



## Water permeability and water/salt selectivity tradeoff in polymers for desalination

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### ABSTRACT

Polymer membrane-based desalination (e.g., reverse osmosis (RO) and nanofiltration (NF)) has been extensively developed since the 1960s and is a well-established process. The separation performance of desalination membranes is usually described in terms of water flux (or permeance) and salt rejection. Based on a survey of available data, water permeance and NaCl rejection are often inversely correlated, and there may be an upper bound, similar to that observed in gas separation membranes, beyond which there are very few data points. However, water permeance and salt rejection are not intrinsic material properties since they are influenced by sample size (i.e., membrane thickness in the case of permeance) and measurement variables (e.g., pressure and salt concentration in the case of salt rejection). Use of water permeability, rather than water flux or permeance, and water/salt permeability selectivity, rather than rejection, in a tradeoff analysis provides a clearer comparison of properties that depend only on the fundamental transport characteristics of the materials under study. When water and salt transport data are presented on a log-log plot of water permeability versus water/NaCl permeability selectivity, a tradeoff relation and upper bound are observed. Both water/NaCl solubility and diffusivity selectivity contribute to high water/NaCl permeability selectivity, but diffusivity selectivity is the dominant factor. Both solubility selectivity and diffusivity selectivity exhibit tradeoff and upper bound features when plotted as a function of water solubility and water diffusivity, respectively; these correlations combine mathematically, in accord with the solution diffusion model, to yield the observed tradeoff relation and upper bound correlation between water permeability and water/salt selectivity.

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### 1. Introduction

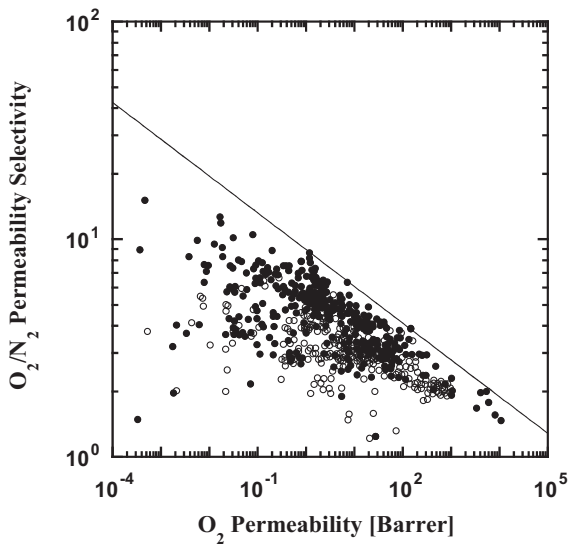
The use of polymer membranes to separate gas mixtures is commercialized for applications including oxygen removal from air, hydrogen separation from nitrogen, carbon monoxide, and light hydrocarbons, CO<sub>2</sub> removal from methane in natural gas, and other applications [1]. In polymers used for gas separations, there is a tradeoff between gas permeability and gas selectivity [1]. Polymers that are more permeable are often less selective and *vice versa*. An example of such a tradeoff relation is presented in Fig. 1 for oxygen and nitrogen. There are essentially no data points above and to the right of the line shown in this figure, which is the so-called “upper bound” for O<sub>2</sub>/N<sub>2</sub> separation and represents the best combinations of permeability and selectivity that have been achieved using poly-

mers. This concept has been demonstrated for many gas pairs by Robeson [2–5], and such a relationship can be derived from theoretical considerations using either activated state [6] or free volume [7] approaches. Permeability and selectivity are intimately linked because increases in permeability are often achieved as a result of increases in gas diffusion coefficients. Polymers having higher diffusion coefficients, and therefore, higher permeability, often have lower diffusivity selectivity (i.e., a weaker ability to discriminate between gas molecules based on their size differences) and, in turn, lower permeability selectivity.

There are suggestions in the literature that such tradeoff and upper bound behavior may not be restricted to polymeric gas separation membranes. For example, Mehta and Zydny found such behavior in porous ultrafiltration membranes and derived a model of the phenomenon [8]. Of course, in this case, the transport mechanism is convective flow through fixed pores, not solution/diffusion transport through a dense material, as it is with polymer membranes used for gas separation, suggesting that the occurrence of permeability/selectivity tradeoffs may be rather general. Robeson and McGrath have suggested that proton conductivity and water

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**Fig. 1.** Tradeoff relation and upper bound (line) observed in polymeric gas separation membranes [2]. ● = rigid, glassy polymers; ○ = rubbery, flexible polymer.

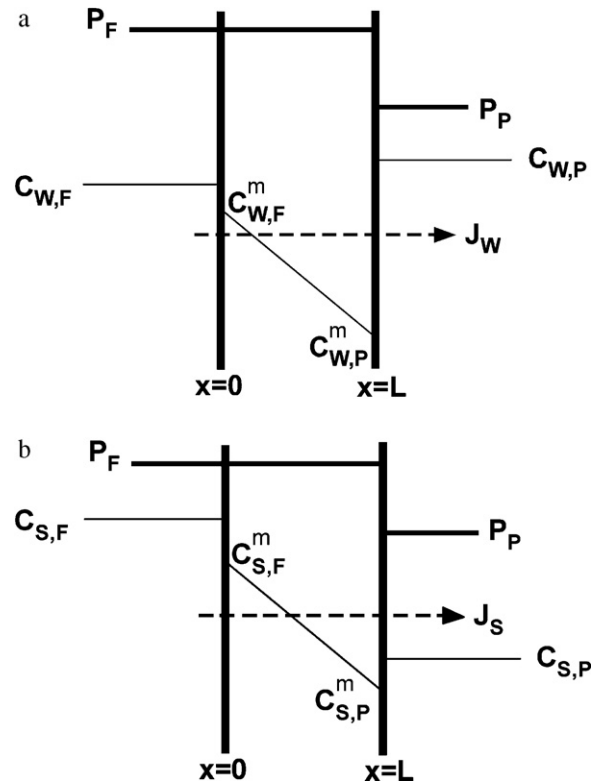
transport in fuel cell membranes are closely coupled in a form of an upper bound relation [9]. However, tradeoff relations between water permeability and water/salt selectivity and upper bound behavior in desalination membranes have not been widely discussed in the literature.

