [39]

$$K_w = \frac{\phi_w^m M_w}{c_w^s V_w} \quad (7)$$

where M_w is the molar mass of water (18 g mol^{-1}), V_w is the molar volume of water ($18 \text{ cm}^3 \text{ mol}^{-1}$), and c_w^s is the concentration of water in the external solution. For pure water, $c_w^s = 1.0 \text{ g cm}^{-3}$, and for a $1.0 \text{ mol (NaCl) kg}^{-1}$ (water) solution, which has a density of 1.04 g cm^{-3} (at $25 \text{ }^\circ\text{C}$ and 1 bar) [73], $c_w^s = 0.98 \text{ g (water) cm}^{-3}$, and the corresponding molar concentration of salt in the solution, c_s^s , is $0.98 \text{ mol(NaCl) L}^{-1}$. Therefore, for many solutions of interest for desalination, the water sorption coefficient is essentially equal to the volume fraction of water in the polymer (i.e., $K_w = \phi_w^m$ since $\frac{M_w}{c_w^s V_w} \approx 1$).

2.3. Salt permeability measurement

Sodium chloride permeability coefficients were measured according to previously reported methods [10]. Film samples were clamped between two chambers of a custom glass diffusion cell (PermeGear Side-bi-Side Diffusion Cell, Hellertown, PA). The upstream chamber, which is the donor cell, was filled with a salt solution of desired concentration, and the downstream chamber, the receiver cell, was filled with DI water. The increase in conductivity of the solution in the receiver cell was measured as a function of time, and these conductivity measurements were converted to salt concentration via a calibration curve. By measuring the thickness of the film, L , after the experiment, the salt permeability could be determined from [10,41]

$$\ln \left[1 - 2 \frac{c_{sL}^s[t]}{c_{s0}^s} \right] = -2 \frac{A}{VL} P_s t \quad (8)$$

where A is the area available for mass transfer (1.77 cm^2), V is the volume of the donor and receiver cells (35 mL), t is time, $c_{sL}^s[t]$ is the salt concentration in the downstream chamber at time t , and $c_{s0}^s[0]$ is the initial salt concentration in the upstream chamber [10]. Eq. (8) is valid when the volumes of the donor and receiver cell solutions are equal to one another. Salt permeability was measured at $25 \text{ }^\circ\text{C}$ and atmospheric pressure, and the salt concentration in the downstream chamber was always more than 2 orders of magnitude lower than the salt concentration in the upstream chamber (i.e., $c_{s0}^s \gg c_{sL}^s$ and $c_{s0}^m \gg c_{sL}^m$ as discussed above).

2.4. Salt sorption measurement

The concentrations of cations and anions sorbed in the polymer films were measured as described previously [44]. Mobile salt sorption was quantified by measuring chloride ion sorption in polymer films that had been equilibrated by soaking them in an aqueous solution containing a desired concentration of sodium chloride. As explained earlier, chloride sorption is representative of mobile salt sorption in both uncharged and cation exchange polymers [44,45]. The sulfonated polymer films were thoroughly equilibrated in a sodium chloride solution of desired concentration, c_s^s , at ambient conditions. This equilibration process involved immersing polymer film samples in salt solutions of desired concentration. However, because the charged polymers considered here were initially in the acid counter-ion form, the pH of the solution decreased as ion exchange from the acid to sodium counter-ion form occurred. Thus, the soaking solution was changed several times to simulate exposing the films to an infinite volume of solution and allow ion exchange to proceed to completion. In some cases, to expedite the equilibration process, dilute sodium hydroxide was added to the equilibration solution to neutralize some of the acid released from the polymer during the ion exchange process. The films were considered equilibrated

when the solution pH stabilized in the range of 5.7–6.0, i.e., at or slightly above the pH of water equilibrated in ambient air. These steps ensured that the films were completely equilibrated in the salt solution at near neutral pH [44]. Once the films reached equilibrium, the volume of each hydrated sample, V_p , was determined geometrically by measuring the diameter and thickness of the circular disk. The uncertainty in V_p was calculated to be roughly 14% based on the typically observed variability in thickness ($< 10\%$) and diameter ($< 2\%$) of each sample [44]. The surface water on the films was completely removed, and the films were subsequently immersed in a known volume, V_d , of DI water; the mobile salt sorbed in the polymer matrix then desorbed from the polymer [41,44,58]. The salt concentration of the desorption solution at equilibrium following the desorption step, c_d , was determined by measuring the concentration of chloride ions in the solution using ion chromatography (ICS-2100, Dionex Corp., Sunnyvale, CA). The desorption volume, V_d , was chosen such that the final concentration of salt in the desorption solution, c_d , would be near or less than $1 \text{ mg(NaCl) L}^{-1}$. This target concentration balanced the competing desires to: (1) extract as many ions from the polymer and reach as high a concentration of ions as possible in the desorption solution in order to accurately measure the ion concentration of the desorption solution and (2) have a sufficiently low concentration of ions in the final desorption solution so that there remains no more than a negligible amount of ions in the polymer following desorption [44]. The anion (i.e., mobile salt) sorption coefficient was then calculated as [44]

$$K_s = \frac{c_d V_d}{c_s^s V_p} \quad (9)$$

The units of K_s are mol(Cl) L^{-1} (swollen film)/ mol(Cl) L^{-1} (external solution). However, for purposes of computing the steady state salt permeability through the polymer (cf. Eqs. (3), (4), and (8)), the mobile salt sorption coefficient is exactly equal to K_s and has units of mol(NaCl) L^{-1} (swollen film)/ mol(NaCl) L^{-1} (external solution).

