Modeling the water permeability and water/salt selectivity tradeoff in polymer membranes

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ABSTRACT

A theoretical framework is proposed to model the observed water/salt permeability, diffusivity, and sorption selectivity tradeoff relationships with water permeability, diffusion, and sorption coefficients. Salt sorption is modeled using an electrostatic (or dielectric) exclusion approach. Water and salt diffusion are modeled using hindered diffusion and free volume theories. The modeling approach suggested here is compared to a set of water and salt transport property data measured using a wide variety of polymers. The models describe the general trends observed in the tradeoff relationships but also situations where penetrant-polymer interactions and/or other system specific effects are likely significant. The approach also highlights the importance of convective frame of reference and thermodynamic correction factors in the analysis of water diffusion in hydrated polymers. These corrections are discussed within the framework of experimental data from a variety of hydrated polymer systems. The expanded tradeoff relationship data set and theoretical framework help to expand insight into the fundamental phenomena that govern water and salt transport in polymer membranes for desalination applications.

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1. Introduction

Growing demand for purified water resources and clean energy coupled with interest in the nexus of food, energy, and water resources has driven significant interest in membrane-based technologies that could help address global need for water and energy [1–10]. Membrane-based technologies, such as reverse osmosis (RO), currently dominate the desalination market, and increases in energy efficiency over several decades have positioned membranes to play an increasingly important role in addressing global water needs [9,11,12]. Furthermore, emerging energy technologies, such as pressure-retarded osmosis (PRO), are of interest for recovering energy, stored as chemical potential, in solutions of different salt concentration [13–18]. Accordingly, there is significant interest in optimizing, preferably inexpensive, polymer membranes for these applications.

Seawater desalination by reverse osmosis is a relatively energy efficient process [9,19–21]. The energy required to desalinate seawater is roughly within a factor of two of the thermodynamic minimum [9]. This efficiency is largely a result of improvements in membranes over several decades and pressure recovery devices that can be incorporated into the process [9,11,22]. On the other hand, brackish water RO is typically less energy efficient compared

to seawater desalination by RO.

Some significant challenges still face membrane desalination technologies. The polyamide-based materials that are commonly used as the active layers of reverse osmosis and nanofiltration membranes are inherently susceptible to degradation by chlorine-containing compounds that are widely used to disinfect water and control membrane biofouling [1,23–27]. Additionally, zero-liquid discharge requirements are subjecting membranes to concentrations of salt that exceed traditional design parameters [19,28,29]. Increasingly contaminated waters that contain a variety of ions and other pollutants also challenge membrane materials that have traditionally been designed to reject sodium chloride [1,24,30–36]. Finally, interest in designing membrane polymers that are both highly selective and simultaneously resistant to fouling presents a significant engineering challenge to the membrane field [29]. In many cases, the literature provides insufficient guidance on the impact of polymer membrane chemistry and structure on the fundamental transport properties that are critical for desalination system performance.

One approach to benchmarking material properties and the influence of polymer chemical and/or structural modification on transport properties is to consider the impact of those modifications on established water/salt permeability, sorption, and/or diffusivity selectivity tradeoff relationships [37]. For a wide range of polymers, a tradeoff relationship is observed whereby materials with higher water/salt permeability selectivity (i.e., the ratio of water permeability to salt permeability) tend to have lower water

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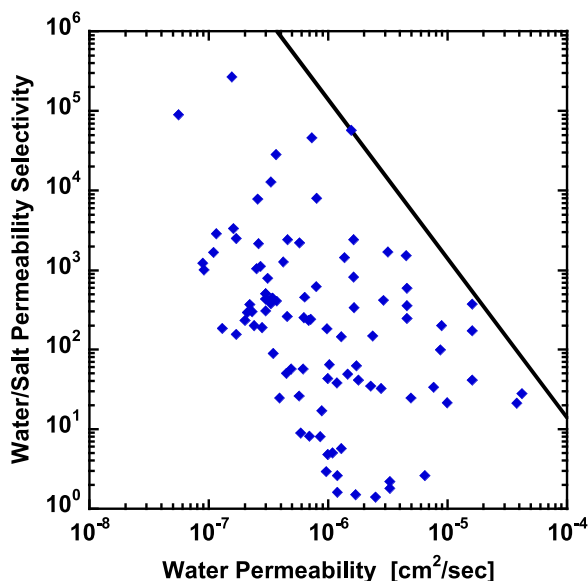*E-mail address:* geise@virginia.edu (G.M. Geise).