Given the shortage of clean water in many parts of the world [10,11], the worldwide market for desalination is growing and is slated to continue to grow rapidly for the foreseeable future [12]. We have recently undertaken fundamental studies characterizing water and salt transport properties in a series of sulfonated polysulfones [13–18] that are highly chlorine-tolerant, a characteristic that may be useful for desalination membranes [19,20]. As part of an effort to develop structure/property relations in such materials and others being considered for desalination, it is of interest to understand whether tradeoff relations between water permeability and water/salt selectivity and upper bound relations such as those that are ubiquitous in gas separation materials are also operative in desalination membrane materials.

The objective of this study was to gather and organize available water and salt solubility, diffusivity, and permeability data from the literature and to search for general tradeoff relations between water permeability and water/salt selectivity and upper bound behavior. Furthermore, we seek to understand if such tradeoff relations derive principally from tradeoffs between water diffusivity and water/salt diffusivity selectivity (as is usually the case in gas separation polymers), water solubility and water/salt solubility selectivity, or both. The existence of such correlations could aid in the development of structure/property guidelines and design rules for new desalination materials as well as stimulate the search for the theoretical underpinning of such relations.

## 2. Theoretical background

Water and salt ions are commonly understood to permeate through nonporous polymeric films according to the solution-diffusion mechanism [21]. Fig. 2a presents water concentration and pressure profiles in a solution-diffusion film. The water concentration in the feed,  $C_{W,F}$  (g H<sub>2</sub>O/cm<sup>3</sup> solution), is in equilibrium with the water concentration in the polymer membrane at the surface contiguous to the feed,  $C_{W,F}^m$  (g H<sub>2</sub>O/cm<sup>3</sup> swollen polymer), where “cm<sup>3</sup> swollen polymer” implies the volume of the polymer together with any absorbed water and salt. Likewise, the water concentration in



**Fig. 2.** Schematic illustration of (a) water and (b) salt concentration profiles in a polymeric membrane. The pressure profile expected for a solution-diffusion membrane is also shown [21,27].

the permeate,  $C_{W,P}$ , is equilibrated with the water concentration in the membrane at the permeate surface of the membrane,  $C_{W,P}^m$ . The water concentration in the feed is drawn slightly lower than that in the permeate since the permeate would typically have less salt and, therefore, slightly higher water concentration, than the feed. The water flux,  $J_W$  (g/(cm<sup>2</sup> s)), can be expressed as follows [21]:

$$J_W = \frac{D_W}{L} (C_{W,F}^m - C_{W,P}^m) = \frac{D_W C_{W,F}^m}{L} \left( 1 - \frac{C_{W,P}^m}{C_{W,F}^m} \right) \quad (1)$$

where  $D_W$  is the average water diffusion coefficient in the film (cm<sup>2</sup>/s),  $L$  is the film thickness (cm),  $C_{W,F}^m$  is the water concentration in the polymer on the feed (or high pressure) side of the film, and  $C_{W,P}^m$  is the water concentration in the polymer on the permeate (or low pressure) side of the film, which is in equilibrium with water in the permeate,  $C_{W,P}$ . In this formulation of Fick's Law, convective contributions to water transport are neglected, and such effects should be small as long as water uptake by the polymer is small (less than about 15 vol%). If the water uptake is higher than this, one can introduce the proper convection correction term into Eq. (1), and this result has been presented in the literature [22]. In this case, the water diffusion coefficient appearing in Eq. (1) should be interpreted as an effective average diffusion coefficient. As shown in the Appendix, the term in parentheses in Eq. (1) is related to the pressure and osmotic pressure difference between the feed and permeate sides of the film, and Eq. (1) is often written as follows [21]:

$$J_W = \frac{D_W C_{W,F}^m}{L} \frac{\bar{V}}{RT} (\Delta P - \Delta \pi) \quad (2)$$

where  $C_{W,F}^m$  is the equilibrium concentration of water in the membrane (g H<sub>2</sub>O/cm<sup>3</sup> swollen polymer); this concentration can be evaluated by measuring the equilibrium uptake of water in the polymer when it is soaking in the feed solution at ambient pressure.

Furthermore, if water uptake varies little with salt concentration over the salt concentration range of interest, then  $C_{W,F}^m$  is approximately the concentration of water in the polymer when it has been equilibrated with pure water at ambient pressure.  $\bar{V}$  is the partial molar volume of water ( $\text{cm}^3/\text{mol}$ ), which is typically well-approximated by the molar volume of pure water [23,24],  $R$  is the gas constant ( $83.1 \text{ cm}^3 \text{ bar}/(\text{mol K})$ ),  $T$  is the absolute temperature (K),  $\Delta P$  is the pressure difference across the membrane (i.e.,  $\Delta P = P_F - P_P$ , where  $P_F$  and  $P_P$  are the feed and permeate pressures, respectively) and  $\Delta\pi$  is the osmotic pressure difference across the membrane (i.e.,  $\Delta\pi = \pi_F - \pi_P$ , where  $\pi_F$  and  $\pi_P$  are the feed and permeate osmotic pressures, respectively).

The water partition (or solubility) coefficient,  $K_W$ , is defined as the ratio of water concentration in the membrane to that in the contiguous solution [25,26]:

$$K_W = \frac{C_{W,F}^m}{C_{W,F}} \quad (3)$$

The units of  $K_W$  are  $[\text{g H}_2\text{O}/\text{cm}^3 \text{ swollen polymer}]/[\text{g H}_2\text{O}/\text{cm}^3 \text{ solution}]$  [26]. For relatively dilute solutions,  $C_{W,F}$  is approximately equal to the density of pure water,  $\rho_W$  [21]. For reverse osmosis membranes,  $K_W$  is usually taken to have the same value on the feed and permeate sides of the membrane, and this assumption can be checked by calculating  $K_W$  values at the feed and permeate interfaces using an appropriate thermodynamic theory (e.g., Flory–Huggins for polymeric materials) [21,27,28]. However, the ratio of the water concentration in the permeate face of the membrane to that in the permeate solution will not be equal to  $K_W$  since the discontinuity in pressure at the permeate face of the membrane contributes to a reduction in  $C_{W,P}^m$  beyond that due to simple partitioning of the water between the permeate water phase and the membrane. This effect is described in more detail in Appendix A and in the literature [20,21].

