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Understanding the influence of sodium chloride concentration on ion diffusion in charged polymers

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ABSTRACT

Previous observations made on sulfonated polysulfones equilibrated with solutions of increasing salinity, where salt diffusion coefficients increase concurrently with reductions in water content driven by osmotic de-swelling, are currently unexplained. To further explain the molecular underpinnings of these observations, we characterized the influence of external salt solution concentration on the average salt and ion diffusion properties of two sulfonated polymers: a model cross-linked material (XLAMPS) and a series of sulfonated polysulfones (HQ: BP – XX). Analysis of the average salt and co- and counter-ion diffusion coefficients in these polymers suggest that the increase in charge screening (of electrostatic interactions between anionic sulfonate groups and co-ions) that occurs with increasing salinity affects the salt diffusion coefficients of sulfonated polysulfone in a manner that is different from what would be expected based on changes in water content alone and from what was observed for XLAMPS. Free volume theory describes the influence of these electrostatic effects on salt diffusion using a parameter related to the characteristic free volume element size necessary for diffusion. The results and analysis suggest that charge screening reduces the characteristic free volume element size necessary for diffusion in sulfonated polysulfone, which provides an explanation for the observed increase in average salt diffusion coefficients with increased salinity.

1. Introduction

Polymer membranes play an important role in desalination where the goal is to separate an undesired solute (e.g., ions) from water [1,2]. The ability of these membranes to desalinate water depends on the relative transport rates of water and salt [1–4]. As such, a key step in engineering polymer membranes for separation processes is to understand how membrane transport properties are related to structural/physical properties so that membranes can be engineered to enhance the transport rate of the desired component relative to the undesired solutes. To this end, many studies have contributed to building polymer structure/property relationships for desalination membranes [1,3,5–14], but further research is needed to understand how specific interactions between polymers and ions influence salt transport properties.

Salt diffusion is a key process that influences salt transport in dense polymer membranes. Salt diffusion often is described by an average salt diffusion coefficient that contains contributions from both cations and anions [15,16]. In hydrated polymers, these diffusion coefficients are typically very sensitive to the water content of the polymer, and diffusion coefficients often decrease as the volume fraction of water in the polymer decreases [11,17]. This influence of water content on salt diffusion in desalination membrane polymers is often rationalized using free volume theory [11,17–19].

Free volume theory suggests that the average salt diffusion coefficient is related to the total amount of hydrated free volume available for salt diffusion in the polymer [11,18,20]. This total amount of hydrated free volume commonly is taken to be proportional to a measure of hydrated polymer water content [11,17]. Within this framework, free volume theory can be used to describe the relationship between polymer structural properties and salt diffusion coefficients. For example, free volume theory helps to explain a fundamental structure/property relationship, observed in sulfonated polysulfone polymers, where tethering additional hydrophilic sulfonate groups to the polymer backbone increases the average salt diffusion coefficient because of the increase in the water volume fraction in the polymer that occurs due to the

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additional sulfonate groups [11].

Free volume theory also explains the influence of external salt concentration on salt diffusion in certain hydrated polymers. Generally, as polymers are exposed to increasing salinity, their water content decreases due to a phenomenon referred to as osmotic de-swelling [1,15]. In many hydrated polymers, such as cross-linked poly (ethylene glycol) diacrylate and a cross-linked charged sulfonated polymer referred to as XLAMPS, average salt diffusion coefficients have also been observed to decrease with increasing salinity due to this osmotic deswelling effect in a manner consistent with free volume theory [1,15,21].

In 2012, Geise et al. reported that the average salt diffusion coefficient in sulfonated polysulfones and sulfonated styrenic block copolymers increased as these charged polymers experienced osmotic deswelling upon exposure to solutions of increasing NaCl concentration [15]. This observation is opposite to the scaling relationship suggested by free volume theory and discussed previously here. At the time, Geise et al. offered possible explanations for the results, but the fundamental underpinning of the observation remained unclear. One explanation is that interactions between ions and the sulfonate fixed charge groups influence salt diffusion to an extent that overshadows the free volume-based effects in the polymers characterized [15]. Understanding these sorts of interactions and when they are relevant would provide information about fundamental structure/property relationships that influence salt transport in charged polymers.

Here, we report the average salt diffusion coefficients for a series of sulfonated polysulfones, referred to as HQ:BP – XX, and XLAMPS polymers equilibrated with 0.5 M, 1 M, and 4 M NaCl solutions. The sulfonated polysulfone materials considered here are similar to those considered previously, but these materials contain hydroquinone linkages not present in the materials originally considered [15]. Consistent with previous measurements made on sulfonated polysulfone, we found that the HQ:BP – XX materials exhibited average salt diffusion coefficients that increased, despite decreased water content, when membranes were equilibrated in NaCl solutions of increasing concentration. Alternatively, XLAMPS polymers exhibited decreased average salt diffusion coefficients when equilibrated in NaCl solutions of increasing concentration [22].

To explore and ultimately explain these observations, we measured individual co- and counter-ion diffusion coefficients. The co-ion diffusion coefficients followed the average salt diffusion coefficient trend suggesting that co-ion diffusion governs the overall average salt diffusion properties of the charged polymers. In XLAMPS, the relative magnitudes of the co- and counter-ion diffusion coefficients were identical to that in external salt solution (i.e., the chloride co-ions diffused more rapidly than the sodium counter-ions), suggesting that in these polymers, ion diffusion was governed by hydrated ion radii. Alternatively, in sulfonated polysulfone, the relative magnitudes of the co- and counter-ion diffusion coefficients were reversed (i.e., the counter-ions diffused more rapidly than the co-ions) suggesting that electrostatic interactions between sulfonate groups (or fixed charges) and the ions governed ion diffusion properties. To quantify the influence of these electrostatic effects on salt diffusion, we applied a free volume-based analysis to the salt, co- and counter-ion diffusion data. We found that, in the sulfonated polysulfones, the characteristic free volume necessary for salt and co-ion diffusion decreases with increasing salinity. This reduction in the characteristic free volume element size necessary for salt diffusion may be related to electrostatic interactions between fixed charges and co-ions and may be an explanation for observed increases in the average salt diffusion coefficient with increasing salinity and decreasing water content. This observation informs relationships between polymer structure, salt transport properties, and external salt solution concentration, which may be useful to guide molecular engineering strategies for desalination polymers.

2. Experimental

2.1. Materials

Two sulfonated polymers were used to study the influence of increased salinity on salt diffusion properties of charged polymers: 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) cross-linked using poly (ethylene glycol) diacrylate (PEGDA), referred to herein as XLAMPS, and a series of sulfonated poly (aryl ether sulfone) random copolymers, where sulfonated and non-sulfonated co-monomers were joined using either hydroquinone (HQ) or biphenol (BP) linkages, referred to herein as HQ:BP – XX. The XLAMPS polymers (Fig. 1) were cross-linked using x and z values of 0.25 and 0.75, respectively (i.e., a 1:3 mass ratio of AMPS to PEGDA) as reported by Ji et al. [23]. The HQ:BP – XX polymers were synthesized using a nucleophilic step growth reaction as reported by Chang et al. [5]. HQ:BP – XX was synthesized with a constant value of y = 0.4, and XX was varied as either 20, 25, or 30 (Fig. 1).

The HQ:BP – XX polymers were chosen to probe the influence of increased salinity on salt diffusion because of their structural similarity to previously characterized biphenol-based sulfonated polysulfones that exhibited the previously discussed unexpected salt diffusion properties where the average salt diffusion coefficients increase with increasing salinity despite reduced water content. Alternatively, XLAMPS polymers were chosen as a control material as, despite containing anionic sulfonate groups, they exhibit average salt diffusion coefficients that decrease as polymer water content decreases with increasing external solution salinity [22]. The physical properties of XLAMPS and HQ:BP – XX equilibrated with 0.5 M NaCl are reported in Table 1.