The concentration of anions sorbed per unit volume of hydrated polymer, c_s^m , was calculated as

$$c_s^m = \frac{c_d V_d}{V_p} \quad (10)$$

Like the salt sorption coefficient, the concentration of anions is equal to the concentration of mobile cations in the polymer, so one may also treat c_s^m as the concentration of mobile salt sorbed in the polymer per unit volume of hydrated polymer.

The concentration of mobile salt in the polymer film or membrane, c_s^m , can be plotted against the salt concentration in the surrounding solution, c_s^s , to generate a salt sorption isotherm. The average mobile salt sorption coefficient for the XLPEGDA hydrogel was determined by linear regression of its mobile salt sorption isotherm. This simplified approach was reasonable for this uncharged polymer because the salt concentration sorbed in the polymer increases linearly with the concentration of salt in the external solution, so the mobile salt sorption coefficient is essentially independent of external salt solution concentration over the ranges of salt concentration considered. However, for the sulfonated polymers described above, K_s is sensitive to the external concentration, for reasons that have been described previously [44].

3. Results and discussion

3.1. Uncharged polymers

As shown in Fig. 3, the XLPEGDA salt permeability decreases slightly as salt concentration increases. Over two orders of magnitude

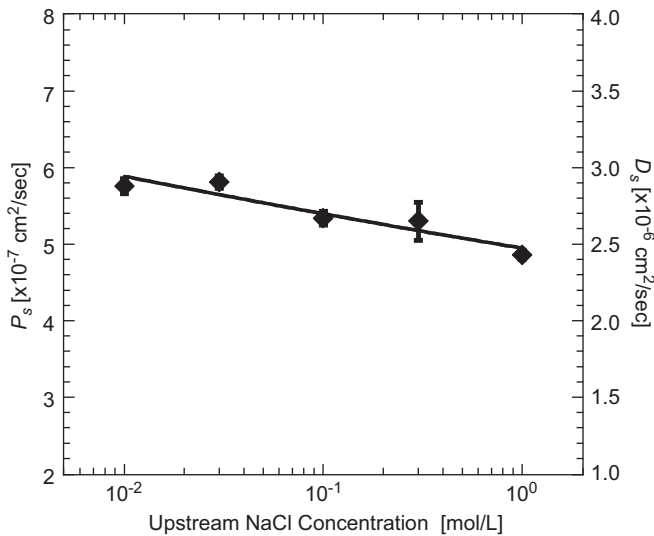


Fig. 3. NaCl permeability and NaCl diffusion coefficients in XLPEGDA versus upstream NaCl concentration. Because the salt sorption coefficient, K_s , for XLPEGDA is constant, both P_s and D_s data may be shown using the same data points, but with different axis labels. Each data point represents the average of measurements made on at least three samples, and the reported uncertainty is one standard deviation from this average.

of salt concentration, the salt permeability decreases by roughly 16%, and this change in salt permeability can be explained within the framework of free volume theory as discussed below. For reference, a salt concentration of 2000 mg(NaCl) L^{-1} , which is often used to test membranes for brackish water desalination, corresponds to 0.034 mol L^{-1} , and a salt concentration of 35,000 mg(NaCl) L^{-1} , which is often used to test membranes for seawater desalination, corresponds to 0.60 mol L^{-1} [12].

As salt concentration in an aqueous solution increases over ranges important for desalination, the thermodynamic activity of water in the solution decreases [74]. Water sorption by a polymer generally decreases as the thermodynamic activity of water surrounding the polymer decreases [75]. The decrease in polymer swelling, due to loss of sorbed water, as the external solution salt concentration increases is called osmotic de-swelling [76]. Table 1 illustrates osmotic de-swelling in the XLPEGDA hydrogel. It shows water uptake and water sorption coefficients, K_w , decreasing with increasing salt concentration in the external solution.

Free volume in water swollen polymers has been found to be proportional to the polymer's water content at least over ranges of water content relevant to the materials considered in this study [40,41,58]. Therefore, as osmotic de-swelling occurs, free volume decreases. Free volume theory has been used to relate average free volume, v_f , in hydrated polymers to the diffusion coefficient of salt, D_s , through such polymers [41,77]:

$$D_s = a \exp \left[-\frac{Yv^*}{v_f} \right] \quad (11)$$

where v^* is the minimum volume of a free volume element required to allow an ion to execute a diffusion step, and a and Y are adjustable constants. When the polymer's free volume is proportional to the polymer's water content (i.e., $v_f = b \times K_w$) [40,41], Eq. (11) can be written as

$$D_s = a \exp \left[-\frac{Yv^*}{bK_w} \right] \quad (12)$$

or (using Eq. (4)):

$$P_s = K_s a \exp \left[-\frac{Yv^*}{bK_w} \right] \quad (13)$$

Table 1
XLPEGDA water uptake and sorption coefficient as a function of NaCl concentration in the external solution at 25 °C.

NaCl concentration (mol L^{-1})	W_w , Water uptake (g(water)/g(dry polymer))	K_w
0	1.02	0.547
0.01	0.948	0.530
0.03	0.930	0.525
0.1	0.924	0.525
0.3	0.892	0.518
1	0.830	0.498

Note: K_w is reported in units of mol(water) L^{-1} (swollen polymer)/mol(water) L^{-1} (solution).