Combining Eqs. (2) and (3) yields [29]:

$$J_W = \frac{D_W K_W}{L} \frac{\rho_W \bar{V}}{RT} (\Delta P - \Delta\pi) = \frac{P_W}{L} \frac{\rho_W \bar{V}}{RT} (\Delta P - \Delta\pi) = A(\Delta P - \Delta\pi) \quad (4)$$

where  $A$  is the effective membrane permeance to water, and  $P_W$  is the membrane permeability to water. Manufacturers often report water flux through membranes in terms of “ $A$ ” values. The product of water density and the water molar volume is  $M_W$ , where  $M_W$  is the molecular weight of water. As indicated in Eq. (4),  $A$  is related to water permeability as follows [29]:

$$A = \frac{P_W M_W}{L RT} \quad (5)$$

Within the context of the solution–diffusion model, the salt flux through the membrane,  $J_S$ , is given by [21,29]:

$$J_S = \frac{P_S}{L} (C_{S,F} - C_{S,P}) = \frac{P_S}{L} \Delta C_S \quad (6)$$

where  $P_S$  is the salt permeability ( $\text{cm}^2/\text{s}$ ),  $C_{S,P}$  and  $C_{S,F}$  are the salt concentrations in the aqueous phases on the permeate and feed sides of the membrane, respectively, and  $\Delta C_S$  is the salt concentration difference (i.e.,  $\Delta C_S = \Delta C_{S,F} - C_{S,P}$ ). Fig. 2b presents a simplified schematic of the salt concentration profile through a membrane of thickness  $L$ . In this picture, and in the discussion below, the focus is on salt and water transport properties through the polymer membrane, so concentration polarization is not considered in this analysis [29]. Often, Eq. (6) is written as follows [29]:

$$J_S = B \Delta C_S \quad (7)$$

where  $B = P_S/L$ . Manufacturers often report salt flux in terms of “ $B$ ” values. Typically,  $\Delta C_S$  and  $\Delta\pi$  are related as follows [30]:

$$\Delta\pi = \Delta C_S RT \quad (8)$$

The ability of a desalination membrane to remove salt from a feed solution is often characterized in terms of salt rejection,  $\mathbf{R}$ , which is defined as [29]:

$$\mathbf{R} = \left( \frac{C_{S,F} - C_{S,P}}{C_{S,F}} \right) \times 100\% \quad (9)$$

Within the context of the solution–diffusion model presented above [29]:

$$\begin{aligned} \mathbf{R} &= \frac{(P_W/P_S)(\bar{V}/RT)(\Delta P - \Delta\pi)}{1 + (P_W/P_S)(\bar{V}/RT)(\Delta P - \Delta\pi)} \times 100\% \\ &= \frac{(A/B)(\Delta P - \Delta\pi)}{1 + (A/B)(\Delta P - \Delta\pi)} \times 100\% \end{aligned} \quad (10)$$

Another common measure of salt rejection is percent salt passage,  $S$ , where  $S = 100\% - \mathbf{R}$  [29]. As indicated by Eqs. (4) and (6), water flux is proportional to the applied pressure difference across the membrane, but salt flux is independent of pressure difference. Thus, salt concentration in the permeate decreases (i.e., rejection increases) as feed pressure increases [31].

From Eq. (10), the salt rejection depends upon the intrinsic water and salt transport properties of the membrane, through  $A$  and  $B$ , and on the conditions at which the desalination membrane is operated, through  $\Delta P$  and  $\Delta\pi$ . Consequently, rejection is not uniquely a material property of the membrane. Tradeoff and upper bound characteristics are typically presented in terms of material properties (i.e., permeability and selectivity) that exhibit less dependence than flux and rejection on the measurement conditions. Therefore, in the following discussion, expressions are presented for water and salt permeability and selectivity, and the tradeoff relations discussed later are presented in terms of permeability and selectivity rather than flux and rejection to minimize, to the greatest extent possible, the influence of measurement conditions and membrane thickness on the tradeoff and upper bound considerations.

According to the solution–diffusion model, water permeability can be expressed as follows [21,26,32,33]:

$$P_W = K_W D_W \quad (11)$$

Similarly, the salt permeability can be written as follows [21,26,32,33]:

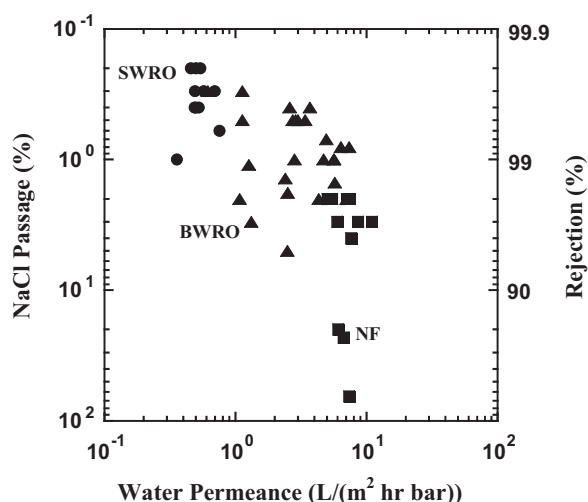
$$P_S = K_S D_S \quad (12)$$

where  $K_S$  is the salt partition coefficient (or salt solubility in the polymer) between the solution and membrane phases (i.e.,  $K_S = C_{S,F}^m/C_{S,F}$ , where  $C_{S,F}^m$  is the salt concentration in the membrane face in contact with the feed solution).  $K_S$  is usually taken to be the same value on both the feed and permeate sides of the membrane. The units of  $K_S$  are  $[\text{g salt}/\text{cm}^3 \text{ swollen polymer}]/[\text{g salt}/\text{cm}^3 \text{ solution}]$ .  $D_S$  is the average salt diffusion coefficient in the membrane.

The ideal water/salt selectivity,  $\alpha_{W/S}$ , is defined as the ratio of water permeability to salt permeability [34]:

$$\alpha_{W/S} = \frac{P_W}{P_S} = \frac{K_W}{K_S} \times \frac{D_W}{D_S} \quad (13)$$

where  $K_W/K_S$  is the water/salt solubility selectivity, and  $D_W/D_S$  is the water/salt diffusivity selectivity. The water permeability appears in the numerator of Eq. (13) because selectivity values are typically defined such that they are greater than 1, and all of the polymers of interest for this work are more permeable to water than to salt. Because the selectivity in Eq. (13) is less dependent on the measurement conditions (pressure and salt concentration) than rejection, correlations between water permeability and water/salt selectivity are the main focus in the following discussion.