2.2. Water content

Polymers were first equilibrated in an aqueous solution of either 0.5 M, 1 M, or 4 M sodium chloride (NaCl, ≥99 %, Sigma-Aldrich) for 24 h. After this initial equilibration period, the polymers were placed in a second (fresh) solution of the same concentration for an additional 24 h to allow the equilibration process to proceed to equilibrium. The external salt concentration range of 0.5 M–4 M NaCl was chosen to probe the influence of increased external salinity on polymer salt diffusion properties, and the use of high concentrations of NaCl provided conditions where electrostatic interactions within the hydrated polymers could be screened to a high extent.

After equilibration, membranes were weighed to determine the wet mass of the hydrated polymer, m_{wet}. Membranes were then dried under vacuum at 80 °C for at least 24 h. The selected drying conditions were sufficient to allow the drying process to reach completion as allowing the drying process to proceed longer had no measurable influence on the water uptake data collected from the experiment. Immediately after drying, samples were weighed again to determine the dry polymer mass, m_{dry}. Water uptake, w_u, was calculated as [1,5,24]:

$$w_u = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad \text{Eq. 1}$$

To determine the dry density of the membrane, ρ_p, samples (immediately following the drying procedure described above) were weighed while immersed in cyclohexane, a non-solvent, auxiliary liquid that does not sorb appreciably into the polymer [5]. Dry density was calculated using Archimedes Principle as [1,5,24]:

$$\rho_p = \frac{m_{dry}}{m_{dry} - m_{aux}}(\rho_{aux} - \rho_{air}) + \rho_{air} \quad \text{Eq. 2}$$

where m_{aux} was the mass of the sample immersed in auxiliary liquid, and ρ_{aux} and ρ_{air} are the densities of cyclohexane and air, respectively. As the auxiliary liquid and air densities used to calculate the polymer density in Eq. (2) are a function of the temperature, the experimental temperature

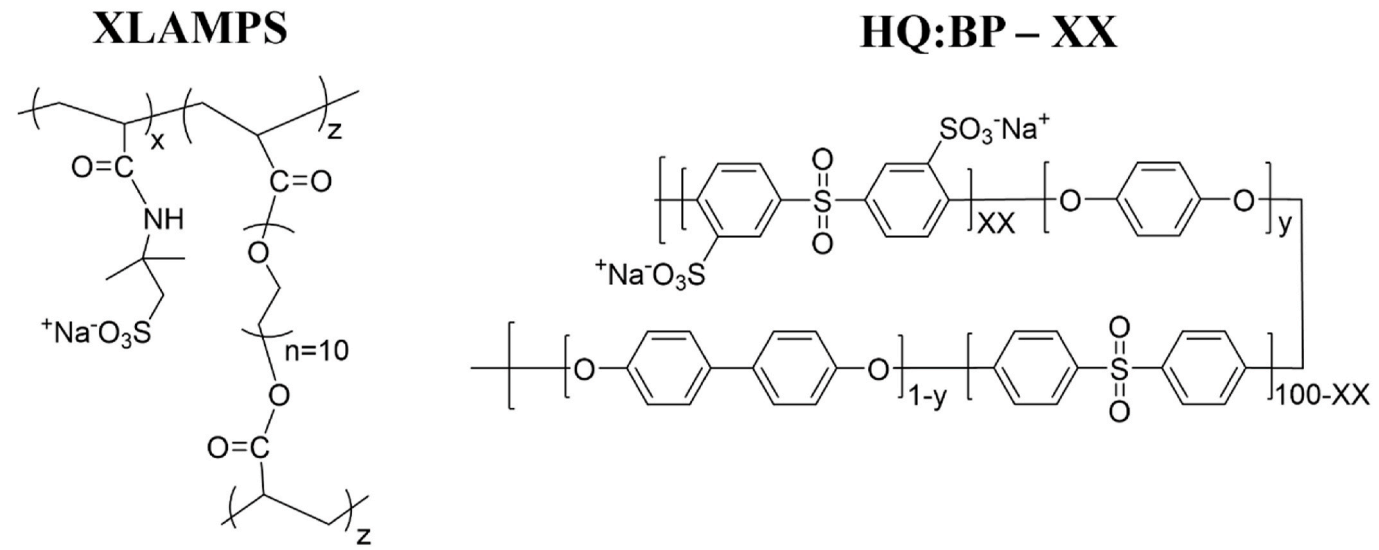

Fig. 1. Chemical structures of XLAMPS and HQ:BP – XX polymers. XLAMPS was prepared with values of x and z set as 0.25 and 0.75, and HQ:BP – XX was prepared with a constant y value of 0.4, and XX values of either 20, 25, or 30.

Table 1
Physical properties of the XLAMPS and HQ:BP – XX materials considered in this study.

Material[a]	IEC[b] [meq/g]	Water uptake, w_u [g (water)/g (dry polymer)]	Dry density, ρ_p [g/cm^3]	Water volume fraction, φ_w	Fixed charge concentration [eq/L (polymer)]	Fixed charge concentration [eq/L (water sorbed)]
XLAMPS	1.09	0.67 ± 0.03	1.36 ± 0.10	0.48 ± 0.04	0.78 ± 0.05	1.6 ± 0.1
HQ:BP – 20	0.83	0.14 ± 0.01	1.37 ± 0.02	0.16 ± 0.01	0.95 ± 0.05	5.8 ± 0.2
HQ:BP – 25	1.01	0.20 ± 0.01	1.50 ± 0.07	0.23 ± 0.01	1.16 ± 0.08	5.0 ± 0.2
HQ:BP – 30	1.19	0.26 ± 0.02	1.43 ± 0.03	0.27 ± 0.02	1.24 ± 0.07	4.6 ± 0.4

[a] Properties of XLAMPS and HQ:BP – XX equilibrated in ambient temperature 0.5 M NaCl solution, which was the lowest salt concentration considered and represents the most hydrated state of the polymers considered in this study.

[b] Reported ion exchange capacity (IEC) calculated based on the synthetic recipe and assuming that all polymers were in the Na$^+$ counter-ion form.

was recorded and used to determine the auxiliary liquid and air densities [25]. The temperatures of all measurements were within at least 1 °C (i.e. 22 ± 1 °C) of each other. The volume fraction of water sorbed in the polymer, ϕ_w, which can be used as a proxy for the total free volume in the polymer [11], was then determined by assuming that the volumes of polymer and sorbed water are additive [1,5,24]:

$$\phi_w = \frac{w_u}{w_u + \frac{\rho_w}{\rho_p}} \quad \text{Eq. 3}$$

where ρ_w is the density of water (1.0 g/cm^3) [25,26]. The volume additivity assumption used to calculate the water volume fraction via Eq. (3) may be influenced by the presence of non-equilibrium excess free volume elements in glassy polymers such as sulfonated polysulfone [11,26].

2.3. Salt transport properties (kinetic desorption)

Salt sorption and diffusion coefficients were measured using a kinetic desorption technique [1,5,27]. First, membranes were cut into 1.83 cm diameter disks and equilibrated in either 0.5 M, 1 M, or 4 M aqueous NaCl solution. The polymers were equilibrated in electrolyte solution for at least 48 h over which the electrolyte solutions were changed at least once. After this equilibration process, the diameter and thickness of the hydrated samples were measured using digital calipers (Item No. 293–344, Mitutoyo). These properties were measured as quickly as possible to minimize de-swelling of the samples in air.

Subsequently, the samples were blotted dry and placed in 100 mL of de-ionized (DI) water, which had been equilibrated under atmospheric conditions to minimize the influence of carbon dioxide adsorption on the experiment, to extract the sorbed salt from the membranes into this desorption solution. These desorption solutions were kept well-mixed by continuous stirring at 400 rpm using a magnetic stir bar to minimize the influence of experimental artifacts, e.g., boundary layers, on polymer salt transport properties. The desorption process was carried out in a sealed temperature controlled jacketed vessel at 22 ± 0.1 °C.

