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# Characterization of a sulfonated pentablock copolymer for desalination applications

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ABSTRACT

Water and salt transport properties were determined in a family of sulfonated pentablock copolymers to characterize their potential as chlorine-tolerant desalination membrane materials. The degree of sulfonation, block molecular weight, and casting conditions can be independently varied to tune the transport properties of these materials. Data for water uptake, water permeability, salt permeability, and apparent surface charge are presented. Apparent diffusion coefficients of water in these materials were calculated using the solution-diffusion theory. Generally speaking, water sorption, water diffusivity, water permeability, and salt permeability increase with increasing degree of sulfonation. As ion exchange capacity increases from 0.4 to 2.0 meq/g (dry polymer), water uptake values vary between 21% and 118%, and water permeability values, in units of $cm^2\ s^{-1}$, vary over 4 orders of magnitude. Salt permeability depends on both the upstream sodium chloride concentration, between 0.01 and 1.0 mol $L^{-1}$, and the degree of sulfonation. Both water permeability and salt permeability are sensitive to the conditions used when casting the polymer films. Apparent surface charge, as characterized by zeta potential, has been shown to be related to the fouling tendency of several membrane materials. In these materials, zeta potential is most negative in samples with low levels of sulfonation and is near neutral in samples with the highest level of sulfonation.

## 1. Introduction

Developing new water sources is critical to address the increasing worldwide shortage of water [1–10]. Saline water, whether from brackish ground water or ocean sources, is a potential supply of water provided it can be sufficiently desalinated. Membrane-based technologies such as reverse osmosis (RO) are among the most effective strategies available to effectively and economically desalinate water [2,11–13].

RO was first developed based on cellulose acetate membranes. Currently, the dominant materials are aromatic polyamide-based thin-film composite membranes [3,14,15]. However, anticipated demands will require improved membranes that not only offer high flux and high salt rejection but are also more robust and durable, e.g., resistant to oxidation by chemicals, such as the chlorine-based disinfectants used in water treatment, highly pH tolerant, and more resistant to fouling than current materials [3,16].

Water must sorb into the polymer membrane to an adequate level to achieve high water flux; however, high water sorption typically reduces salt rejection. Optimizing membrane performance requires careful management of this tradeoff. One possible strategy is to make a more robust and durable material by selecting polymers that feature chemically resistant backbones; unfortunately, these materials are often very hydrophobic. Sulfonation is one way to introduce hydrophilic character into an otherwise hydrophobic polymer [17–28]. The degree of sulfonation can be varied to optimize the water flux/salt rejection tradeoff. Compared to weakly charged or uncharged polymers, strongly charged sulfonated polymers could be expected to exhibit different salt sorption and transport behavior, due to the presence of the fixed charges on the polymer [16,29].

Sulfonated poly(arylene ether sulfones) have been studied as potential desalination membranes [20,21,30,31]. However, the degree of sulfonation is limited because, at high sulfonation levels, these random copolymers become water soluble. Block copolymer architectures have been considered as a way to achieve high levels of sulfonation without strong losses in mechanical stability [31,32]. Sulfonated poly(styrene-b-hydrogenated butadiene-b-styrene) or SEBS triblock copolymers have been studied [32–35], but the sulfonation of their styrene end blocks leads to uncontrolled swelling and, thus, poor mechanical properties when hydrated.

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This report presents water and salt transport in a new styrenic pentablock copolymer platform. Shown in Fig. 1, Nexar™ polymers, produced by Kraton Performance Polymers, Inc. (Houston, TX), are symmetric pentablock copolymers consisting of *tert*-butyl styrene end blocks, hydrogenated isoprene inner blocks, and a middle block that is selectively and randomly sulfonated to a desired degree, *x*, using a post-polymerization sulfonation process [32].

Unlike SEBS materials, when sulfonation is limited to the middle block, the result is a polymer with controlled swelling and good mechanical properties in the hydrated state [32,36]. For this sulfonated pentablock copolymer, the *tert*-butyl styrene end blocks do not undergo sulfonation since the favorable para and ortho positions of the phenyl ring are protected from sulfonation by the *tert*-butyl group and the polymer backbone, respectively. The hydrogenated isoprene block gives the copolymer additional toughness. Hydrophilic and hydrophobic micro-domains have been observed in this material [37]. The pentablock copolymer architecture of the material affords a unique opportunity to tune the hydrophilic and hydrophobic character almost independently.

## 2. Experimental

### 2.1. Materials

Sulfonated pentablock copolymer films were cast from a micellar solution [37] using one of two procedures [36]. The polymer solution was hand-cast onto a silane treated glass plate using a casting knife to draw down a uniform film of desired thickness. Solvents were evaporated at room temperature in a nitrogen environment with ~20% relative humidity. Alternatively, a machine-cast method used commercial equipment to cast the polymer solution onto a silane treated polyester substrate. Solvent evaporation was accelerated by using higher evaporation temperatures. The transport property implications of these two casting methods will be discussed in the Results and discussion section.