**Fig. 3.** Correlation between water permeance and NaCl passage of commercial desalination membranes (manufacturers: Nitto Denko Hydranautics, Dow FilmTec, and GE Osmonics) (● = SWRO: Sea Water Reverse Osmosis, ▲ = BWRO: Brackish Water Reverse Osmosis, ■ = NF: Nanofiltration). Temperature = 25 °C; feed pressure = 75–230 psi (5–15.7 atm) (NF), 800 psi (54.4 atm) (SWRO) and 100–600 psi (6.8–40.8 atm) (BWRO); feed pH = 7.5–8; feed NaCl concentration = 500–2000 ppm (NF and BWRO), and 32000 ppm (SWRO); and recovery = 8–15% [35–37].

### 3. Results and discussion

Evidence for a tradeoff between water transport and salt rejection characteristics in desalination membranes is shown in Fig. 3, which presents water permeance (i.e., the  $A$  value referred to in Eq. (5) and NaCl salt passage for a variety of commercial seawater, brackish water reverse osmosis membranes, and nanofiltration membranes [35–37].<sup>1</sup> These data provide examples of the performance of current commercially available desalination membranes. From this figure, membranes exhibiting higher permeance often have higher salt passage (i.e., lower salt rejection) and *vice versa*. There are no data in the upper right hand corner of this figure (i.e., at high permeance and high rejection), suggesting the possibility of an upper bound relation. While data are commonly reported in terms of permeance (or flux) and salt passage (or, equivalently, salt rejection) as indicated in Fig. 3, these parameters are not solely determined by the water and salt transport properties of the membrane material, so it is difficult to separate the fundamental transport behavior of the materials from the operating conditions, which, as indicated in the caption of Fig. 3, are different for seawater, brackish water, and nanofiltration-based desalination.

Another challenge in demonstrating a tradeoff between water and salt transport properties using water permeance or water flux data from thin-film composite membranes, which is the source for the data in Fig. 3, is that the thicknesses of these membranes are not reported and are not necessarily the same from one membrane to another. In fact, it may be difficult to determine accurately the effective thickness of the active separating membrane in a thin-film composite membrane, which may be of the order of 100 nm. Therefore, the data cannot be readily normalized with respect to membrane thickness and, as such, the water permeance data are not intrinsic material properties of the polymer, since they inherently depend on membrane thickness (cf., Eq. (5)). Additionally,

as indicated above, rejection and salt passage depend upon the experimental conditions, such as pressure difference and salt concentration difference across the membrane, as well as the material properties of the membranes. Therefore, salt passage (or rejection) *per se* is not purely a material property. So, although the data in Fig. 3 show hints of a tradeoff between water throughput and salt retention, it is difficult to definitively conclude that such a trend is due to intrinsic membrane material properties.

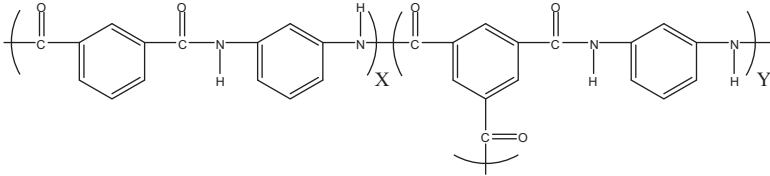
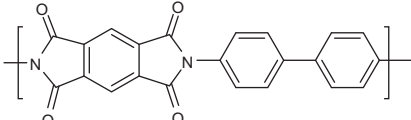
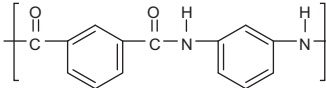
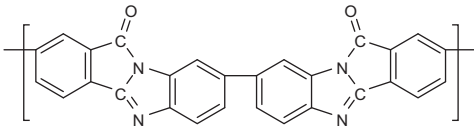
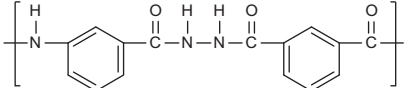
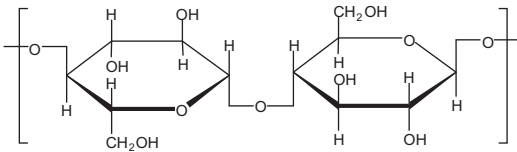
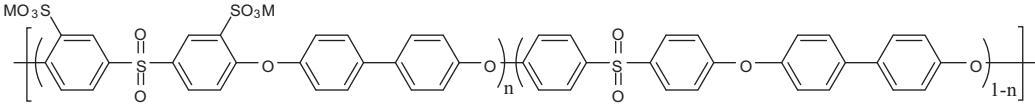
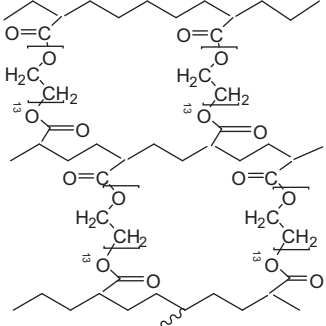
To separate the influence of material properties on the water/salt tradeoff and upper bound behavior from the influence of membrane thickness and operating parameters, the analysis below includes only literature data where fundamental salt and water transport properties have been measured on polymers of defined thickness. These data permit the calculation of water and salt permeability, diffusivity, and solubility. While this approach does not utilize the data reported by membrane manufacturers, which is typically given for composite membranes where the membrane thickness is not specified, it provides an easier path to analyze the data in terms of parameters that are more closely related to the intrinsic material properties of the polymers considered. In all cases, the experimental data were reported at or near room temperature, so this factor is approximately the same for all materials. The chemical structure of the traditional crosslinked polyamide that forms the basis for many of the current desalination membranes and the structures of the other materials considered are presented in Table 1. Data have also been included for a cross-linked polyethylene glycol hydrogel to provide an example of the transport properties of such materials and to understand where such highly hydrated materials fit into this framework [38]. Most of the materials in Table 1 are aromatic polymers considered to have relatively rigid chain structures, which might be expected to encourage high diffusion selectivity for water over salt.