Kamcev et al. suggested that the dissociation and subsequent speciation of carbon dioxide in the desorption solution may result in ion exchange phenomena that could influence the conductivity of the desorption solution [28]. This phenomenon is not likely to influence desorption experiments performed using sodium-form sulfonated polymers (because ion exchange from a sodium counter-ion form to acid counter-ion form is generally a thermodynamically non-favorable process) [28,29]. The influence of this potential artifact, however, was further mitigated by ensuring that the concentration of NaCl in the desorption solutions was at least an order of magnitude larger than the concentration of acid in the atmospherically equilibrated de-ionized water.

The conductivity and temperature of the desorption solution was measured as a function of time using a conductivity meter (Cond 7310, WTW). A calibration curve was used to convert desorption solution conductivity into salt concentration. The relationship between conductivity and concentration is temperature dependent, so the calibration curve data were measured at the experimental temperature (22 ±

0.1 °C). Desorption solution conductivity increased as salt desorbed from the membrane and was measured until it stabilized to a constant value. Stabilization generally occurred at times that were at least five times the sample's characteristic time for diffusion, and this value was used to determine the long-time, or final, mass of salt desorbed from the polymer during the experiment, M_∞.

The conductivity of the solution was related to the concentration of the desorption solution using the calibration curve, and the mass of salt, M_t, desorbed from the polymer as a function of time, t, was determined using the time-dependent concentration data and solution volume. The average salt diffusion coefficient, D_s, was determined from the short-time desorption solution conductivity data using a flat-sheet desorption model [30]:

$$D_s^m = \frac{\pi\delta^2}{16}\left[\frac{\mathrm{d}(M_t/M_\infty)}{\mathrm{d}(t^{1/2})}\right]^2 \qquad \text{Eq. 5}$$

where δ is the thickness of the polymer sample. Further discussion of Eq. (5) and sample kinetic desorption analysis for XLAMPS and HQ:BP – 25 are provided as Section S1, but effectively, the bracketed term can be determined by performing a linear regression of M_t/M_∞ and $t^{1/2}$ for times where $M_t/M_\infty < 0.6$.

The salt sorption coefficient, K_s, was calculated from the long-time desorption data as [1,5,27]:

$$K_s \equiv \frac{C_s^m}{C_s^s} = \frac{C_d V_d}{C_s^s V_p} \qquad \text{Eq. 6}$$

where C_d is the salt concentration of the desorption solution calculated from the long-time desorption solution conductivity using the calibration curve, V_d is the volume of the desorption solution, and V_p is the volume of the swollen polymer, which can be geometrically determined by measuring the thickness and area of a sample before the salt extraction process. The units of the salt sorption coefficient calculated via Eq. (6) are [mol/L (swollen polymer)]/[mol/L (solution)].

2.4. Conductivity

The ionic conductivity of the polymers was measured using a direct-contact electrochemical impedance spectroscopy (EIS) technique previously described by Kamcev et al. [31]. First, polymers were equilibrated in either 0.5 M, 1 M, or 4 M NaCl solution, for at least 48 h, as previously described (Section 2.2). After this initial equilibration period, polymers were quickly dipped in a 5 M NaCl solution and clamped in between two gold electrodes. The 5 M NaCl dip helps eliminate resistance contributions from solution layers between the polymer and electrode that can introduce experimental artifacts [31]. The time-scale of this dipping procedure is on the order of magnitude of seconds, which is considerably shorter than the characteristic time-scale for diffusion, and is therefore likely not long enough to induce additional ion-sorption in the polymer that would influence the measurement [31].

Impedance was measured using a potentiostat (BioLogic SP-300) to impose an oscillating potential with a 10 mV amplitude over a frequency range of 7 MHz–100 Hz. The apparent resistance of the polymer, R_m, was calculated via the obtained Nyquist plot as the value of the real impedance when the imaginary impedance was equal to zero. Example spectra are provided in Section S2. The ionic conductivity of the polymer, κ, was calculated from the apparent resistance as [31]:

$$\kappa = \frac{\delta}{R_m A} \qquad \text{Eq. 7}$$

where A is the active area of the electrode (which was 0.218 cm^2).

3. Results and discussion

3.1. Water content and salt diffusion data

As discussed in the introduction, variations in polymer chemistry or external conditions that influence the salt diffusion properties in hydrated polymers can generally be explained by free volume theory where the average salt diffusion coefficient is related to the water content of the polymer [11,15,17,22,29,32–34]. Therefore, it is generally expected that, under circumstances where polymer water content decreases, the average salt diffusion coefficient of the polymer decreases as well. It is for this reason that the average salt diffusion coefficients reported by Geise et al. [15], which stand in contrast to what is observed for many other polymers, motivate this study. Here, we discuss how changes in polymer water content, induced by both the degree disulfonation of HQ:BP – XX and external salt concentration, influence salt diffusion.

XLAMPS is generally considered to be a high-water content polymer (i.e., when fully hydrated, the water volume fraction is larger than 0.4) [34]. The water content of XLAMPS decreases as the external salt solution concentration increases (Fig. 2), consistent with previous observations of the influence of external salt concentration on water content in XLAMPS that are described by osmotic de-swelling [21,22,35]. The average salt diffusion coefficients of XLAMPS decrease with increasing salt concentration as well (Fig. 3A), and this relationship between average salt diffusion coefficients and external salt concentration is expected, because qualitatively, as the water content decreases (or, as the polymer exhibits osmotic de-swelling), the salt diffusivity decreases as well. These observations are consistent with previous observations and suggest that salt diffusion in XLAMPS is well described by the previously discussed free volume theory [22].

The sulfonated polysulfones are generally considered low water content polymers (i.e., the water volume fractions of HQ:BP – XX are less than 0.4 (Fig. 2)). The water volume fraction of the HQ:BP – XX polymers increases with degree disulfonation (Fig. 2), and likewise, the average salt diffusion coefficients also increase with increasing degree

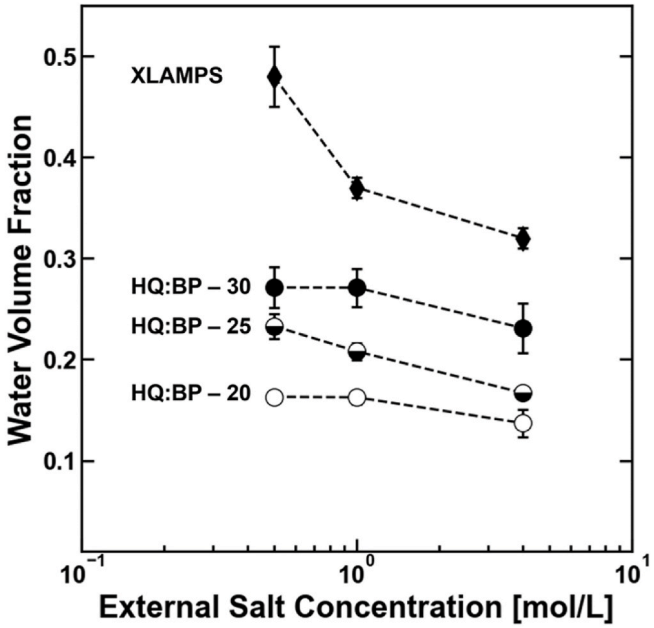

Fig. 2. Water volume fraction data for aqueous sodium chloride solution equilibrated XLAMPS (◆), HQ:BP – 20 (○), HQ:BP – 25 (◒), and HQ:BP – 30 (●) reported as a function of external NaCl concentration. The dashed lines are intended to guide the eye. The uncertainty was determined as the standard deviation from the mean of three measurements.