Two base copolymers (A and B) with varying levels of sulfonation were the focus of this study. Table 1 shows the block molecular weights in the two copolymers relative to that of the middle styrene block [38]. More detailed information about the molecular weights has been reported elsewhere [38]. Copolymer B has hydrophobic blocks, relative to the middle styrene block, that are larger than those of copolymer A. The transport property implications of this adjustment will be described in the Results and discussion section.

Table 2 lists the relevant sulfonated pentablock copolymers that were prepared from each base block copolymer. The degree of sulfonation is represented both by the ion exchange capacity of the material, defined with units of milli-equivalents (meq) per gram of dry polymer, and the fraction of sulfonation of the middle block styrene repeat units.

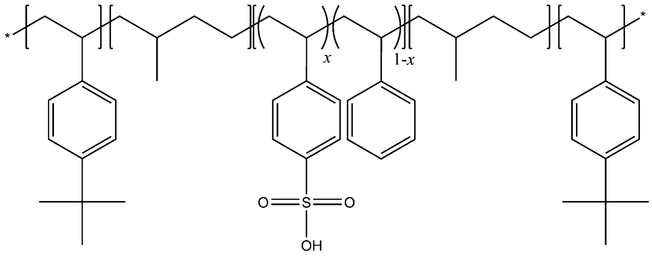

**Fig. 1.** Structure of the sulfonated pentablock copolymer.

**Table 1**
Relative block compositions (normalized by the middle styrene block molecular weight) for the two base block copolymers.

| Block Copolymer | Relative Block Composition (by mass) | | |
|---|---|---|---|
| | *tert*-butyl styrene | Hydrogenated isoprene | Styrene |
| A | 0.62 | 0.64 | 1.00 |
| B | 1.04 | 0.72 | 1.00 |

### 2.2. Methods

Sulfonated pentablock copolymer samples were received from Kraton Performance Polymers, Inc. as uniform thickness films in the acid form, e.g., the counter-ion for the sulfonate group was a proton as shown in Fig. 1. Since the material was produced via post-polymerization sulfonation, any by-products remaining in the polymer from the sulfonation step needed to be removed before transport measurements were performed. These by-products, such as residual acids, were removed by soaking and washing the film samples at ambient conditions in de-ionized water (Millipore Advantage A10) until the soaking solution stabilized at pH = 5.7. De-ionized water, equilibrated with atmospheric carbon dioxide, has a pH of 5.7 [39]. This pH stabilization was achieved after replacing the de-ionized soaking water 3 times over a period of 3 h. To insure that all acids and water extractable molecules were removed, samples were soaked in de-ionized water at room temperature for 24 h. During the first 3 h, the samples were transferred to fresh de-ionized water every hour. Finally, 1 h before use in an experiment, the sample was transferred to a fresh volume of de-ionized water.

#### 2.2.1. Water uptake measurement

Water uptake was measured gravimetrically at room temperature. First, the polymer was equilibrated in de-ionized water and the sample's wet mass, $m_{\mathrm{wet}}$, was measured. Next, the sample was dried under vacuum at room temperature until its mass stabilized and an apparent dry mass, $m_{\mathrm{dry}}$, was measured. The water uptake of each sample was calculated using:

$$\text{Water Uptake} = \mathrm{WU} = \frac{m_{\mathrm{wet}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}} \tag{1}$$

The mass fraction of water in the hydrated sample, $w_{w0}^{m}$, was calculated using:

$$w_{w0}^{m} = \frac{m_{\mathrm{wet}} - m_{\mathrm{dry}}}{m_{\mathrm{wet}}} \tag{2}$$

The mass concentration of water in the hydrated polymer, $C_{w0}^{m}$, can be calculated by assuming volume additivity applies

$$C_{w0}^{m} = (\mathrm{WU})\rho_m = \frac{m_{\mathrm{wet}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}\left(\frac{w_{tBS}}{\rho_{tBS}} + \frac{w_{HI}}{\rho_{HI}} + \frac{w_S}{\rho_S} + \frac{w_{SS}}{\rho_{SS}} + \frac{\mathrm{WU}}{\rho_w}\right)} \tag{3}$$

where $\rho_m$ is the mass of polymer per hydrated sample volume, $w_i$ is the mass of component $i$ per total mass of dry polymer, and $\rho_i$ is the

**Table 2**
Ion exchange capacities (IECs) and the sulfonation fraction of middle block styrene repeat units for the two base block copolymers.

| Block copolymer A | | Block copolymer B | |
|---|---|---|---|
| IEC [meq/g] | Sulfonation fraction | IEC [meq/g] | Sulfonation fraction |
| 1.46 | 0.30 | 0.4 | 0.10 |
| 1.6 | 0.33 | 0.7 | 0.18 |
| 2.0 | 0.41 | 1.0 | 0.26 |
| | | 1.5 | 0.39 |
| | | 2.0 | 0.52 |