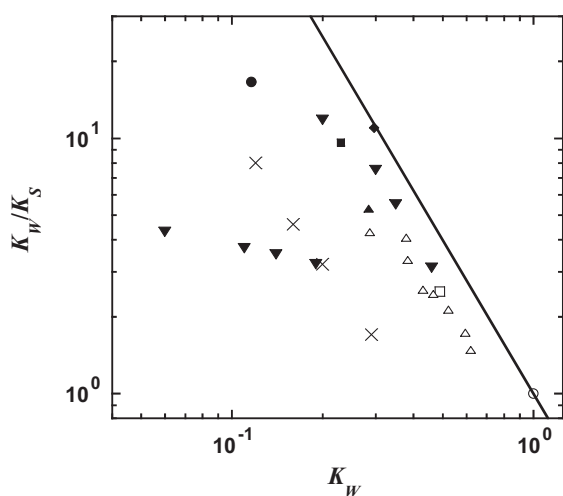
Based on the solution–diffusion mechanism, the ability of polymers to separate water from salt can be characterized in terms of water/salt solubility selectivity and water/salt diffusivity selectivity, and correlations of such data will be presented below. The detailed molecular theory for the transport of salt and water through such membranes as it applies to tradeoff relations has not been worked out to the same extent as it has for gas separations, so there is no theoretical model for tradeoff relations in desalination membranes. As such, the data below will be presented in an empirical form that is analogous to the way such data are presented when discussing gas separation tradeoff data [2,3]. That is, the solubility, diffusivity, or permeability of the more permeable species, water in this case, will be correlated with the water/salt solubility, diffusivity, or permeability selectivity. It is hoped that this work will stimulate further fundamental study and the development of models of this phenomenon for water/salt separation membranes. Furthermore, the absence of substantial amounts of data for salts other than NaCl in a wide variety of materials does not allow the development, at this time, of correlations between, for example, ion and water molecule size and the slopes of the upper bound relation to be presented. For comparison, the slopes of gas separation permeability/selectivity tradeoff curves are proportional to the difference in the square of the diameters of the two gases being considered [2,3,6].

The correlation between the water partition coefficient, or water uptake, and the ratio of water to salt partition coefficients (i.e., the water/salt solubility selectivity) is presented in Fig. 4. In general, water/salt solubility selectivity decreases as water uptake, or equivalently, water partition coefficient, increases. That is, polymers that absorb less water generally exhibit a better ability to selectively sorb water relative to sodium chloride. This trend has also been observed by Yasuda et al. in hydrogel polymers [39]. At low water uptake values (i.e.,  $K_W < 0.2$ ), Yasuda et al. reported that the salt partition coefficient,  $K_S$ , was significantly less than  $K_W$ . Fur-

<sup>1</sup> Arguably, the data in Fig. 3 should be limited to brackish and sea water desalination membranes, since there are reports that some high flux nanofiltration membranes are more properly regarded as having a significant amount of transport through small, but relatively non-selective pores and, as such, would not be expected to strictly obey the solution–diffusion transport mechanism discussed in this study [29,38,39].

**Table 1**  
Polymers considered in this study.

Polymer	Chemical structure
Commercial crosslinked polyamide membrane [52]	
Aromatic polyimide (PI) [53]	
Aromatic polyamide (PA1 [53] and PA2 [40])	
Polybenzimidazopyrrolone (PBP) [53]	
Polyamide-hydrazide (PAH) [53]	
Cellulose acetate (CA) [32,33]	
Sulfonated poly(arylene ether sulfone) (BPS) (M = H <sup>+</sup> or Na <sup>+</sup> ) [17,18,42]	
Crosslinked poly(ethylene glycol) [38]	



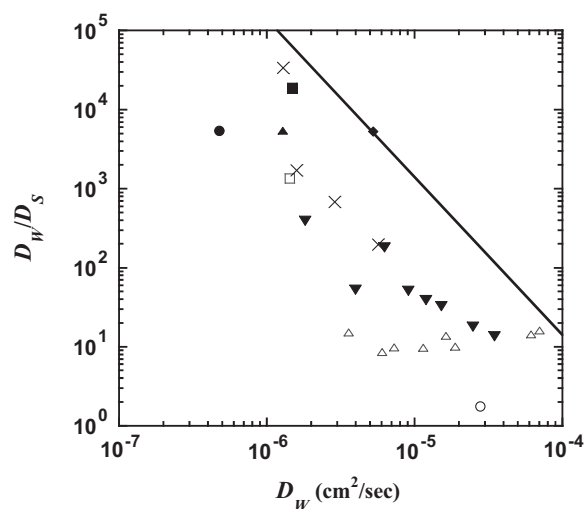
**Fig. 4.** Correlation between water/NaCl solubility selectivity,  $K_W/K_S$ , and water partition coefficient,  $K_W$  for PI (polyimide, ●), PA1 (aromatic polyamide, □), PBP (polybenzimidazolepyrrolone, ◆), PAH (polyamide-hydrazide, ▲), CA (cellulose acetate, ×), PA2 (aromatic polyamide, ■), BPS (sulfonated poly(arylene ether sulfone), ▼), and PEG (crosslinked poly(ethylene glycol), △). The structures of these materials and literature references are recorded in Table 1. For comparison, a point is shown for a hypothetical membrane made of pure water; in this case, both the water and salt partition coefficients are taken to be equal to one (○). The line is the empirical upper bound relation ( $K_W/K_S = \lambda_K/(K_W)^{\beta_K}$  where  $\lambda_K$  and  $\beta_K$  are constant;  $\lambda_K = 1$  and  $\beta_K = 2$ ).

thermore, the deviation of  $K_S$  from  $K_W$  depended on the chemical nature of polymers. However, at higher  $K_W$  values, the salt partition coefficient was nearly equal to  $K_W$  if there were no strong polymer-water interactions [39]. The solubility selectivity values in Fig. 4 range from less than 2, in the case of the PEG hydrogels and cellulose acetate, to as high as 20 for the aromatic polyimide. Thus, these solubility selectivity values span a considerable range from one material to another. This result is qualitatively different from that observed in gas separation polymers, where solubility selectivity values for light gases (e.g.,  $O_2/N_2$ ) vary little from one polymer to another [2,3].

To further place the data in Fig. 4 in perspective, one can consider the case of a hypothetical membrane made of water. In this case,  $K_W$  and  $K_W/K_S$  would both be equal to 1, representing a possible limit on the tradeoff plot. This point is included in Fig. 4.

Based on the data in Fig. 4, there appears to be a type of upper bound line beyond which there are very few data points. That is, there are no data in the upper right-hand corner of this graph, which would correspond to materials with very high water uptake and also very high water/salt solubility selectivity. The line in this figure was drawn empirically to provide, roughly, a cap or outer boundary on the data in the literature. The materials considered in this figure are selective for water over salt in that they have higher water solubility than salt solubility, and this property assists them in being more permeable to water than to salt.