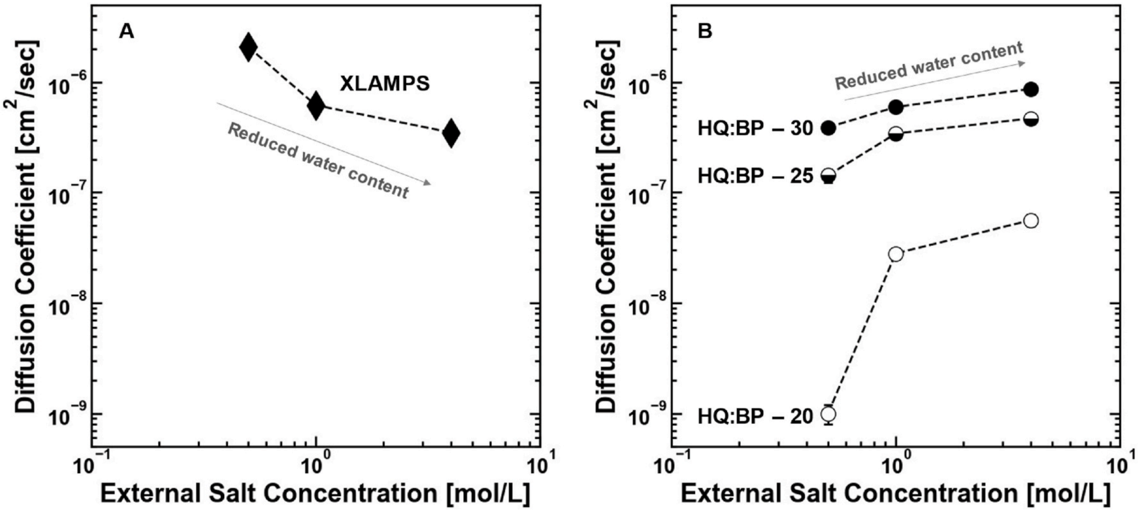

Fig. 3. Average salt diffusion coefficient data for hydrated (A) XLAMPS (◆) and (B) HQ:BP – 20 (○), HQ:BP – 25 (◒), and HQ:BP – 30 (●) reported as a function of external NaCl concentration. The dashed lines are intended to guide the eye. The uncertainties were determined as the standard deviation from the mean of three measurements.

disulfonation (value of XX in HQ:BP – XX data in Fig. 3B). These observations are expected based on the previously discussed free volume-based relationship between water content and the average salt diffusion coefficient, and they are consistent with previous reports in the literature where the water content and average salt diffusion coefficient both increase as the polymer degree of disulfonation increases [11,13].

Similar to observations for XLAMPS, the sulfonated polysulfones exhibit osmotic de-swelling, i.e., their water content decreases as external salt concentration increases (Fig. 2). However, unlike XLAMPS, the average salt diffusion coefficients of the sulfonated polysulfones increase with increasing external salt concentration (Fig. 3B), and this observation is inconsistent with the previously discussed free volume-based relationship between average salt diffusion coefficients and water content. This observation is paradoxical, because when the water content of the sulfonated polysulfones is reduced via polymer chemistry (i.e., degree disulfonation), the average salt diffusion coefficients decrease as expected, but when the water content of the polysulfones is reduced via osmotic de-swelling, the average salt diffusion coefficients increase.

External salt concentration can influence electrostatic interactions between fixed charges, and chloride co-ions and sodium counter-ions. These electrostatic interactions can also influence salt diffusion in charged polymers [1,22,33,36,37], and therefore the salt diffusion properties observed in HQ:BP – XX may be consistent with a physical picture where electrostatic effects influence salt diffusion in addition to free volume-based effects. To probe the influence of electrostatic effects on ion diffusion in the polymers (and why these effects may influence salt diffusion differently in HQ:BP – XX than XLAMPS) we characterized the co- and counter-ion diffusion coefficients for the charged polymers.

3.2. *Ion diffusion*

Ion diffusion coefficients (D_g^m for counter-ions and D_c^m for co-ions) were calculated by combining salt sorption data (Section S3) and average salt diffusion data (both measured in the kinetic desorption experiment) with ionic conductivity data (Section S4) measured using EIS [33,38,39]. The average salt diffusion coefficient, measured via kinetic desorption, can be related to the counter- and co-ion diffusion coefficients via the Nernst-Planck equation [29,33,38]:

$$D_s = \frac{D_g^m D_c^m \left(z_g^2 C_g^m + z_c^2 C_c^m \right)}{z_g^2 C_g^m D_g^m + z_c^2 C_c^m D_c^m} \qquad \text{Eq. 8}$$

where C_g^m and C_c^m are the concentrations of the counter- and co-ions, respectively. The ionic conductivity, κ, is related to the counter- and co-ion diffusion coefficients as [29,33,38]:

$$\kappa = \frac{F^2}{RT} \left(z_g^2 D_g^m C_g^m + z_c^2 D_c^m C_c^m \right) \qquad \text{Eq. 9}$$

In both Eq. (8) and Eq. (9), z_g and z_c are the counter and co-ion valences, respectively. The counter- and co-ion diffusion coefficients were calculated by solving Eq. (8) and Eq. (9) simultaneously [5,33,38]. It is important to note that the Einstein equation, a relationship between ionic mobilities and diffusivities that is valid for aqueous salts at infinite dilution, is assumed to be valid in the derivation of Eq. (8) and Eq. (9) [33,40,41].

Generally, the observed relationships between external salt concentration, polymer structure, and the co-ion diffusion coefficients are identical to those of the average salt diffusion coefficients (cf. Figs. 3 and 4). The co-ion diffusion coefficients decrease with increasing salinity for the XLAMPS polymers (Fig. 4A) and increase with increasing salinity and degree disulfonation for the sulfonated polysulfones (Fig. 4B). This result is consistent with theory [29] and with experimental observations [23,33], which were made using other charged polymers, suggesting that co-ion diffusion properties govern the overall salt diffusion properties of charged polymers.

In all the materials considered, the counter-ion diffusion coefficients were less sensitive to the variables in this study compared to the co-ion diffusion coefficients. For example, from 0.5 M NaCl to 4 M NaCl, the co-ion diffusion coefficients decrease and increase by almost an order of magnitude for XLAMPS and HQ:BP – XX respectively (Fig. 4), whereas the counter-ion diffusion coefficients are all within the same order of magnitude for XLAMPS and HQ:BP – XX over the range of external salt concentrations (Fig. 5). Similarly, the co-ion diffusion coefficients for HQ:BP – XX equilibrated with 0.5 M NaCl span three orders of magnitude over the range of degree disulfonation (Fig. 4B), whereas the counter-ion diffusion coefficients are all the same order of magnitude over this range (Fig. 5B).