**Table 3**
Legend for non-pentablock copolymer data shown in Fig. 6.

| Symbol | Sample name |
|---|---|
| ▽ | Methyl methacrylate/glycerol methacrylate copolymer |
| □ | Hydroxypropyl methacrylate/methyl methacrylate copolymer |
| ◇ | Hydroxypropyl methacrylate/glycidyl methacrylate copolymer |
| × | Hydroxyethyl methacrylate/methyl methacrylate copolymer |
| + | Hydroxyethyl methacrylate hydrogel |
| △ | Hydroxyethyl methacrylate/glycerol methacrylate hydrogel |
| ⊠ | NaCl diffusion coefficient in water at 25 °C ($1.5 \times 10^{-5}$ cm$^2$ s$^{-1}$) [74] |

density of component *i*. The densities of the components were taken as follows: *t*-butylstyrene (*tBS*) 0.947 g cm$^{-3}$ [40], hydrogenated isoprene (*HI*) 0.85 g cm$^{-3}$ [41], styrene (*S*) 1.048 g cm$^{-3}$ [40], styrene sulfonic acid (*SS*) 1.47 g cm$^{-3}$ [42], and water (*w*) 1.00 g cm$^{-3}$ [43].

The dry mass, which was measured gravimetrically, may neglect a small amount of residual tightly-bound water [44–47] that hydrates the sulfonic acid groups; however, the amount of this residual water was shown to be very small, relative to the high water uptake of the material, by Karl Fischer titration [48].

Water uptake was also measured after the polymer sample was equilibrated in a salt solution of desired concentration. The rest of the experiment was identical to that described above. Based on observation, the sample did not lose salt during the drying process, and the small amount of salt sorbed into the polymer during hydration is negligible compared to the water uptake.

### 2.2.2. *Water permeability measurement*

Pure water permeability of the sulfonated pentablock copolymer films was measured at ambient temperature, ranging from 24 °C to 27 °C, using a stainless steel dead-end cell (HP4750 Stirred Cell, Sterlitech, Corp., Kent, WA). The sample was mechanically supported in the cell by a porous stainless steel disc. A piece of filter paper was placed between the sample film and the porous stainless steel disc to prevent sample rupture. The dead-end cell was filled with de-ionized water, sealed and pressurized with compressed nitrogen to a desired pressure that did not exceed 800 psig (approximately 55.2 bar). The pressure was varied only to control the duration and, thus, the accuracy of the experiment; the applied pressure does not appreciably affect the pure water permeability of these materials over the pressure range considered [49].

The simple form of the solution-diffusion theory of reverse osmosis [49,50] gives the following expression for the water flux

$$n_w = \frac{P_w}{l}\frac{\overline{V}_w}{RT}[\Delta p - \Delta\pi] = \frac{D_w C^m_{w0}}{l}\frac{\overline{V}_w}{RT}[\Delta p - \Delta\pi] \tag{4}$$

where $D_w$ is the apparent diffusion coefficient of water in the hydrated polymer, $\overline{V}_w$ is the partial molar volume of water (18 cm$^3$ mol$^{-1}$) [51], *R* is the gas constant, *T* is the absolute temperature of the feed solution, $\Delta p$ is the applied pressure difference, is the osmotic pressure difference across the film, and *l* is hydrated sample thickness that was measured immediately following the experiment using a Mitutoyo Litematic VL-50A micrometer. Sample thicknesses ranged from 25 to 60 μm, and the variability of the measured sample thickness was typically around 5%.

Rigorously speaking, this hydrated thickness should be defined based upon the water content of the film during the experiment. This thickness is not the same as either the dry thickness or the thickness when the sample is equilibrated in water since, during a water permeability experiment, there is a gradient in water content across the sample, which will cause a gradient in swelling across the sample, leading the thickness of the membrane to be potentially different during the permeation experiment than when it is fully hydrated with water; this effect has been discussed in the literature and can be significant for situations such as, for example, organic liquid permeation through highly swollen rubbers [49,52]. In our experiments, the characteristic timescale for diffusion of water in the IEC 1.0–2.0 materials (calculated as $l^2/D_w$ [53]) was less than the amount of time required to remove the sample from the dead-end cell and measure its thickness (which was approximately 2–3 min). Consequently, the measured sample thickness was essentially equal to the thickness of samples equilibrated by soaking in water. For the IEC 0.4 and IEC 0.7 materials, the differences between the water equilibrated thickness and the dry thickness were 3% and 6%, respectively. As a result, the differences between the water equilibrated thickness and the thickness during the water permeability experiment were within the variability of the thickness measurement.