Fig. 5 presents a correlation of water diffusion coefficients and water/salt diffusion selectivity in the materials whose structures are given in Table 1. The data for the sulfonated poly(arylene ether sulfones) and poly(ethylene glycols) were obtained using water uptake and water permeability measurements to estimate water diffusion coefficients, and kinetic salt desorption experiments to measure salt diffusion coefficients [17,18,38–42]; the other data are from the literature [18,32–34,40]. Water/salt diffusion selectivity values range from less than 10 in some of the more highly hydrated sulfonated poly(arylene ether sulfones) to as high as about 33,000 in CA (43.2% degree of acetylation), so diffusivity selectivity varies over a much wider range than the salt/water solubility selectivity data presented in Fig. 4. This trend is qualitatively similar to that



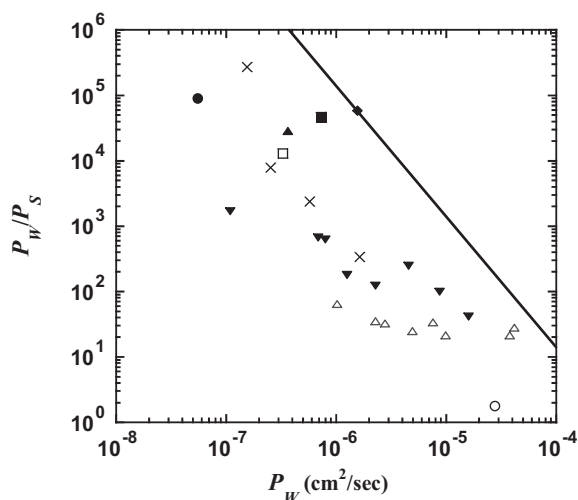
**Fig. 5.** Correlation between water/NaCl diffusivity selectivity,  $D_W/D_S$ , and water diffusion coefficient,  $D_W$  for PI (polyimide, ●), PA1 (aromatic polyamide, □), PBP (polybenzimidazolepyrrolone, ◆), PAH (polyamide-hydrazide, ▲), CA (cellulose acetate, ×), PA2 (aromatic polyamide, ■), BPS (sulfonated poly(arylene ether sulfone), ▼), and PEG (crosslinked poly(ethylene glycol), △). For comparison, a point is shown indicating the self-diffusion coefficient of water and the ratio of the diffusion coefficient of NaCl in water to the self-diffusion coefficient of water (○). The literature sources for these data are provided in Table 1. The line is the empirical upper bound relation ( $D_W/D_S = \lambda_D/(D_W)^{\beta_D}$  where  $\lambda_D$  and  $\beta_D$  are constant;  $\lambda_D = 1.4 \times 10^{-7}$  and  $\beta_D = 2$ ).

observed in materials for gas separation, where diffusivity selectivity is the primary contributor to variations in the permeability selectivity of light gases from one material to another [2,3,6,43]. This high diffusivity selectivity is qualitatively consistent with the fact that there are rather large differences between the effective diameter of a water molecule (2.65 Å, kinetic diameter) [44] and that of hydrated salt ions (e.g.,  $Na^+$ : 7.2 Å;  $Cl^-$ : 6.64 Å) [45].

As Fig. 5 shows, materials having higher water diffusion coefficients often have a weaker ability to sieve water relative to salt and *vice versa*. There are very few data points above and to the right of the empirically drawn upper bound line in Fig. 5, suggesting that this line may represent an upper bound. Using the self-diffusion coefficient of water at 25 °C ( $2.8 \times 10^{-5}$  cm<sup>2</sup>/s) [46] and the diffusion coefficient of NaCl in water at 25 °C ( $1.6 \times 10^{-5}$  cm<sup>2</sup>/s),  $D_W/D_S$  may be calculated for a hypothetical membrane made of water. This point is included in Fig. 5 for comparison.

In Fig. 5, water diffusion coefficients for some of the highly swollen materials exceed the self-diffusion coefficient of water. This phenomenon can be understood by considering convective effects that are a result of the highly swollen nature of these materials, not pore flow [22]. The data in Fig. 5 have not been corrected for this effect, so Fig. 5 presents effective average diffusion coefficients to highlight the salt and water transport as would be experienced in a desalination process.

Fig. 6 presents a correlation between water permeability and water/salt permeability selectivity. On these coordinates, a trend appears with polymers that are more permeable to water often being less able to separate water from salt ions, and *vice versa*. There are virtually no points above and to the right of the line shown in this figure, which has been drawn empirically based upon the data in the figure, suggesting an upper bound for the separation properties of water and salt using polymers such as those presented in Table 1. The permeability selectivity varies more than 5 orders of magnitude, based primarily on variations in diffusivity selectivity, while the water permeability varies by nearly 2 orders of magnitude, influenced mainly by variations in water diffusion coefficients among the materials shown in Fig. 5. The inverse correlation



**Fig. 6.** Correlation between water/NaCl permeability selectivity,  $P_w/P_s$ , and permeability coefficient,  $P_w$  for PI (polyimide, ●), PA1 (aromatic polyamide, □), PBP (polybenzimidazolepyrrolone, ◆), PAH (polyamide-hydrazide, ▲), CA (cellulose acetate, ×), PA2 (aromatic polyamide, ■), BPS (sulfonated poly(arylene ether sulfone), ▼), PEG (crosslinked poly(ethylene glycol), △) and pure water, (○). The literature sources for these data are provided in Table 1. The line is the empirical upper bound relation ( $P_w/P_s = \lambda/(P_w)^\beta$  where  $\lambda$  and  $\beta$  are constant;  $\lambda = 1.4 \times 10^{-7}$  and  $\beta = 2$ ).

between water uptake and water/salt solubility selectivity presented in Fig. 4 also contributes to the tradeoff behavior observed in Fig. 6, but to a lesser extent than the diffusion coefficients and diffusivity selectivity.

To put these values in perspective, a point is shown in Fig. 6 for a hypothetical membrane composed of water. In this case, the water permeability was estimated as the product of the self-diffusion coefficient of water is  $2.8 \times 10^{-5} \text{ cm}^2/\text{s}$  [46] and the water partition coefficient (i.e., 1), and the salt permeability was estimated as the product of the measured NaCl diffusion coefficient in water and taking the salt partition coefficient to be one. The resulting calculated salt permeability coefficient is  $1.6 \times 10^{-5} \text{ cm}^2/\text{s}$ . The water permeance for such a membrane, if it were 100 nm thick (similar in thickness to current commercial desalination membranes), would correspond to an A value of 73 L/(m<sup>2</sup> h bar).