Parity plots, where the individual ion diffusion coefficients are plotted as a function of the average salt diffusion coefficient (Fig. 6), can be used to compare the relative magnitudes of the co-ion, counter-ion, and average salt diffusion coefficients. Co- and counter-ion diffusion data for XLAMPS polymers reported by Yan et al. [22] are included in Fig. 6A as well. The data reported by Yan et al. represent XLAMPS synthesized over an IEC range of 0.01–1.93 meq/g (dry polymer) and

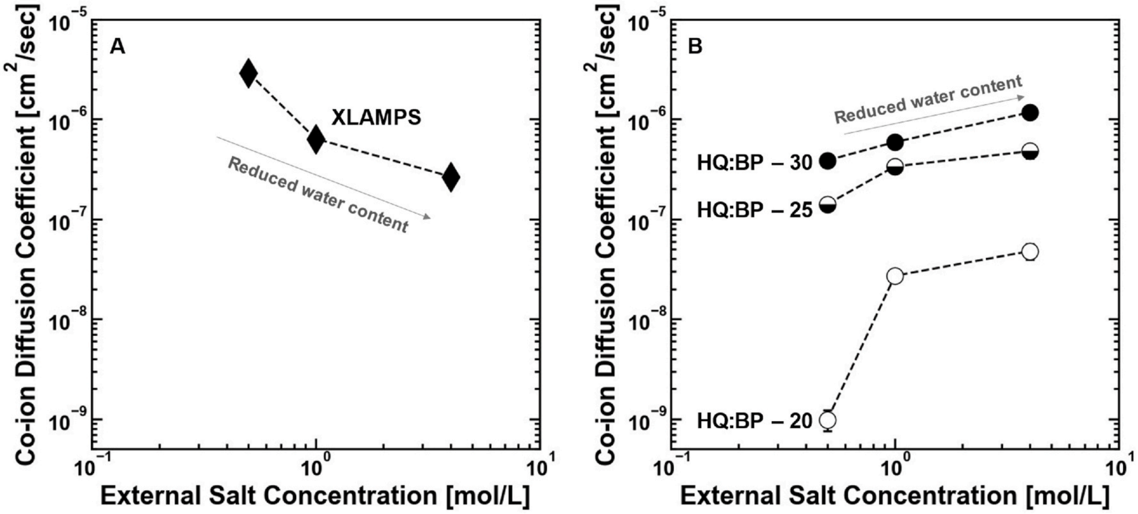

Fig. 4. Co-ion diffusion coefficient data for hydrated (A) XLAMPS (◆) and (B) HQ:BP – 20 (○), HQ:BP – 25 (◒), and HQ:BP – 30 (●) reported as a function of external NaCl concentration. The dashed lines are intended to guide the eye. The uncertainties were determined as the standard deviation from the mean of three measurements.

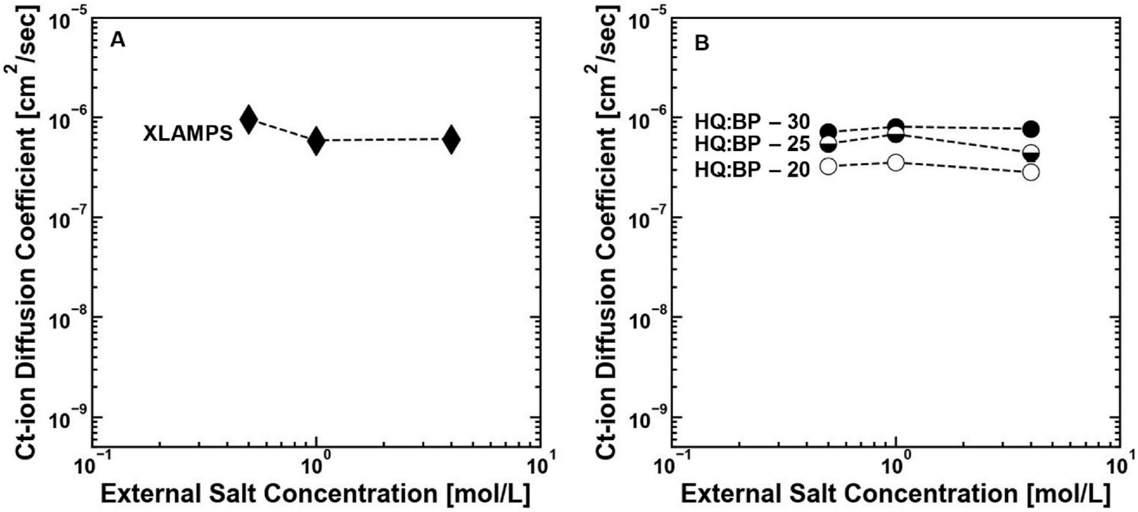

Fig. 5. Counter-ion (Ct-ion) diffusion coefficient data for hydrated (A) XLAMPS (◆) and (B) HQ:BP – 20 (○), HQ:BP – 25 (◒), and HQ:BP – 30 (●) reported as a function of external NaCl concentration. The dashed lines are intended to guide the eye. The uncertainties were determined as the standard deviation from the mean of three measurements.

equilibrated with external salt solutions with concentrations ranging from 0.01 to 1 M NaCl, so this data set expands upon the synthetic and experimental conditions of the XLAMPS polymers characterized in this report to provide additional context for the subsequent analysis [22].

In XLAMPS, the co-ion diffusion coefficients generally are larger than the counter-ion diffusion coefficients, so the absolute values of the average salt diffusion coefficients were generally between the corresponding co- and counter-ion diffusion coefficient (Fig. 6A). On average, the co-ion diffusion coefficients were approximately 1.35 times larger than the counter-ion diffusion coefficients, which is comparable to observations made in aqueous NaCl where the self-diffusion coefficient of chloride is approximately 1.5 times that of a sodium ion [33,42]. In aqueous solution, ion diffusion coefficients are proportional to their hydrated radii so that smaller chloride ions (hydrated radius of 3.32 Å) have larger diffusion coefficients than sodium ions (hydrated radius of 3.58 Å) [42,43]. Given the similarity between ion diffusion properties observed in solution and in XLAMPS, the ion diffusion properties of the XLAMPS polymers are influenced, likely predominately, by ion size effects, and specific ion-polymer interactions, such as electrostatic effects, may be less relevant. These results are consistent with the previous conclusion that salt diffusion in XLAMPS equilibrated with increasing salinity is governed by free volume-based effects (i.e., water content).

Alternatively, in HQ:BP – XX, the counter-ion diffusion coefficients were larger than the co-ion diffusion coefficients, which were effectively equal to the average salt diffusion coefficients within experimental uncertainty (Fig. 6B). In HQ:BP – XX, the difference between the co- and counter-ion diffusion was inversely related to both the external salt concentration and degree disulfonation (Fig. 6B). For example, in HQ:BP – 20 equilibrated with 0.5 M NaCl (i.e., the lowest degree disulfonation and external salt concentration) the counter-ion diffusion coefficient was 320 times larger than the co-ion diffusion coefficient whereas in HQ:BP – 30 equilibrated with 4 M NaCl, (i.e., the largest degree disulfonation and fixed charge concentration) the ratio of co- and counter-ion diffusion coefficients is approximately unity (Fig. 6B).

The observation that co-ion diffusion coefficients are smaller than counter-ion diffusion coefficients in HQ:BP – XX is consistent with observations of co- and counter-ion diffusion coefficients in other charged polymers where electrostatic effects, to a greater extent than free