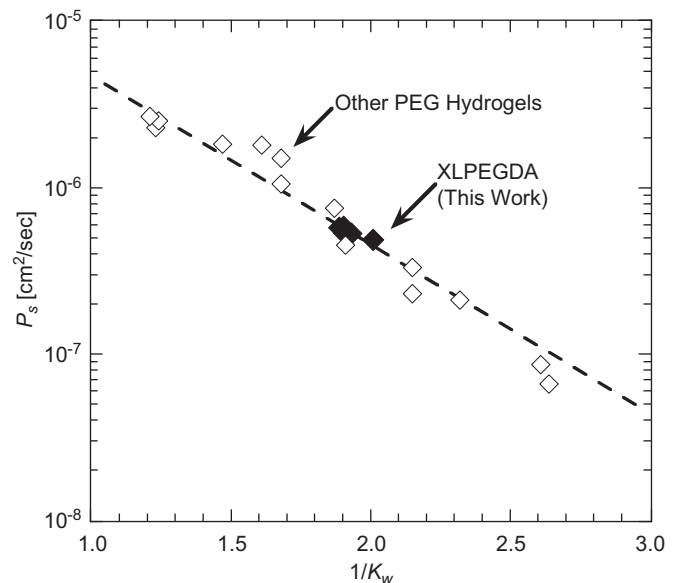


Fig. 4. XLPEGDA NaCl permeability correlated with $1/K_w$ (according to Eq. (13)) and compared to other cross-linked PEG hydrogels where K_w was varied by changing the concentration of water in the solution prior to cross-linking or incorporating a co-monomer [58,78].

where b is an adjustable constant. If K_s is constant, then Eq. (13) suggests that the logarithm of salt permeability should vary linearly with reciprocal water uptake. The salt permeability data from Fig. 3 are presented in the form suggested by Eq. (13) in Fig. 4. The data from Fig. 3, where the water content in the polymer was varied by adjusting the salt content in the external solution, are compared with data for other poly(ethylene glycol) (PEG) hydrogels where the water content has been varied by changing the crosslink density of the polymer by varying either the concentration of water in the pre-polymerization mixture or by incorporating a co-monomer such as poly(ethylene glycol acrylate) in the hydrogel [58,78]. Regardless of whether water content is varied by changing the amount of water in the pre-polymerization mixture, adding a co-monomer, or immersing a film in salt solutions of different concentrations, Fig. 4 shows that the salt permeability data correlate with $1/K_w$ as anticipated by Eq. (13). Based upon this simple picture, exposing XLPEGDA hydrogels to salt solutions of different concentrations changes the water content of the hydrogel which, in turn, changes the hydrogel's free volume, salt diffusion coefficients and, therefore, salt permeability coefficients through the hydrogel.

Using Eq. (4), the salt permeability values in Fig. 3 were combined with the mobile salt sorption coefficient to calculate

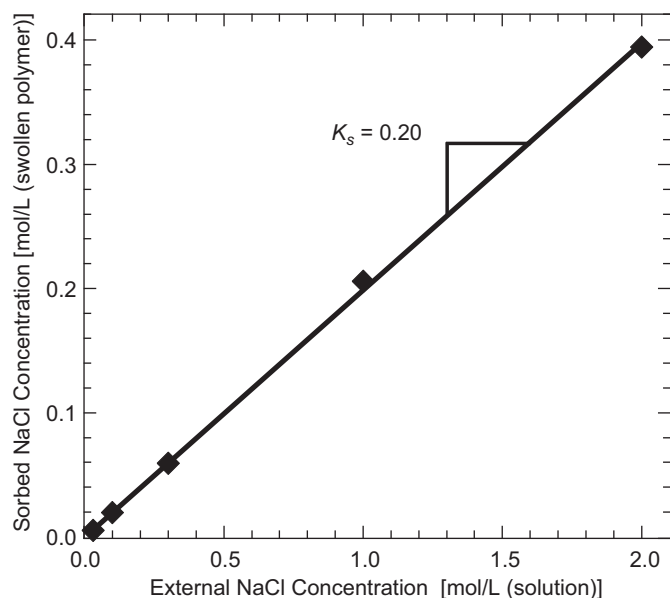


Fig. 5. NaCl sorption isotherm for the XLPEGDA hydrogel. The slope of the line defines the polymer's salt sorption coefficient, which is essentially constant at $K_s = 0.20 \pm 0.003$.

the salt diffusion coefficients in Fig. 3. The mobile salt sorption coefficient was determined from the salt sorption isotherm shown in Fig. 5. Because XLPEGDA does not contain any charged groups, the molar concentrations of sodium and chloride ions dissolved in the polymer are, within the uncertainty of the measurements, exactly equal to each other at each data point, and thus, the mobile salt sorption coefficient is representative of both cation and anion sorption, as expected [44]. The salt concentration in the polymer is reasonably described by a constant K_s value, and constant values of the salt sorption coefficient are typical for such uncharged polymers [44,55,79]. From Fig. 5, the salt sorption coefficient is $K_s = 0.20 \pm 0.003$, which agrees well with previously reported XLPEGDA salt sorption coefficients measured at only a single external salt solution concentration [58].

Because the mobile salt sorption coefficient is independent of salt concentration, the salt diffusion coefficient exhibits the same dependence on salt concentration as salt permeability (cf., Fig. 3). Therefore, for XLPEGDA, the modest decrease in P_s and D_s with increasing external solution salt concentration results from changes in free volume stemming from the depression of water sorption in the polymer due to the decrease in the activity of water as external salt solution concentration increases (i.e., osmotic de-swelling). However, for charged polymers, D_s does not follow the trend observed for XLPEGDA in Fig. 4, and these data will be discussed below.