According to Eq. (13), the empirical upper bound relationship shown in Fig. 6 should be the product of the inverse correlations presented in Figs. 4 and 5:

$$\frac{P_w}{P_s} = \frac{K_w}{K_s} \times \frac{D_w}{D_s} = \frac{\lambda_K}{(K_w)^{\beta_K}} \times \frac{\lambda_D}{(D_w)^{\beta_D}} \quad (14)$$

The empirical fitting parameters,  $\lambda_K$ ,  $\beta_K$ ,  $\lambda_D$ , and  $\beta_D$ , are listed in the captions of Figs. 4 and 5. In the most straightforward application of the solution diffusion model, the empirical parameters,  $\beta_K$  and  $\beta_D$ , should be equivalent. With this approach, the empirical upper bound relationship between water permeability and water/salt selectivity (Fig. 6) is

$$\frac{P_w}{P_s} = \frac{\lambda_K}{(K_w)^{\beta_K}} \times \frac{\lambda_D}{(D_w)^{\beta_D}} = \frac{\lambda_K \lambda_D}{(K_w D_w)^\beta} = \frac{\lambda}{(P_w)^\beta} \quad (15)$$

where  $\lambda = \lambda_K \lambda_D$  and  $\beta$  has replaced  $\beta_K$  and  $\beta_D$ . The caption of Fig. 6 contains the numerical values of  $\lambda$  and  $\beta$ . The upper bound relationship observed in Fig. 6 follows the relationship shown in Eq. (15).

While these results only address the transport of sodium chloride through dense polymer films, they suggest that permeability/selectivity tradeoff and upper bound relations similar to those found in gas separation and ultrafiltration membranes may also be observed in desalination membranes. Currently, there are not

enough data in the open literature to prepare robust versions of such tradeoff plots for other salts. However, if this phenomenon is general, and there is reason to suspect that it is, based upon the similarity in transport mechanism (i.e., solution–diffusion) between water, salt, and gas permeability, it could provide guidance for the design of new materials or for the calculation of the performance that might be obtained if materials could be developed with properties along this tradeoff line.

In the gas separation tradeoff relationship, the empirical parameters,  $\lambda$  and  $\beta$ , are backed by fundamental theory. The slope of the tradeoff line,  $\lambda$ , is proportional to the difference in the squares of the gas molecule diameters, and the shift factor,  $\beta$ , is related to the size of the gas molecules, and their solubility in the polymer matrix [6]. Sufficient data do not presently exist to suggest fundamental physical meaning for  $\lambda$  and  $\beta$  in desalination materials. However, it is likely that the physical parameters that enter into  $\lambda$  and  $\beta$  in the gas separation case (i.e., penetrant size and solubility) will also enter into  $\lambda$  and  $\beta$  in the desalination case. Additionally, variables such as ionic charge on the polymer and salt, which have no role in the gas separation case, may also make important contributions to the  $\lambda$  and  $\beta$  parameters in the desalination case.

#### 4. Conclusions

Literature data for the transport of water and sodium chloride through polymers reveals the existence of permeability and selectivity tradeoff relations and points to the existence of so-called upper bound relations, similar to those observed in polymers considered for gas separation. This finding, though preliminary and based upon a small number of data points, suggests that materials more permeable to water will naturally tend to have less ability to separate water from mixtures with salt and *vice versa*. Furthermore, most of the tradeoff behavior between water permeability and water/salt permeability selectivity derives from the tradeoff between water diffusion coefficient and water/salt diffusion selectivity. Comparison of desalination data on a permeability and selectivity basis, rather than a permeance and rejection basis, provides a clearer picture of the impact of the polymer material, rather than its thickness or operating conditions such as feed pressure and salt concentration, on the observed behavior. Future studies directed at understanding whether such tradeoff relations extend to other salts and to other polymers being considered for desalination would be useful. Eventually, perhaps it will be possible to model these tradeoff relations in much the same way as they have been modeled in gas separation membranes.

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#### Appendix A. Relation between pressure difference across a membrane and the water concentration difference that drives water diffusion through the membrane

The applied pressure difference across a solution–diffusion membrane causes a water concentration difference across the

membrane, and this concentration difference is the driving force for diffusion of water across the membrane. While this fact was recognized some time ago [27], a short summary of the key equations linking the pressure difference to the concentration difference is given to provide a self-contained basis for the calculations and approach used in this work. Additionally, presenting this information provides an opportunity to review key assumptions in the solution–diffusion theory of reverse osmosis.

As indicated in Eq. (1), the flux of water through the membrane is related to the water concentration difference across the membrane:

$$J_W = \frac{D_W C_{W,F}^m}{L} \left( 1 - \frac{C_{W,F}^m}{C_{W,P}^m} \right) \quad (\text{A1})$$

The term in parentheses in Eq. (A1) is related to the pressure difference across the membrane via the chemical potential difference between the water in the feed and permeate solutions.

The chemical potential of water in the feed solution,  $\mu_{W,F}$ , can be expressed as follows:

$$\mu_{W,F}(T, C_{S,F}, P_F) = \mu_W^0(T, P_P) + RT \ln a_{W,F} + \bar{V}(P_F - P_P) \quad (\text{A2})$$

where  $\mu_{W,F}$  depends on temperature ( $T$ ), salt concentration in the feed ( $C_{S,F}$ ), and feed pressure ( $P_F$ ). The reference state is taken to be pure water at the permeate pressure and temperature, so  $\mu_W^0(T, P_P)$  is the chemical potential of pure water at these conditions. The influence of salt concentration on the water chemical potential in the feed enters through the activity of the water in the feed,  $a_{W,F}$ . Finally, the pressure dependence of the chemical potential of the feed water is given by the product of the partial molar volume of water in the feed solution,  $\bar{V}$ , and the difference between the reference pressure,  $P_P$ , and the feed pressure,  $P_F$ . This representation presumes that the water partial molar volume is independent of pressure over the range of interest, which is reasonable.