As has been described elsewhere, the pressure dependence of water flux is thermodynamic in nature, not hydrodynamic [16,49]. Equation (4) defines the water permeability, which consists of diffusion and solubility terms:

$$P_w = D_w K_w$$

where

$$K_w \equiv \frac{C^m_{w0}}{C^s_{w0}} \tag{5}$$

where $C^s_{w0}$ is the concentration of water in the upstream solution and is essentially constant for many solutions of interest. For example, $C^s_{w0}$ at 25 °C was taken to be 1.00 g/cm$^3$ [43]. Equation (4) can be used to calculate water permeability when $[\Delta p - \Delta\pi]$ is held constant, and $n_w$ and $l$ are measured.

### 2.2.3. *Salt permeability measurement*

The salt flux is negligibly influenced by pressure and is given by

$$n_s = \frac{D_s}{l}[C^m_{s0} - C^m_{sl}] = \frac{D_s K_s}{l}[C^s_{s0} - C^s_{sl}] \tag{6}$$

where $C^m_{s0}$ and $C^m_{sl}$ are the concentrations of salt in the membrane at the upstream and downstream faces, respectively [50]. Likewise, $C^m_{s0}$ and $C^m_{sl}$ are the bulk solution concentrations on the upstream and downstream sides of the membrane, respectively. Equation (6) defines the salt permeability

$$P_s = D_s K_s \tag{7}$$

where $D_s$ is the apparent diffusion coefficient of salt, and the effective salt partition coefficient, $K_s$, characterizes the concentration of salt in the membrane to that in the bulk solution.

Sodium chloride permeability was measured using a diffusion cell where the membrane separated two chambers of equal volume (customized 35 mL PermeGear Side-bi-Side Diffusion Cell, Hellertown, PA). The donor cell chamber (upstream) was filled with an aqueous solution of desired salt composition while the receiver cell chamber (downstream) was filled with de-ionized water. The salt concentration in the receiver cell was determined as a function of time by measuring conductivity and converting to salt concentration via a calibration curve. Solutions in both cells were stirred using magnetic stirbars. The donor and receiver cells were jacketed, and water from a circulation bath was passed through the jacket continuously to maintain the temperature at 25 °C. The steady-state salt permeability, $P_s$, was calculated from [54]

$$\ln\left[1 - \frac{2C^s_{sl}[t]}{C^s_{s0}[0]}\right] = -\left(\frac{2AP_s}{Vl}\right)t \tag{8}$$

where $C^s_{sl}[t]$ is the downstream bulk solution concentration of salt at time *t*, $C^s_{s0}[0]$ is the upstream bulk solution concentration of salt

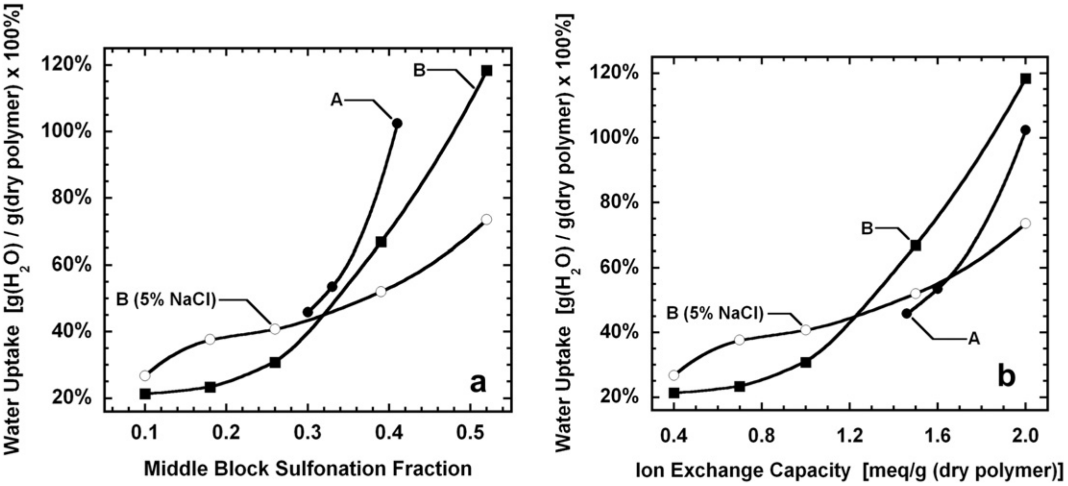

**Fig. 2.** Pure water uptake for copolymers A (●) and B (■) and water uptake of base copolymer B in a 5% NaCl solution (○) versus the sulfonation fraction of middle block repeat units (a) and ion exchange capacity (b).

at $t = 0$, $A$ is the sample area, and $V$ is the volume of liquid in each cell; the donor and receiver cell volumes must be equal to employ this equation. The effective membrane area was 1.77 $cm^2$ and 35 mL solution volumes were used in the donor and receiver cells.