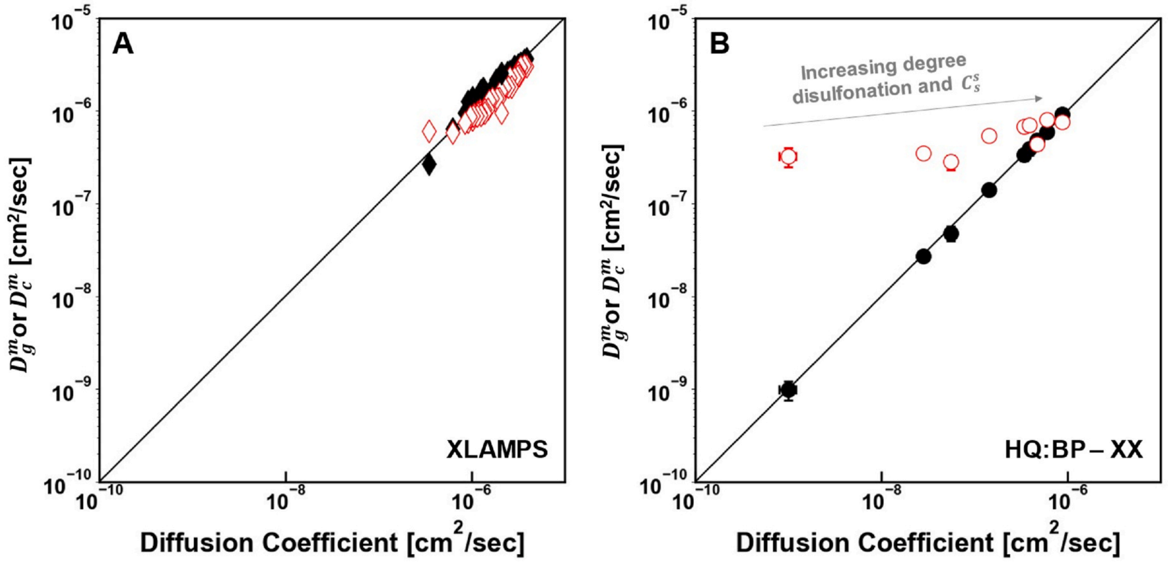

Fig. 6. Counter- or co-ion diffusion coefficients for hydrated (A) XLAMPS and (B) HQ:BP – XX reported as a function of the average salt diffusion coefficient, D_s. The unfilled symbols represent counter-ion diffusion coefficients, and the filled symbols represent co-ion diffusion coefficients. The solid line represents parity between ion diffusion coefficients (vertical axes) and the average salt diffusion coefficient (horizontal axes). The uncertainties were determined as the standard deviation from the mean of three measurements.

volume-based effects, govern ion diffusion [33,38]. For example, thermodynamically non-ideal coulombic interactions between fixed charges and ions can influence ion diffusion, and in other charged polymers, ion diffusion is described by a physical picture where co-ion diffusion is suppressed by thermodynamically non-favorable repulsive interactions with fixed charges, and counter-ion diffusion is promoted by thermodynamically favorable interactions with fixed charges (i.e., counter-ion condensation) [33]. Previously, we found that ionic interactions in these sulfonated polysulfones, equilibrated with sodium chloride, were primarily governed by ion-fixed charge and dielectric exclusion interactions [44], but other ionic interactions (e.g., ion pairing) may influence ion transport as well [45,46].

Interactions between ions and fixed charges are generally considered strongest in polymers with high fixed charge concentrations [34,35]. As the external salt concentration increases, the concentration of ions sorbed in the polymer increases as well (Fig. S3), and due to the increased ionic strength of the solution sorbed in the polymer matrix, electrostatic (e.g., coulombic) interactions between ions and fixed charges become increasingly screened [47]. This physical picture explains the observation that the difference between co- and counter-ion diffusion coefficients is inversely related to both the degree disulfonation (i.e., directly related to fixed charge concentration (Table 1)) and external salt concentration because the repulsive coulombic interactions between co-ions and fixed charges are progressively screened with increased concentrations of salt sorbed in the polymer matrix (i.e., increased external salt concentration). This relationship is discussed in more detail in Section S5.

This charge-screening based analysis also provides a physical explanation for the observation that average salt diffusion coefficients increase with increasing salinity in HQ:BP – XX polymers. Because co-ion diffusion effectively governed the average salt diffusion properties of HQ:BP – XX (Fig. 6B), the repulsive ion-fixed charge interactions that suppress co-ion diffusion effectively suppress the overall salt diffusion in HQ:BP – XX as well, and with increasing salinity, the average salt diffusion coefficients increase as these interactions are screened. A quantitative model describing the influence of polymer structural properties (e.g., fixed charge concentration) on these interactions between ions and fixed charges and the resulting salt diffusion properties would provide additional support for the proposed physical picture and would be helpful to guide molecular engineering strategies where polymer salt diffusion properties are modified through modifications of polymer structure.

Recently, the Manning-Meares model has been used to quantify the influence of both ion/fixed charge interactions and water content-based effects (i.e., hindered diffusion) [32,33] on ion diffusion in hydrated charged polymers [23,33,34], and we attempted to use the Manning-Meares model to describe salt diffusion in HQ:BP – XX and XLAMPS (Section S6). One advantage of the Manning-Meares model is that it is derived from theoretical considerations alone and has no adjustable parameters. To a first approximation, the Manning-Meares model qualitatively supports the proposed physical picture and predicts that electrostatic interactions should hinder co-ion diffusion to a lesser extent in polymers equilibrated with increasing salinity due to charge screening phenomenon (Fig. S7B). The model also qualitatively predicts that ion/fixed charge interactions influence co-ion diffusion to a greater extent in HQ:BP – XX than XLAMPS (Fig. S7B) because the dimensionless fixed charge concentration of HQ:BP – XX (i.e., the fixed charge concentration normalized by the sorbed salt concentration) is orders of magnitude larger in HQ:BP – XX than XLAMPS (Fig. S8).

However, limitations of the Manning-Meares model result in poor quantitative agreement between the model predictions and experimental data for HQ:BP – XX (Fig. S7). For example, the Manning model is derived using an assumption that co- and counter-ions only interact with a single polymer chain, which is approximated as a uniformly charged line, and because co- and counter-ions likely interact with many polymer chains in the polymer matrix, the Manning model may underpredict the contribution of electrostatic interactions on salt diffusion properties in the highly-charged HQ:BP – XX polymers (Section S5). The Manning model also does not account for electrostatic interactions, other than ion-fixed charge interactions, that may contribute to ionic non-idealities and salt diffusion in charged polymers (e.g., dielectric exclusion [44] and ion-pairing [45,46]). Additionally, the hindered-diffusion effects described by the Mackie and Meares model are most applicable to high water content polymers and therefore may be an inappropriate choice to describe the influence of free volume-based effects on salt transport in low water content HQ:BP – XX [19,33]. Free volume theory, despite having an adjustable parameter, may be more applicable to describe salt diffusion in polymers with low to moderate water content, such as HQ:BP – XX [19]. In the subsequent section, we discuss how the relationship between water content, external salt concentration, and average salt diffusion coefficients in HQ:BP – XX can be quantified through an application of free volume theory where the influence of electrostatic effects on ion diffusion are described using the characteristic free volume element size necessary for diffusion.

3.3. Free volume theory

Free volume theory provides a framework to describe salt diffusion in hydrated polymers. Cohen and Turnbull's free volume theory suggests that the diffusion coefficient of a penetrant in a polymer, D_i, is related to the total amount of free volume in the polymer v_f, as:

$$\ln(D_i) \sim -\frac{v^*}{v_f} \qquad \text{Eq. 10}$$

where v^* is the characteristic size of a free volume element necessary for diffusion [18]. Yasuda et al. applied Cohen and Turnbull's theory to salt diffusion in hydrated polymers by suggesting that the total free volume available for salt to diffuse through a hydrated polymer is proportional to polymer water content [17]. In the original Yasuda et al. report, the mass fraction of water in the polymer was used as the metric for polymer water content, but the volume fraction of water (i.e., $v_f \sim \phi_w$) is commonly used currently (Fig. 7). In principle, the suggestion by Yasuda et al. implied that any changes in polymer water content – whether via the incorporation of hydrophilic fixed charge groups or osmotic de-swelling – would influence the average salt diffusion coefficient in the polymer.

The free volume theory framework developed by Yasuda et al. leads to a semi-empirical expression for the diffusion coefficient of i in a polymer with water volume fraction ϕ_w:

$$\ln(D_i) = \ln\left(D_i^0\right) - \left[b\left(\frac{1}{\phi_w} - 1\right)\right] \qquad \text{Eq. 11}$$

This model, the one-parameter free-volume theory [19], is constrained so that a penetrant diffusing through a hypothetical membrane of pure water (i.e., $\phi_w = 1$) would have a diffusion coefficient of D_i^0, (which, in aqueous solutions at infinite dilution, is equal to 1.51×10^{-5} cm^2/sec for NaCl, 2.01×10^{-5} cm^2/sec for a chloride ion and 1.34×10^{-5} cm^2/sec for a sodium ion) [17,42]. In the model, the parameter b is related to the characteristic free volume element size necessary for diffusion (i.e., $b \sim v^*$) [17]. As a result, a proxy for this characteristic size of a free volume element necessary for diffusion, v^*, can be obtained by fitting polymer salt diffusion and water content data to the one-parameter free volume theory (Eq. (11)) to obtain the parameter b.