3.2. Charged sulfonated polymers

Charged polymers differ fundamentally from uncharged polymers because the fixed charges (i.e., sulfonate groups in the materials considered in this study) on the polymer can exert a strong influence on ion sorption properties, above and beyond that associated with the effect of these charged groups on water content in the polymer. For at least this reason, charged groups on a polymer have a strong influence on salt transport properties [12,44,47,48]. At salt solution concentrations of interest for applications such as desalination, sulfonated polymers can sorb considerably more cations, on an equivalent basis, than anions [44]. As a result, sorption and transport of anions in sulfonated

polymers critically influence mobile salt sorption and transport properties [12,45,49–51].

As shown in Fig. 6, and in striking contrast to the XLPEGDA data, the sulfonated polymer salt permeability coefficients increase by more than an order of magnitude as upstream external salt solution concentration increases over 2 orders of magnitude. This behavior is qualitatively representative of many sulfonated polymers [10,12,80]. To some extent, this increase in P_s with increasing upstream salt concentration should be expected for charged polymers because the mobile salt sorption coefficient, K_s , in charged polymers can increase significantly with increasing external solution salt concentration due to enhanced screening of fixed charge groups on the polymer at higher salt concentrations, which limits Donnan exclusion of co-ions (i.e., mobile salt) [44]. This factor alone would tend to increase salt permeability with increasing salt concentration [12]. However, as discussed below, increases in both K_s and D_s with increasing upstream salt solution concentration contribute to the salt permeability behavior in Fig. 6.

To calculate the salt diffusion coefficients from the permeability data, the mobile salt (i.e., anion) sorption coefficients for BPSH-32, sPBC-1.5, and sPBC-2.0 are needed. These coefficients were reported previously, and the data are summarized in Fig. 7 [44]. Unlike the XLPEGDA mobile salt sorption coefficient, which is independent of external salt solution concentration, the sulfonated polymer mobile salt sorption coefficients depend sensitively on external solution salt concentration [44].

The mobile salt sorption coefficients presented in Fig. 7 can be combined with salt permeability measurements from Fig. 6 to calculate salt diffusion coefficients using Eq. (4). The results are presented in Fig. 8. The salt permeability, sorption, and diffusion coefficients from the sPBC materials have not been corrected for the complex phase separated morphology of these materials. In this sense, the sPBC salt permeability and diffusion coefficients are apparent values that should be expected to be sensitive to the polymer's morphology. While the equilibrium salt sorption data can be readily adjusted to account for the fact that the salt

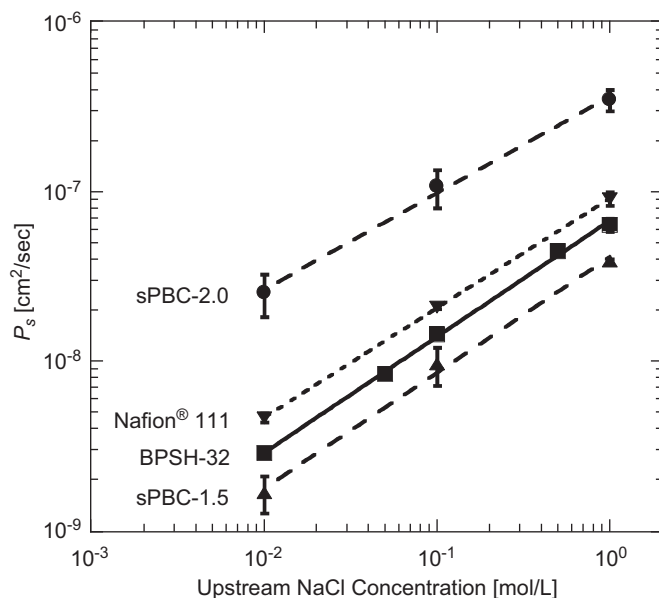


Fig. 6. NaCl permeability versus upstream NaCl concentration for sulfonated polymers [10]. Data for Nafion[®] 111 (a sulfonated perfluoropolymer) are included for comparison. The Nafion[®] 111 films had an IEC of 0.909 meq g⁻¹ (dry polymer), and the dry films were approximately 25 μm thick [81]. Each data point represents the average of measurements made on at least three samples, and the reported uncertainty is one standard deviation from this average.

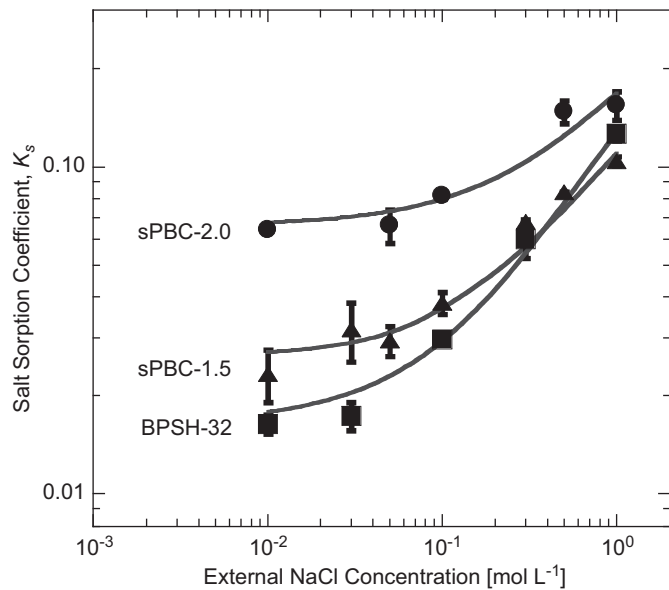


Fig. 7. Mobile salt (i.e., anion) sorption coefficients as a function of salt concentration. The lines are drawn according to a salt sorption model previously reported [44]. Each data point represents the average of measurements made on at least three samples, and the reported uncertainty is one standard deviation from this average. Reprinted from Journal of Membrane Science, G. M. Geise, et al., Sodium chloride sorption in sulfonated polymers for membrane applications, <http://dx.doi.org/10.1016/j.memsci.2012.08.014>, Copyright 2012, with permission from Elsevier.