### 2.2.4. Zeta potential measurement

Zeta potentials of the sulfonated and unsulfonated pentablock copolymers were calculated, using the Fairbrother–Mastin approximation, from streaming potential measurements made at ambient conditions using an Anton Parr SurPASS Electrokinetic Analyzer fitted with a clamping cell at a system pressure of 300 mbar [55–57]. A 10 mM NaCl electrolyte was used in these measurements, and pH was varied by addition of NaOH or HCl solutions as necessary. The pH was ramped at increments of ΔpH ~0.3 from pH 10 to 3 using the instrument's automated titrator. At each pH value, streaming potential was measured 4 times and these data were averaged.

The streaming potential measurements on acid form sulfonated polymer samples were erratic, likely due to ion exchange between the NaCl electrolyte solution and the polymer. This ion-exchange effect can be observed in simple soaking experiments: the pH of the external solution containing an acid form sample decreases when salt is added [58]. While the streaming potential was being measured, the pH and conductivity of the solution in the instrument were being altered by the ion exchange process. To resolve this, film samples were soaked in solutions of 10 mM NaCl until no pH change was observed in the soaking solution, i.e., samples were converted to the sodium counter-ion form, before running the streaming potential experiment. This step mimics the situation in a desalination process where one would expect the polymer to be in a salt form, due to the large volume of saline water being treated. After this process was adopted, the streaming potential results were very reproducible.

## 3. Results and discussion

### 3.1. Water uptake

Water uptake data for the sulfonated pentablock copolymers are presented in Fig. 2; the unsulfonated pentablock copolymer had negligible water uptake. As the degree of sulfonation increased, water uptake increased, as expected.

The ion exchange capacities for members of the copolymer B family of materials correspond to higher degrees of sulfonation compared to those of copolymer A materials because of the increased hydrophobic end block size of copolymer B. The water uptake of copolymer A materials was higher than those of copolymer B materials, indicating that increases in the mass of the hydrophobic end blocks restricts swelling. The water uptake of copolymer B materials is somewhat different when the polymer is

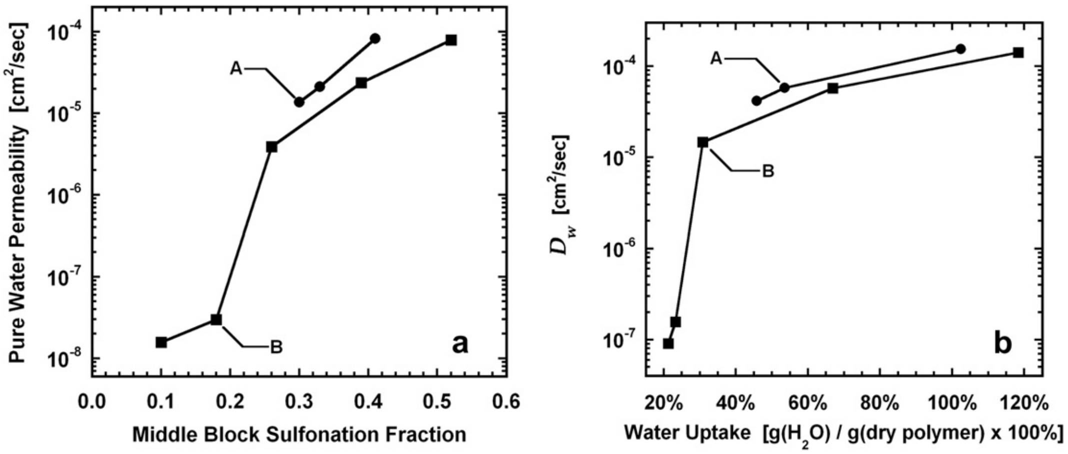

**Fig. 3.** Pure water permeability (a) and the apparent water diffusion coefficient as defined in Equation (4) (b) for the two base block copolymers.

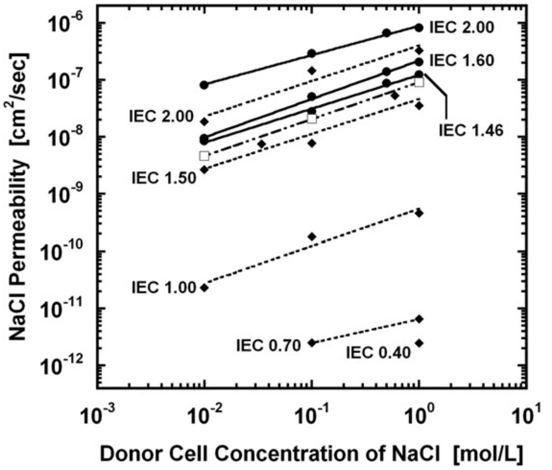

**Fig. 4.** Sodium chloride permeability as a function of donor cell salt concentration for the sulfonated pentablock copolymers A (●) and B (◆) and Nafion® 111 (□) – IECs for the sulfonated pentablock copolymers are listed in units of meq/g (dry polymer).

equilibrated in a 5% NaCl solution, i.e., converted to the sodium form. Decreases in water uptake have been observed upon neutralization of acid form sulfonated polymers [20,59,60]. For copolymer B samples with IEC values in the range of 0.4–1.0 meq/g (dry polymer), the pure water uptake is lower than the water uptake in the 5% NaCl solution; the fundamental origin of this behavior is not fully understood at this time.