Yasuda et al. applied their model to a series of uncharged hydrogels equilibrated with 1 M NaCl, and they reported that their one-parameter free volume theory model accurately described the scaling relationship between the average salt diffusion coefficient and water content of the polymers (Fig. 7A) [17]. In Yasuda et al.'s investigation, the water content of the hydrogels was varied via modifications of polymer structure [17]. Yasuda et al.'s results suggest that the salt diffusion properties of hydrated polymers scale according to free volume theory when water content is varied via modifications of polymer structure. Because the visual agreement between the model and experimental data is reasonable (i.e., all data were described by a single line) (Fig. 7A), this result suggests that the characteristic free volume size necessary for diffusion is similar for all the uncharged hydrogels characterized by Yasuda et al. [17].

Here, the observation that the average salt diffusion coefficients decrease in XLAMPS polymers equilibrated with increasing salinity suggest that the salt diffusion properties of XLAMPS scale according to the one-parameter free volume theory when the water content was varied via osmotic de-swelling (due to equilibration with external salt solutions of increasing concentration) (Fig. 7B). These results are consistent with previously reported data for XLAMPS equilibrated with 0.01–1 M NaCl [22] (Fig. 7B), as well as other reports in the literature that show similar scaling relationships in uncharged [6,10,15,48] and charged [33,36,37] polymers when water content was varied due to osmotic de-swelling. Similar to Yasuda et al.'s data, the one-parameter free volume theory also describes the relationship between the average salt diffusion coefficient and water content in the XLAMPS polymers (both those synthesized by Yan et al. [22] and those synthesized in this investigation) equilibrated with 0.01–4 M NaCl only using a single line (Fig. 7B). This result suggests that the characteristic free volume element size necessary for diffusion (related to b) is not appreciably influenced by the external salt concentration in the charged XLAMPS polymers.

The average salt diffusion coefficients and inverse water volume fraction of the sulfonated polysulfones scale according to the one-parameter free volume theory when the water content is varied via the incorporation of hydrophilic fixed charge groups (Fig. 7C). However, the average salt diffusion coefficients and inverse water content of the sulfonated polysulfones do not scale according to the theory when the water content is varied via osmotic de-swelling (i.e., increasing external salt solution concentration) (Fig. 7C), which is consistent with observations made in other sulfonated polysulfones and sulfonated polystyrene [15]. This unexpected result is consistent with the physical picture that salt diffusion in HQ:BP – XX equilibrated with increased

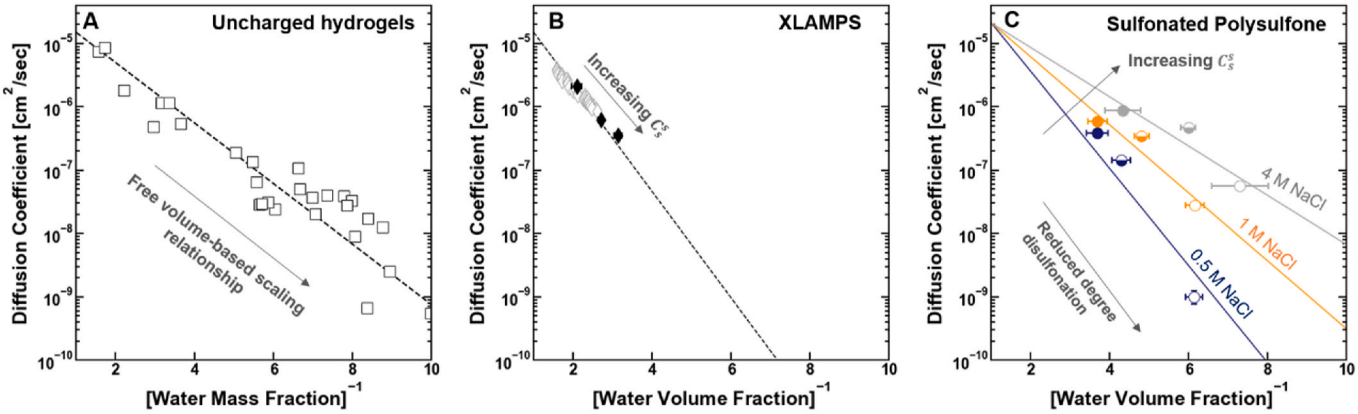

Fig. 7. Average salt diffusion coefficient data reported as a function of inverse water content for hydrated (A) uncharged hydrogels equilibrated with 1 M NaCl [17], (B) XLAMPS equilibrated with 0.5–4 M NaCl (◆) and XLAMPS as synthesized by Yan et al. (◇) [22], and (C) HQ:BP – 20 (○), HQ:BP – 25 (◒), and HQ:BP – 30 (●) equilibrated with 0.5–4 M NaCl. The lines in (A), (B) and (C) are calculated by fitting the data to the one parameter free volume theory (Eq. (11)). The uncertainties were determined as the standard deviation from the mean of three measurements, and uncertainty in the inverse water volume fraction was calculated using standard error propagation.

salinity is influenced by differences in other interactions (e.g., electrostatic interactions between co-ions and fixed charges) and not necessarily free volume-based effects alone.

Within the context of the one parameter free volume theory, an increase in the average salt diffusion coefficient despite a reduction in the water content may be explained by a simultaneous reduction in the parameter related to the characteristic free volume element size necessary for diffusion, b (Eq. (11)). This parameter b may be influenced by electrostatic interactions between polymer fixed charges and ions, so that within the context of free volume theory, the influence of external salt concentration on salt diffusion may be described by considering the influence of external salt concentration on b. In the subsequent section, we use the one-parameter free volume theory to probe the influence of ion/fixed charge interactions on the characteristic free volume element size necessary for salt, co-, and counter-ion diffusion (via the parameter b) in the HQ:BP – XX materials.

3.3.1. *Influence of salt concentration on the parameter* ***b*** *for sulfonated polysulfone*

The one-parameter free volume theory was applied to HQ:BP – XX at constant external salt concentrations (Fig. 7C) because free volume theory accurately described the scaling relationship between polymer water content and average salt diffusion coefficient in HQ:BP – XX when the water content was varied via degree disulfonation. At a given external salt concentration, the model describes the influence of degree disulfonation on the relationship between water content and salt diffusion reasonably well (i.e., within similar degrees of scatter around the trend line as Yasuda et al.'s data) (Fig. 7C). This result suggests that at a given external salt concentration, ion-fixed charge interactions, which may influence the characteristic free volume element size necessary for salt diffusion, are similar in HQ:BP – XX, which is consistent with the observation that the dimensionless fixed charge concentration was generally independent of the degree disulfonation (Section S5). To describe the influence of increased salinity on the HQ:BP – XX salt diffusion data, the slope of the line decreases with increasing salinity (Fig. 7C). This application of free volume theory effectively suggests that the characteristic free volume element size necessary for diffusion (related to the parameter b) decreases as external salt concentration increased (Table 2).

To explain the molecular underpinnings of the observed reduction of b for HQ:BP – XX equilibrated with increasing salinity we applied this free volume-based analysis to the co- and counter-ion diffusion data (Fig. 8). The parameter, b, is largest for co-ions, and smallest for counter-ions (Table 2). This parameter is identical for co-ions and average salt (Table 2), further supporting the conclusion that co-ion diffusion governs average salt diffusion in HQ:BP – XX.