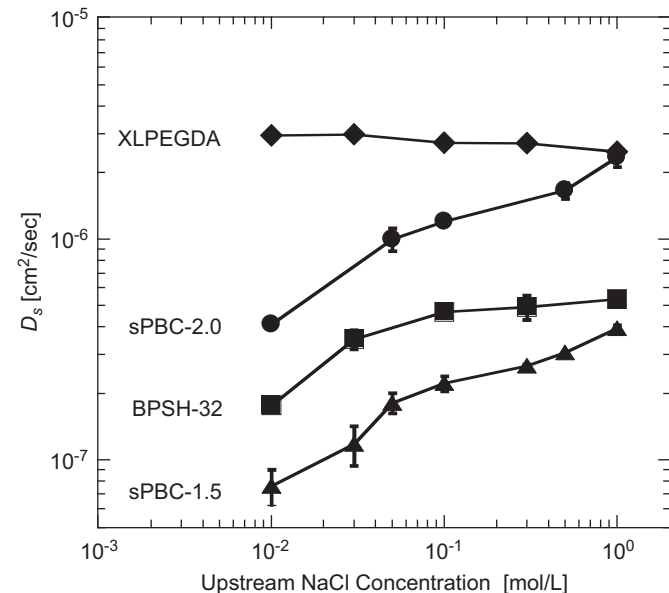


Fig. 8. Salt diffusion coefficients plotted versus NaCl concentration. The lines have been drawn to guide the eye. Each data point represents the average of values from at least three samples, and the reported uncertainty is one standard deviation from this average.

sorption is essentially restricted to the polymer's hydrophilic micro-domains [44], sufficiently detailed information regarding the morphological structure of these materials is not available to make the corresponding adjustments to the salt permeability and diffusion coefficient data [82]. The XLPEGDA salt diffusion coefficient data are also presented in Fig. 8 for comparison. As explained earlier, the D_s values of XLPEGDA decrease slightly with increasing salt concentration. In contrast, the sulfonated polymer D_s values increase with increasing salt concentration.

Table 2
Water uptake and sorption coefficient values for the sulfonated polymers as a function of NaCl concentration.

NaCl concentration (mol L ⁻¹)	BPSH-32		sPBC-1.5		sPBC-2.0	
	w_u	K_w	w_u	K_w	w_u	K_w
0	0.484	0.395	0.669	0.408	1.18	0.553
0.01	0.431	0.368	0.363	0.272	1.01	0.515
0.03	0.414	0.359	0.337	0.258		
0.05					0.897	0.487
0.1	0.408	0.357	0.322	0.250	0.874	0.480
0.3	0.401	0.353	0.290	0.231		
0.5					0.613	0.392
1	0.395	0.347	0.258	0.209	0.497	0.342

Note: Water uptake, w_u , is reported in units of g(water)/g(dry polymer).

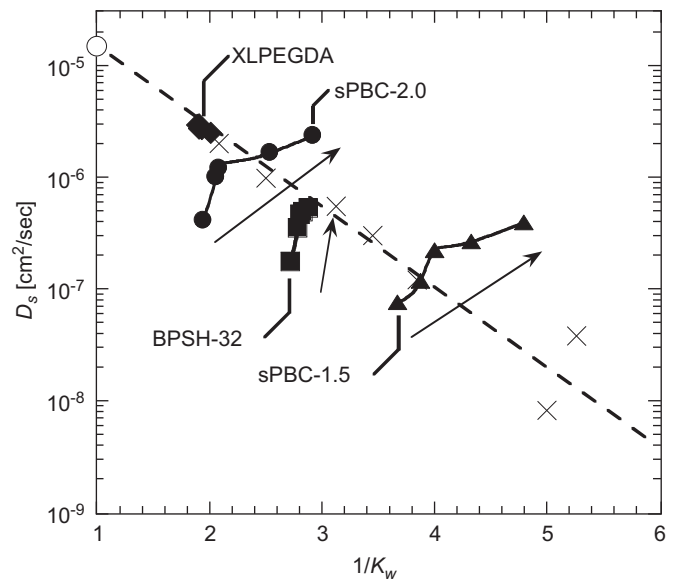


Fig. 9. Relation between equilibrium water sorption coefficients, K_w , and salt diffusion coefficients, D_s , in uncharged and sulfonated polymers. The \times symbols represent previously reported D_s from sulfonated polysulfone measured using a kinetic desorption technique after equilibrating the polymers with 1 mol L⁻¹ aqueous NaCl solution; K_w values for these sulfonated polysulfones were varied by changing the polymer's degree of sulfonation [39]. The diffusion coefficient of NaCl in water is shown as \circ [83]. The dashed line, motivated by Eq. (12), is drawn according to the \times and \circ data. D_s for XLPEGDA (\diamond), BPSH-32 (\blacksquare), sPBC-1.5 (\blacktriangle), and sPBC-2.0 (\bullet) are plotted versus $1/K_w$ where the water sorption coefficients were varied by changing the salt concentration. For these polymers, the arrows denote increases in salt concentration from 0.01 to 1.0 mol L⁻¹. The solid lines connecting the data points are drawn to guide the eye.