### 3.2. Pure water permeability

As the polymer's degree of sulfonation increases, its water uptake increases. This rise in water sorption correlates strongly with an increase in water permeability as shown in Fig. 3. Additionally, as the water content of the material increases, plasticization of the polymer by water increases the diffusion coefficient of water as shown in Fig. 3.

Fig. 3 also shows the effect of varying the hydrophobic character of the base polymer. Copolymer B is less able to swell in water due to increased length of the hydrophobic end blocks, as discussed earlier in this section. Lower water permeability is expected from materials, such as copolymer B, with reduced water content.

The apparent water diffusion coefficients, defined by Equation (4), are shown in Fig. 3. At higher levels of sulfonation, both copolymer A and B materials exhibit similar behavior. However, at a lower degree of sulfonation a large decrease in the apparent diffusion coefficient was observed for copolymer B. These data suggest that a fundamental change in material properties occurs between IEC 0.7 and IEC 1.0. This may be due to a morphological reorganization leading to a greater degree of phase continuity of the water swollen hydrophilic micro-domains of the block copolymer.

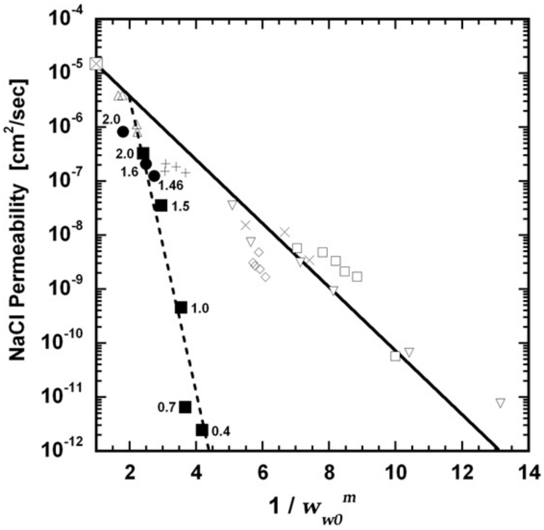

**Fig. 6.** Sodium chloride permeability of sulfonated pentablock copolymers A (●) and B (■), labeled with the material's IEC in units of meq/g (dry polymer), compared to data published by Yasuda et al. [54,72] for the product of the sodium chloride diffusion and solubility coefficient ($D_sK_s = P_s$) versus the reciprocal of the mass fraction of water in the hydrated polymer with a 5% sodium chloride solution. The legend for non-pentablock copolymer data is shown as Table 3.

### 3.3. Salt permeability

Contrary to expectations for an unchanged hydrophilic polymer, the salt permeability of a highly charged material is expected to depend on the upstream, or donor cell, salt concentration [16]. Generally, this dependence on salt concentration is not observed for materials such as cellulose acetate [50,61]. However, exceptions have been noted as cellulose acetate exhibits a weak ion exchange capacity, as a function of both pH and external salt solution concentration, owing to the carboxyl groups in the cellulose acetate polymer [62–64]. The sodium chloride salt permeability of the

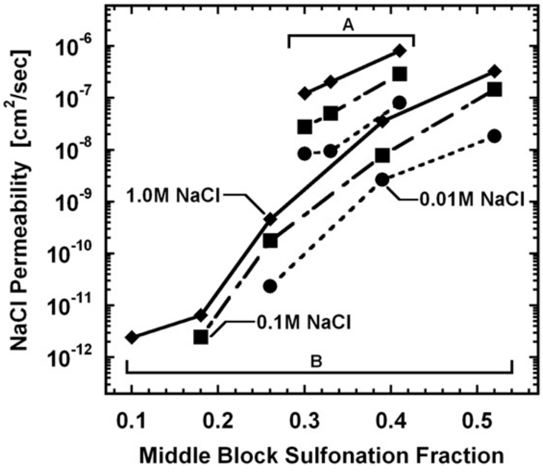

**Fig. 5.** Sodium chloride permeability for different donor cell concentrations as a function of degree of sulfonation for the two base block copolymers.