The chemical potential of water in the membrane at the face of the membrane in contact with the feed solution at  $x=0$  (cf., Fig. 2a),  $\mu_{W,F}^m$ , is given by:

$$\mu_{W,F}^m(T, C_{S,F}, P_F) = \mu_W^0(T, P_P) + RT \ln a_{W,F}^m + \bar{V}_W(P_F - P_P) \quad (\text{A3})$$

where  $a_{W,F}^m$  is the activity of water in the membrane at the feed–membrane interface (i.e., at  $x=0$ ), which may be calculated using, for example, the Flory–Huggins theory of polymer solution thermodynamics to relate the water activity in the membrane to the water concentration in the membrane,  $C_{W,0}^m$ .  $\bar{V}_W$  is the partial molar volume of water in the polymer membrane. At equilibrium, the chemical potentials of water in the feed solution and in the membrane at the feed–membrane interface are equal (i.e.,  $\mu_{W,F} = \mu_{W,F}^m$ ); equating Eqs. (A2) and (A3) yields:

$$RT \ln a_{W,F}^m = RT \ln a_{W,F} + \bar{V}(P_F - P_P) - \bar{V}_W(P_F - P_P) \quad (\text{A4})$$

In desalination applications, the activity of water in the feed solution is typically written in terms of the feed osmotic pressure,  $\pi_F$  [21,30]:

$$RT \ln a_{W,F} = -\pi_F \bar{V} \quad (\text{A5})$$

Eq. (A4) illustrates an important point regarding the effect of pressure on water uptake in the polymer. For simplicity, consider the case where pure water is equilibrated with the membrane, so  $a_{W,F} = 1$ . If the partial molar volume of the water in the feed solution,  $\bar{V}$ , is equal or nearly equal to the partial molar volume of water in the polymer,  $\bar{V}_W$ , then an increase in feed pressure will increase the chemical potential of the water in the feed solution and in the membrane by the same amount, so no change in water concentration in the membrane (i.e., no change in  $a_{W,F}^m$ ) is required to re-establish equilibrium at the higher pressure. This result is a consequence of the fact that, in the solution–diffusion model, the membrane experiences a uniform pressure  $P_F$  throughout its thickness (cf., Fig. 2).

That is, the water concentration in the polymer at the feed–polymer interface, which influences  $a_{W,F}^m$ , will not change as feed pressure changes so long as  $\bar{V} \approx \bar{V}_W$ . It is reasonable to assume that the partial molar volume of water is approximately the same in the feed solution and in the polymer, so the concentration of water in the polymer and the polymer–feed interface should be independent of pressure. This expectation has been confirmed experimentally for solvent absorption in polymers [47–49] and for water dissolved in polymers [50]. Thus, in reverse osmosis, the water concentration in the feed side of the membrane is expected to be independent of pressure and can be evaluated at any convenient pressure (e.g., atmospheric).

In a similar fashion, one may equate the chemical potential of the water in the membrane at the membrane–permeate interface (i.e., at  $x=L$  in Fig. 2) with the chemical potential of water in the permeate to obtain:

$$RT \ln a_{W,P}^m = RT \ln a_{W,P} + \bar{V}(P_P - P_P) - \bar{V}_W(P_F - P_P) \quad (\text{A6})$$

The term involving  $\bar{V}_W(P_F - P_P)$ , which corresponds to the effect of pressure on chemical potential of the water in the membrane at the permeate face of the membrane, contains  $(P_F - P_P)$  because, as indicated earlier (cf., Fig. 2), the pressure in the membrane at the permeate face is  $P_F$ . The term involving  $\bar{V}(P_P - P_P)$ , which corresponds to the effect of pressure on the chemical potential of the water in the permeate solution, is zero because the permeate water is at the reference pressure,  $P_P$ . The activity of water in the permeate is typically written in terms of the osmotic pressure of the permeate solution:

$$RT \ln a_{W,P} = -\pi_P \bar{V} \quad (\text{A7})$$

In this derivation, the partial molar volume of water is assumed to be independent of pressure, which is reasonable given the pressure ranges encountered in typical desalination applications.

Combining Eqs. (A4)–(A7) yields:

$$\begin{aligned} \frac{a_{W,P}^m}{a_{W,F}^m} &= \exp \left[ -\frac{\bar{V}}{RT} ((P_F - P_P) - (\pi_F - \pi_P)) \right] \\ &= \exp \left[ -\frac{\bar{V}}{RT} (\Delta P - \Delta \pi) \right] \end{aligned} \quad (\text{A8})$$

In arriving at this result, the water partial molar volume in the polymer and in the feed and permeate solutions are taken to be equal to one another (i.e.,  $\bar{V} = \bar{V}_W$ ). The water activity can be related to the concentration of water by any convenient thermodynamic model, such as the Flory–Huggins model for polymer solutions [51]. In many cases of practical interest, the water concentration is low enough that the ratio of activities may be effectively replaced by their corresponding ratio of water concentrations in the membrane at the feed and permeate faces of the membrane, so that:

$$\frac{a_{W,P}^m}{a_{W,F}^m} = \frac{C_{W,P}^m}{C_{W,F}^m} = \exp \left[ -\frac{\bar{V}}{RT} (\Delta P - \Delta \pi) \right] \quad (\text{A8}')$$

Eq. (A8') provides the concentration ratio required by Eq. (A1). Combining (A8) and (A1) yields:

$$J_W = \frac{D_W C_{W,F}^m}{L} \left( 1 - \exp \left[ -\frac{\bar{V}}{RT} (\Delta P - \Delta \pi) \right] \right) \quad (\text{A9})$$

Based on Eq. (A9), water flux will be a nonlinear function of  $\Delta P$  and reach a ceiling value (or upper limit) as  $\Delta P$  increases. That is, water flux will not increase without bound at higher and higher feed pressures. In fact, this phenomenon has been observed for the transport of organic liquids through polymer membranes [21,28,47]. However, for desalination of water, the partial molar volume of water (approximately  $18 \text{ cm}^3/\text{mole}$ ) is so small, relative



to  $RT$  and the pressures normally encountered in desalination (e.g.,  $\Delta P$  is often less than 70 bar even for seawater desalination [29], which is the highest pressure desalination processes commonly encounter), that the exponential term in Eq. (A9) can be replaced without error by the first term in its Taylor series expansion:

$$J_W = \frac{D_W C_{W,F}^m \bar{V}}{L} \frac{\bar{V}}{RT} (\Delta P - \Delta \pi) \quad (\text{A10})$$

which is the desired result (i.e., Eq. (2)).

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