Like the XLPEGDA hydrogel, the concentration of water sorbed in the sulfonated polymers decreases as external salt solution concentration increases. Table 2 presents the equilibrium water uptake and water sorption coefficient data for the sulfonated polymers as a function of NaCl concentration in the external solution. However, despite the decrease in water content as external salt concentration increases, the salt diffusion coefficients from the sulfonated polymers increase significantly. This result is quite different from that observed in the uncharged hydrogel, where a decrease in water content in the polymer was accompanied by a decrease in salt diffusion coefficients (cf., Fig. 4), in accordance with free volume theory. The results summarized in Figs. 7 and 8 show that, for the charged polymers, both mobile salt solubility and diffusivity increases contribute to the increase in salt permeability as salt concentration in the upstream solution increases.

To underscore the striking departure of the salt diffusion coefficient data in charged polymers from expectations based on free volume theory, Fig. 9 presents salt diffusion coefficient data as a function of reciprocal water content, following the model set forth in Eq. (12). Previously reported salt diffusion coefficients, which were measured directly using a kinetic desorption technique [41], from sulfonated polysulfone films define the dashed line in Fig. 9. These sulfonated polysulfone films were equilibrated with 1 mol L⁻¹ aqueous sodium chloride solution prior to the kinetic desorption process used to measure D_s [39]. That is, they were all measured at a fixed salt concentration. The water sorption coefficient for the sulfonated polysulfone materials was adjusted by changing the polymer's degree of sulfonation [39]. Additionally, the dashed line in Fig. 9 is drawn to intersect the diffusion coefficient of NaCl in water (1.5×10^{-5} cm² s⁻¹ at 25 °C and 9 mmol L⁻¹ NaCl [83]) when $1/K_w$ is equal to unity, which represents a hypothetical membrane made of water, as discussed elsewhere [10,39,58].

Salt diffusion coefficient data are also plotted in Fig. 9 as a function of reciprocal water sorption coefficient where K_w is varied by changing the concentration of the salt solution used during the measurements. The XLPEGDA data shown in Fig. 9 lie along the dashed line indicating, as mentioned previously, that decreased water sorption, which occurs as the concentration of the contiguous salt solution increases, results in a decrease in the material's salt diffusion coefficient that is consistent with free volume theory [41,58]. In remarkable contrast to this behavior, the salt diffusion coefficients measured in the sulfonated polymers as a function of increasing salt concentration (i.e., BPSH-32, sPBC-1.5, and sPBC-2.0) increase as water sorption decreases, opposite to expectations from free volume theory.

As the external salt solution concentration increases, the concentration of ions sorbed in the polymer increases [44]. In the sulfonated polymers considered in this study, in particular, the concentration of anions (i.e., chloride ions) increased by approximately 2.5–3 orders of magnitude as the external salt concentration increased by approximately 2 orders of magnitude, largely due to reduced Donnan exclusion at higher salt concentrations [44]. Based upon the results in Figs. 8 and 9, changes in the electrical interactions between the polymer's fixed charge groups and the diffusing ions may influence mobile salt diffusion.

The dashed line in Fig. 9 is a fit to free volume theory (i.e., Eq. (12)) of previously reported salt diffusion coefficient data in sulfonated polysulfone samples measured at a constant salt solution concentration (1 mol L⁻¹) (cf. \times symbols in Fig. 9) [39]. This empirical relationship between D_s and K_w should also be observed when the polymer's water content changes as a result of equilibrating the sample in salt solutions of different concentrations, and indeed, such a relationship is observed for XLPEGDA (cf. \blacklozenge symbols in Fig. 9). Presumably, the same relationship between D_s and K_w exists in the sulfonated polymers, but it is masked by the strong increase in D_s with increasing salt concentration due to phenomena other than the effect of changing water uptake on free volume and, in turn, salt diffusion coefficients. If the effects of water content were taken into account (as approximated by the dashed line in Fig. 9), the increase in D_s with increasing salt concentration would be even stronger than that shown in Fig. 8. The next section discusses possible explanations for the observed results in the sulfonated polymers.

3.3. Diffusion coefficient analysis

The Maxwell–Stefan (MS) equations have been successfully used to describe transport of small molecules in polymers [38,53,84–87]. For salts containing only monovalent ions, such as NaCl, the MS equations for cation and anion transport in a

polymer reduce to the Nernst–Planck equations when coupling effects are neglected and when no electric current is passed across the film [12,47]. The diffusion analysis presented in this section also assumes that the velocity, i.e., flux, of water through the film is equal to zero.

For uncharged polymers, the steady state salt flux, n_s , is given by [12]

$$n_s = - \left[\frac{D_M D_X}{D_M + D_X} \left(\frac{\partial \ln a_s^m}{\partial \ln c_s^m} \right) \right] \frac{dc_s^m}{dx} \quad (14)$$

where a_s^m is the thermodynamic activity of salt in the polymer, and D_M and D_X are average diffusion coefficients for cations (M) and anions (X), respectively. These average diffusion coefficients account for the mass transfer resistances, per the MS equations, experienced by the ions as they travel through the swollen membrane [12].