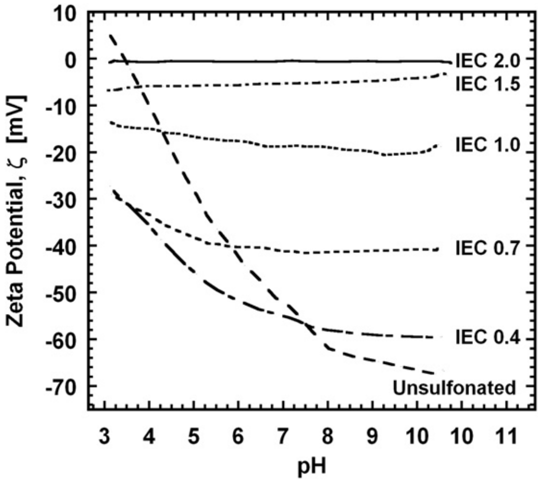

**Fig. 7.** Zeta potential as a function of pH for the block copolymer B materials.

sulfonated pentablock copolymer materials increased as the donor cell salt concentration increased as seen in Fig. 4. Nafion® 111 (IEC = 0.909 meq/g(dry polymer))[65] films showed similar behavior and these results were included in Fig. 4 for comparison.

The variation in salt permeability as a function of donor cell salt concentration may be due to Donnan exclusion, that is, an electric potential acts to exclude co-ions (anions for sulfonated polymers) from the polymer matrix [16,29,66,67]. Donnan exclusion is more pronounced at lower salt concentrations [29]. As salt concentration decreases, sorption of chloride ions in the polymer matrix decreases [16]. This reduction in salt sorption, effectively a decrease in $K_s$, reduces salt permeability, as would be expected from Equation (7). At higher salt concentrations, the ionic strength of the solution becomes large relative to the fixed charge concentration of the polymer, which tends to overwhelm the Donnan exclusion effect. As a result, the salt permeability increases with increasing salt concentration [16,29]. Therefore, the change in permeability observed in Fig. 4 may result from changes in salt sorption. The apparent salt diffusion coefficient, however, may be sensitive to chain stiffening as a result of ion exchange [68–70] or water sorption variations that may result from salt concentration variations [59,60,71]. To determine whether salt sorption, salt diffusion, or both phenomena drive the dependence of salt permeability on concentration, additional experiments need to be performed.

As the ion exchange capacity increases, the salt permeability increases as seen in Fig. 4. This may seem contrary to the Donnan exclusion argument presented above; however, the water uptake of the polymer increases with the degree of sulfonation (or IEC), and this trend will tend to increase the salt partition coefficient as shown for cellulose acetate materials [50]. In addition, the previously mentioned plasticization effect with increasing water content will cause penetrant diffusion coefficients to increase. Thus, it is not surprising that materials with increased degree of sulfonation are more permeable to salt as shown in Fig. 5.

As the swelling of copolymer B is restricted relative to that of copolymer A, salt permeability is generally lower in copolymer B than in A. This decrease in salt permeability is greater than the decrease in water permeability shown in Fig. 3, thus, the permeability selectivity, defined as the ratio of water permeability to salt permeability, of copolymer B is greater than that of copolymer A. This increase in selectivity is believed to be a result of the changes in water content and, thus, plasticization discussed previously and not a result of increases in the fixed charge concentration of the membrane.

It is helpful to review the effect of water content on permeability of salt through other hydrated membrane materials. In the late 1960s, Yasuda et al. [54,72] reported salt permeability versus the reciprocal of the equilibrium mass fraction of water, $1/w_{w0}^{m}$, for several hydrated hydrogel materials. Their work showed a strong correlation between salt permeability and water content. Ju et al. reported a similar correlation between salt permeability and water content in several cross-linked poly(ethylene glycol) hydrogels [73]. Fig. 5 compares results for sulfonated pentablock copolymers with those for hydrogels studied by Yasuda et al. [54,72] Salt permeability and water uptake values for the sulfonated pentablock copolymer were determined using a 5% sodium chloride feed solution as employed by Yasuda et al.

Fig. 6 shows that the salt permeabilities for the sulfonated pentablock copolymers are, at comparable levels of water uptake, lower than those for the hydrogel materials considered by Yasuda et al. This result may be due, in part, to Donnan exclusion of salt from the polymer matrix, which would not be operative in the hydrogels considered by Yasuda et al., which are, for the most part, uncharged. However, there may also be some effect from the domain structure of the block copolymer material. These materials have hydrophobic domains where water and salt transport should be negligible compared to the hydrophilic sulfonated domains of the copolymer. The salt permeability values for the block copolymer are averages over the entire heterogeneous structure while many of the hydrogels studied by Yasuda et al. were homogeneous materials.

Evidence of this effect can be seen in the limit of high water content where the salt permeability values of the hydrogel materials approach the limit of diffusion of salt in water. The sulfonated block copolymer data, at high water content, do not intersect the diffusion coefficient of salt in water because significant portions of the polymer cannot transport salt. Thus, the best fit line of the block copolymer data intersects the best fit line of the data from Yasuda et al. at an *x*-axis value that appears to correspond with the inverse mass fraction of hydrated polymer in the swollen block copolymer, which is approximately 2.

### 3.4. *Surface charge (zeta potential)*

Since the surface charge of a membrane can influence its tendency to undergo fouling [55,56,75,76], the zeta potential was determined for the copolymer B films. These results are shown as a function of pH in Fig. 7.