Fig. 1. Water/salt permeability selectivity plotted versus diffusive water permeability for a series of reported polymer membrane transport property data, characterized using sodium chloride [23,37,46–58].

permeability and vice versa (Fig. 1). The water/salt permeability selectivity tradeoff with water permeability can be split into sorption and diffusivity tradeoff relationships because permeability is defined, in these materials, as the product of a sorption coefficient and an average diffusion coefficient [1,24,37–40]. These empirical tradeoff relationships allow for comparison of a variety of materials based on fundamental transport properties (i.e., permeability and selectivity as opposed to flux and rejection [1]). As has been recognized in other areas of the membrane field [41–45], they can be used to illustrate the current state-of-the-art and/or emphasize needed property improvements [10].

One limitation of the fundamental tradeoff relationships for desalination membranes is that the intrinsic water and salt transport properties, e.g., permeability, sorption, and diffusion coefficients, must be known. Accurate measurement of these properties is difficult for heterogeneous thin film composite membranes such as the polyamide materials that are used in commercial desalination processes [37,59], and this situation, in many cases, frustrates efforts to establish fundamental structure-property relationships in such materials. Tradeoff relationships, however, can also be developed based on water and salt permeance data that are available for such materials [10,37,60].

While the empirical water permeability and water/salt selectivity tradeoff relationship, introduced in 2011 [37], provides a starting point for benchmarking polymers that are of interest for desalination applications, a theoretical framework would be helpful in further understanding the fundamental origins of the tradeoff relationship. Here we incorporate additional data into the tradeoff relationship (relative to the initial report). Additionally, we incorporate theory to identify the contributions of electrostatic interactions, hindered diffusion, and free volume transport in polymers to the tradeoff relationships. Finally, we seek to gain insight into the fundamental phenomena that result in the tradeoff relationship.

2. Theoretical background

Transport of water and salt through polymeric materials that are of interest for desalination applications is typically described using the solution-diffusion model where penetrant sorption at the upstream face of the membrane precedes diffusion down a concentration gradient and is followed by desorption at the downstream face of the membrane [39,40]. The solution-diffusion model describes the overall permeability of a polymer to a given penetrant in terms of sorption and diffusive contributions to transport:

$$P_i = K_i \times D_i \tag{1}$$

where P_i is permeability, K_i is the sorption coefficient, and D_i is the diffusion coefficient of component i in the polymer [39,40]. Eq. (1) follows from analysis of the governing flux equations [1,3,24,40]. While the separation of permeability into sorption and diffusion components using Eq. (1) appears relatively straightforward, describing the fundamental underpinnings of the sorption and diffusive properties and their connections to polymer chemistry and/or structure is often much more challenging [1,24,37].

The intrinsic permeability selectivity of a material can be defined as a ratio of permeability values. For desalination, selectivity is often defined as the ratio of the water permeability to the salt permeability, and as shown in Eq. (1), permeability can be split into sorption and diffusion components [37]. The water/salt permeability selectivity and corresponding sorption and diffusivity selectivity expressions are related as:

$$\frac{P_w}{P_s} = \frac{K_w}{K_s} \times \frac{D_w}{D_s} \tag{2}$$

Permeability selectivity can be determined by independently measuring water and salt permeability values (i.e., the so-called ideal selectivity), or the selectivity can be determined from simultaneous water and salt transport experiments. The latter can be particularly important when osmotic de-swelling or other ion-polymer interactions influence the water content and, thus, the water permeability of the polymer [61]. Presently, the tradeoff relationships do not distinguish between these experimental methods.

2.1. The sorption component of transport

The sorption coefficient can be defined, at equilibrium, as the ratio of the concentration of a component i in the polymer membrane, c_i^m, to the concentration of component i in the external solution, c_i^s [39,40]:

$$K_i \equiv \frac{c_i^m}{c_i^s} \tag{3}$$

For desalination applications, sorption coefficients are typically defined for water, K_w, and either individual ions (e.g., K_+ or K_-) or overall salt, K_s [1,24,37]. The water sorption coefficient is often approximately equal to the volume fraction of water sorbed in the polymer, and it is convenient, and often appropriate, to use K_w and the volume fraction of water interchangeably [1,62]. For salt sorption in hydrated polymers, the concentrations in Eq. (3) are typically defined as mol of i per kg or L of water sorbed in the polymer [63].

The concentrations used to define the salt sorption coefficient, K_s, depend on the nature of the electrolyte and whether the polymer is uncharged (e.g., poly(ethylene oxide)) or charged (e.g., cation or anion exchange materials) [1,3,24,63–65]. The salt sorption coefficient for binary monovalent electrolyte sorption in an uncharged polymer can be calculated using either the cation or anion concentrations [1,3,65]. In charged polymers, however, the co-ion concentrations (i.e., anions in cation exchange materials and cations in anion exchange materials) are used to define the salt sorption coefficient, K_s [1,3,65]. Here we will focus on the overall salt sorption and water sorption coefficients, K_s and K_w,