The term in square brackets in Eq. (14) is the mutual diffusion coefficient for salt transport through an uncharged, swollen polymer, D_{sp} :

$$D_{sp} = \frac{D_M D_X}{D_M + D_X} \left(\frac{\partial \ln a_s^m}{\partial \ln c_s^m} \right) \quad (15)$$

Eq. (14) can be integrated across the film, from $x=0$ to L , to give Eq. (1) where D_s is a concentration averaged salt diffusion coefficient defined using Eqs. (2) and (15). According to Eq. (15) for an uncharged polymer, D_{sp} (and, thus, D_s) depends on the mobilities of the cations and anions in the polymer and a thermodynamic factor (the derivative term in Eq. (15)) that describes the non-ideality of the salt–water–polymer mixture [53,84,88].

The derivative in parenthesis in Eq. (15) can be calculated using the XLPEGDA ion sorption data (cf. Fig. 5) and the assumption that, at equilibrium, the activity of salt in the external solution (calculated using the Pitzer model [89]) is equal to the activity of salt sorbed in the polymer, a_s^m , which is reasonable because XLPEGDA is not a charged polymer, and the hydrostatic pressures in the polymer and contiguous solutions were equal during the experiments. The derivative, $(\partial \ln a_s^m / \partial \ln c_s^m)$, calculated using these assumptions and the experimental salt sorption data, is effectively constant over the range of salt concentrations considered here and equal to 0.96. Thus, the change in the salt diffusion coefficients for XLPEGDA as salt concentration increases (cf. Fig. 3) results from changes in ion mobilities as a result of the change in water sorption that occurs as the concentration of the external salt solution changes. Additionally, $(\partial \ln a_s^m / \partial \ln c_s^m) = 0.96$ is close to unity indicating that sorption of salt in XLPEGDA is reasonably thermodynamically ideal.

For diffusion of a monovalent salt in a charged, cation exchange material, when the water flux is set equal to zero in the MS equations, the salt flux is given by [12]

$$n_s = - \left[\frac{(c_A^m + c_s^m) D_M D_X}{(c_A^m + c_s^m) D_M + c_s^m D_X} \right] \left(\frac{\partial \ln a_M^m a_X^m}{\partial \ln c_s^m} \right) \frac{dc_s^m}{dx} \quad (16)$$

where c_A^m is the fixed charge concentration in the polymer, which is the volumetric sulfonate group concentration in the polymer for sulfonated polymers, and D_M , D_X , a_M^m , and a_X^m are average diffusion coefficients for and thermodynamic activities of cations (M) and anions (X) sorbed in the polymer, respectively. Using an approach similar to that described above, the mutual diffusion coefficient for salt transport through the charged swollen polymer is

$$D_{sp} = \left[\frac{(c_A^m + c_s^m) D_M D_X}{(c_A^m + c_s^m) D_M + c_s^m D_X} \right] \left(\frac{\partial \ln a_M^m a_X^m}{\partial \ln c_s^m} \right) \quad (17)$$

Eq. (16) can be integrated from $x=0$ to L to obtain Eq. (1) where D_s is once again a concentration averaged salt diffusion coefficient determined using Eqs. (2) and (17).

The difference between the salt diffusion coefficients for the uncharged and charged polymers can be observed by comparing D_{sp} for each case (i.e., comparing Eqs. (15) and (17)). For charged polymers, D_{sp} (and, thus, D_s) depends upon the fixed charge and mobile salt concentrations in the polymer, the diffusion coefficients of the cations and anions, and a thermodynamic factor (i.e., the derivative in parenthesis in Eq. (17)) that describes the non-ideality of the ion-swollen polymer mixture. For uncharged polymers, D_{sp} (and, thus, D_s) does not depend on the concentrations of ions in the polymer because all of the ions sorbed in the polymer are mobile. As discussed previously, the thermodynamic factor for the uncharged polymer appears to be constant over the range of salt concentrations considered. Evaluating the thermodynamic factor for the charged polymers (i.e., the term in parenthesis in Eq. (17)), however, is not straightforward because the molar concentrations of ions sorbed in the polymer are not equal to one another, preventing extension of the assumption regarding the activity of salt sorbed in the uncharged polymer (discussed earlier) to the charged polymer case. Even though a value for this derivative cannot presently be calculated owing to the difficulties in determining the activities of cations and anions sorbed in the charged polymers, absent other information to the contrary, the charged polymer thermodynamic factor is presumed to be also relatively independent of salt concentration, by analogy to the uncharged polymer case.

In the simplest case, if D_M and D_X are independent of salt concentration, the term in square brackets in Eq. (17) must decrease as salt concentration increases (as described in more detail in the [Supplementary Material](#)). Since D_s in the charged polymers increases with increasing salt concentration, the mobility of cations and anions in the charged polymers must change with salt concentration because the term in brackets in Eq. (17) cannot decrease with increasing salt concentration unless D_M and D_X are sensitive to salt concentration. Furthermore, in cases of greatest interest to the use of such materials as membranes to regulate the transport of water and ions, the mobile salt concentration in the polymer is typically much smaller than the fixed charge concentration, i.e., $c_s^m \ll c_A^m$. In this limit and when the mobility of the anion is at least comparable to if not less than that of the cation, which is reasonable [90], the diffusion coefficient for salt transport through a charged polymer (Eq. (17)) becomes [12]

$$D_{sp} = D_X \left(\frac{\partial \ln a_M^m a_X^m}{\partial \ln c_s^m} \right) \quad (18)$$

because the $c_s^m D_X$ term is small relative to the $(c_A^m + c_s^m) D_M$ in the denominator of the bracketed term in Eq. (17). In this case, the salt diffusion coefficient is governed by the mobility of the anions, which is reasonable. Therefore, the experimental results suggest that anion diffusion coefficients must increase substantially with increasing salt concentration, despite the decreasing water content of the polymer.