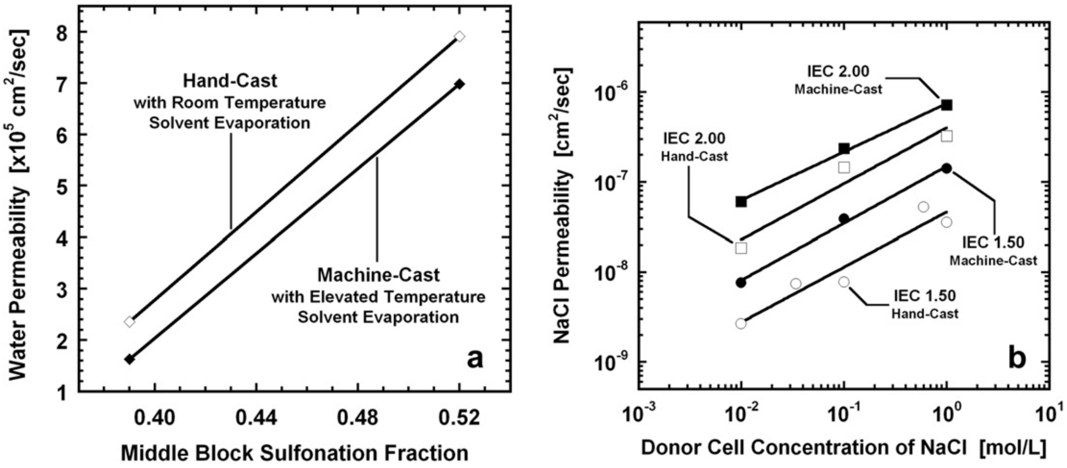

**Fig. 8.** Pure water permeability versus middle block sulfonation fraction (a) and sodium chloride permeability versus donor cell concentration of sodium chloride (b) for copolymer B materials cast by both the hand-cast and machine-cast procedures.

Interestingly, the zeta potentials become more neutral and less pH dependent as the sulfonation of the material, i.e., IEC, increases. The unsulfonated membrane appears to be negatively charged over most of the pH range considered; this result is similar to zeta potential data for other hydrophobic polymers [77]. It seems initially counterintuitive that such a membrane would become less negatively charged as sulfonate groups are incorporated. However, it has been suggested that anionic species, such as hydroxide ions, may sorb preferentially to the surface of hydrophobic polymers yielding zeta potentials similar to those observed for the unsulfonated pentablock copolymer [78,79]. Sulfonation of a polymer may block surface sorption of anionic species and attract positively charged species to the surface resulting in more neutral zeta potentials as seen in Fig. 7. These effects have been observed for other sulfonated polymers [80], and no generally accepted explanation has been advanced to explain this behavior.

### 3.5. *Effect of casting conditions*

Polymer films were formed from the sulfonated pentablock copolymer solutions by hand-cast and machine-cast procedures as described in the Methods section. The transport properties of the different films are shown in Fig. 8. It is reasonable to expect different transport properties, such as seen in Fig. 8, since the domain morphologies of these block copolymer systems most likely reflect non-equilibrium states. Variations in the casting procedure may provide access to different non-equilibrium states and different transport properties. It is possible, if not likely, that these non-equilibrium states will be kinetically trapped, since a significant fraction of the block copolymer is composed of glassy polymer.

## 4. Conclusions

A series of pentablock copolymers with a selectively sulfonated middle styrene block and glassy hydrophobic end blocks have been characterized to evaluate their potential as desalination membrane materials. The degree of sulfonation, block molecular weights, and film casting technique can be varied to tune transport properties.

Both water uptake and water permeability increase with degree of sulfonation. A jump in both water permeability and the apparent water diffusion coefficient suggest some morphological change between IEC 0.7 and IEC 1.0. Salt permeability depends on upstream salt solution concentration suggesting that Donnan exclusion effects are operative in these materials; however, additional experiments are needed to determine whether the dependence of salt permeability on upstream salt concentration results from sorption, diffusion, or both phenomena. Higher salt permeability is observed for materials with higher water content, highlighting the need to control water swelling. Larger hydrophobic blocks restrict swelling and result in a material with increased permeability selectivity. This increase in selectivity is likely related to the decrease in water content imposed by the larger hydrophobic end blocks.

Surface charge measurements revealed that the unsulfonated pentablock copolymer exhibits negative zeta potential over most of the pH range studied. Sulfonation of the polymer reduces the magnitude of the zeta potential until the material is essentially neutrally charged across the pH range considered. In addition, the zeta potential becomes less sensitive to changes in pH as degree of sulfonation increases.

Two solution casting procedures were studied, and material transport properties are sensitive to the method used to cast the film. This observation is likely due to the existence of kinetically trapped non-equilibrium morphological states. This result provides a further avenue for tuning transport properties in these sulfonated pentablock copolymers.

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