These results effectively suggest that the characteristic free volume element size necessary for diffusion is larger for co-ions than it is for counter-ions, and this result may also be explained through an analysis of electrostatic interactions between fixed charges, co-ions, and counter-ions. For example, repulsive interactions between co-ions and fixed charges may effectively increase the characteristic free volume element size necessary for diffusion, because non-favorable thermodynamic interactions (i.e., electrostatic repulsion) between co-ions and fixed charges are theoretically minimized when the two charges are separated by larger distances [49,50]. Alternatively, thermodynamically favorable interactions between counter-ions and fixed charges may effectively reduce the characteristic free volume element size necessary for counter-ion diffusion because associative interactions between counter-ions and fixed charges, (e.g., counter-ion condensation) may allow counter-ions to diffuse through the polymer via migration along polymer fixed charges [33]. This diffusion mechanism, which would allow counter-ions to diffuse through the polymer more quickly than if they were diffusing through the polymer free volume alone, may provide a physical explanation for the reduced characteristic free volume element size necessary for counter-ion diffusion.

Table 2
Eq. (11) parameter, ***b***, reported for average salt, co-ion, and counter-ion diffusion in the HQ:BP – XX polymers.

External salt concentration [mol/L]	Parameter related to the characteristic free volume element size necessary for diffusion, b		
	NaCl	Co-ion (Cl^-)	Counter-ion (Na^+)
0.5	1.67 ± 0.33	1.76 ± 0.30	0.84 ± 0.21
1	1.14 ± 0.14	1.23 ± 0.14	0.77 ± 0.16
4	0.81 ± 0.12	0.88 ± 0.13	0.69 ± 0.20

The values of b were calculated by fitting the experimental diffusion and water content data to the one-parameter free volume theory (Eq. (11)) and experimental errors are reported as the standard deviation calculated from the variance of the fit parameter.

As the co-ion and average salt diffusion coefficients were effectively equal, the parameter, b, for co-ion diffusion also decreased with increasing salinity (Table 2). Alternatively, for the counter-ion diffusion data, b was effectively independent of the external salt concentration (Table 2) (i.e., all data, regardless of the external salt concentration, effectively fall on the same line (Fig. 8B)). At 4 M NaCl, the values of b for co-ion and salt diffusion decrease so that they are effectively equal to b for counter-ion diffusion (Table 2).

The observed reduction in b for co-ion diffusion with increasing salinity suggests that the characteristic free volume element size necessary for co-ion diffusion may decrease with increasing salinity. This result may be explained with the previously proposed physical picture where increased charge screening with increasing salinity decreases the length scale over which repulsive electrostatic interactions are significant, and under such circumstances, the characteristic free volume element size necessary to accommodate a fixed charge, and counter- and co-ion, is reduced. For counter-ion diffusion, observations that b is effectively independent of the external salinity suggest that the characteristic free volume element size necessary for counter-ion diffusion may be independent of external salt concentration. This result may be consistent with previous observations that counter-ion condensation occurs in these sulfonated polysulfones over the entire range of external NaCl concentrations [44] so that counter-ions can migrate along the polymer backbone over the entire range of NaCl concentrations. These results may explain the observation that co-ion diffusion coefficients in the sulfonated polysulfone change by an order of magnitude over the salt concentration range while counter-ion diffusion coefficients remain relatively constant (Figs. 3 and 4). Generally, these observations support the proposed physical picture where salt diffusion in the sulfonated polysulfones is governed by electrostatic interactions between ions and fixed charges and provide additional evidence that the observed increase in the average salt diffusion coefficients of HQ:BP – XX with increasing salinity despite reduced water content is a result of the progressive screening of co-ion fixed charge interactions with increased ionic strength of the solution sorbed in the polymer (i.e., salinity).

4. Conclusions

The average salt diffusion coefficients for a series of sulfonated polysulfone polymers (referred to as HQ:BP – XX) increased when the polymers were equilibrated with sodium chloride solutions of increasing concentration despite reductions in polymer water content. This observation stands in contrast to observations made in charged XLAMPS polymers, where both the average salt diffusion coefficient and water content decrease in polymers equilibrated with increasing salt concentration. We explain these observations using a physical picture where

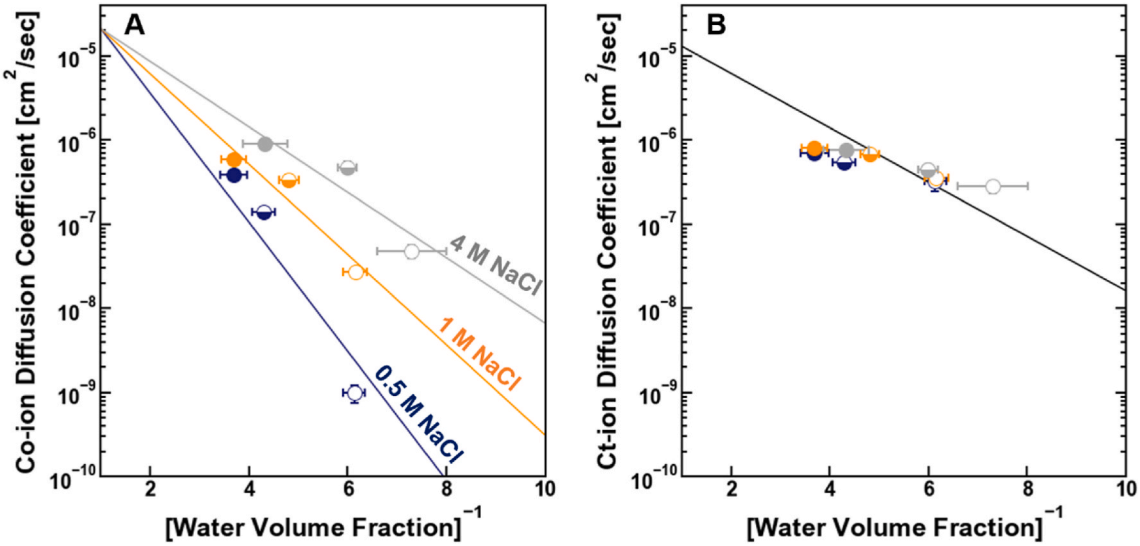

Fig. 8. (A) Co-ion and (B) counter-ion diffusion coefficient data reported as a function of inverse water volume fraction for HQ:BP – 20 (○), HQ:BP – 25 (◒), and HQ:BP – 30 (●) equilibrated with 0.5–4 M NaCl. The external salt concentration is denoted by color, and data for polymers equilibrated with 0.5 M NaCl, 1 M NaCl, or 4 M NaCl are navy, orange, or gray, respectively. The lines in (A) were calculated by fitting the co-ion diffusion data (at constant external salt concentration) to the one parameter free volume theory, and the line in (B) was calculated by fitting the counter-ion data at all external salt concentrations to the one-parameter free volume theory. The uncertainties were determined as the standard deviation from the mean of three measurements, and uncertainty in the inverse water volume fraction was calculated using standard error propagation.

electrostatic interactions influence average salt diffusion to a greater extent in HQ:BP – XX than XLAMPS. To quantitatively describe the influence of these electrostatic effects on salt diffusion in charged polymers, we propose an application of free volume theory where electrostatic interactions are described using the characteristic free volume element size necessary for salt diffusion. Through this application of free volume theory, we found that the influence of external salt concentration on salt diffusion in HQ:BP – XX may be governed by a reduction in the characteristic free volume element size necessary for diffusion with increasing salinity. These results provide a physical explanation for previously unexplained salt diffusion phenomenon observed in charged polymers, which may be helpful to guide molecular engineering strategies that modify polymer salt diffusion properties via modifications of polymer structure.

CRediT authorship contribution statement

Sean M. Bannon: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Ethan Kutner:** Investigation. **Benjamin Garretson:** Investigation. **Geoffrey M. Geise:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Geoffrey M. Geise reports financial support was provided by National Science Foundation. Sean M. Bannon reports financial support was provided by National Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2024.123197.

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