For the sulfonated polymers considered in this work, the concentration of mobile salt is much less than the polymer's fixed charge concentration. For example, when the external salt concentration is 1 mol L^{-1} (the highest value considered in these studies), c_s^m values in BPSH-32, sPBC-1.5, and sPBC-2.0 polymers are nearly an order of magnitude lower than c_A^m , and at 0.5 or 0.3 mol L^{-1} , c_s^m is even more than an order of magnitude smaller than c_A^m . Therefore, Eq. (18) should be a good approximation for the sulfonated polymers considered in this study.

Although the molecular basis for the increase in salt diffusion coefficients with increasing salt concentration in charged polymers is not known at this time, several factors are proposed which may contribute to this phenomenon. If the thermodynamic factor in Eq. (18) does not vary considerably over the ranges of sorbed mobile salt concentration in these polymers, then, based on Eq. (18), the presence of fixed charge groups on the polymer

backbone might act to influence the mobility of the anion, and thus mobile salt, in the polymer.

Due to weakening of Donnan exclusion of anions from the polymer as salt concentration increases, the anion partition coefficient increases significantly in these polymers as external salt solution concentration increases [44]. One might hypothesize that the electrostatic effects acting to preclude chloride ion sorption into sulfonated polymers at low salt concentration may also act to slow diffusion of anions through the polymer, since some region around a sulfonate group would be effectively inaccessible to chloride, forcing chloride ions to take a circuitous path through the polymer to minimize such interactions. The strength of electrostatic interactions should be sensitive to the concentration of ions in the polymer matrix because the strengths of similar interactions in aqueous solution are sensitive to the ion concentration, or ionic strength, of the solution [74]. As salt concentration increased, these repulsive interactions between chloride ions and sulfonate groups would be weakened, which would limit the ability of the sulfonate groups to preclude chloride ion sorption and hinder chloride ion mobility.

The literature supports the hypothesis that the presence of fixed charge groups on a polymer backbone influences salt diffusion. The activation energy for salt diffusion in a polyphosphazene cation exchange material is ~ 1.4 times higher than that in a similar uncharged polyphosphazene polymer doped with salt to maintain similar ion concentrations in both polymers, and this result suggests that the fixed nature of the polymer's charge acts to hinder salt diffusion [91]. Additionally, molecular dynamics simulations suggest that ion self-diffusion coefficients in a nano-porous matrix of charged obstacles (similar, in principle, to the charged polymers considered in the present work) tend to increase with increasing salt concentration, provided that the mobile salt concentration is sufficiently less than the fixed charge concentration (a condition obeyed by the materials considered in this study [44]) [92].

Ions are understood to diffuse together with the water molecules hydrating the ions, which makes the diffusing species larger than the bare ions alone [74]. Thus, another hypothesis to describe the trend of increasing diffusion coefficients as salt concentration increases is that the extent of ion hydration changes as salt concentration and ionic environment in the polymer change. This effect could change the effective size of the diffusing ions [93]. In aqueous solutions, ion hydration decreases as salt concentration increases [94], so if the ions are effectively smaller at higher salt concentrations, this could explain their increased mobility. For example, as the concentration of aqueous NaCl changes from 0.01 to 1.0 mol kg^{-1} (water), the number of water molecules associated with the sodium and chloride ions changes from 25 to 20 [94]. However, it is not known why this effect would influence ion diffusion coefficients much more strongly in the sulfonated polymers than in the uncharged polymer.

Yet another hypothesis is ion pairing between Cl^- and Na^+ in the polymer [93]. If ions in the polymer pair together (or 'undissociate'), these NaCl pairs may be effectively smaller (i.e., more mobile) than dissociated and hydrated Cl^- and Na^+ ions [93]. Ion pairing in polymers has been discussed largely for pairing between counterions and fixed charge groups [95,96], and evidence of NaCl pairing behavior in the polymers used in this study is not presently available. Again, it is not known why this effect would influence ion diffusion coefficients much more strongly in the sulfonated polymers than in the uncharged polymer.

4. Conclusions

The average salt diffusion coefficients for three sulfonated polymers, BPSH-32, sPBC-1.5, and sPBC-2.0, were calculated as a

function of external salt concentration based on previously measured salt permeability and sorption data. These data were compared with those for an XLPEGDA uncharged polymer. The salt diffusion coefficients of the charged sulfonated polymers increase markedly as salt concentration increases while the salt diffusion coefficients of the XLPEGDA polymer decrease only slightly as salt concentration increases. The decrease in the salt diffusion coefficients in the uncharged XLPEGDA material occurs because increased salt concentration depresses the polymer's water content via osmotic de-swelling, thereby reducing the free volume of the hydrated polymer which, in turn, reduces diffusion coefficients and permeability coefficients. In contrast, the salt diffusion coefficients from the charged sulfonated polymers increase with increasing salt concentration even as water content (and, therefore, free volume) decreases. Presumably, interactions between the diffusing ions and the swollen polymer matrix are responsible for this behavior. Diffusion coefficient analysis using a Maxwell–Stefan/Nernst–Planck approach suggests that the anion mobility (i.e., the mobility of mobile salt) is likely increasing in the charged polymer systems as salt concentration increases. Various hypotheses have been suggested to explain the trend of D_s with the external upstream solution salt concentration, but further study is required to fully understand such trends.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2012.09.029>.

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