



Specific co-ion sorption and diffusion properties influence membrane permselectivity

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ABSTRACT

The apparent permselectivity of three cation exchange membranes (CEMs) was measured using four monovalent strong electrolytes (sodium chloride, sodium bromide, sodium nitrate and sodium perchlorate). The salt (co-ion) sorption and diffusion coefficients of a crosslinked sulfonated polymer, based on the sodium salt form of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), were measured to describe the influence of sorption and diffusion properties on apparent permselectivity. Three models were used (in conjunction with electroneutrality and thermodynamic equilibrium conditions) to probe the influence of electrostatic and dispersion energy forces on specific co-ion sorption. Dispersion forces appear to be important for capturing specific co-ion sorption properties. A model combining the Mackie and Meares hindered diffusion theory and Manning's counter-ion condensation theory was used to explore the influence of electrostatics and polymer tortuosity on co-ion diffusion. Ion-polymer complexation interactions between sodium perchlorate and the poly(ethylene oxide)-based crosslinker used in the sulfonated polymer significantly influenced sorption and diffusion properties. The occurrence of these ion-polymer complexes was supported by salt sorption measurements made on three uncharged, crosslinked poly(ethylene oxide)-containing polymers with 3, 10, or 13 ethylene oxide repeat units between crosslinks. Ion specific sorption, diffusion, and ion-polymer complexation phenomena influence apparent permselectivity properties of charged polymers, and the sorption and complexation phenomena appear to affect apparent permselectivity properties to a greater extent compared to ion specific diffusion effects other than size-based differences.

1. Introduction

Ion exchange membranes (IEMs) often are prepared using charged polymers, and such polymers have ionizable fixed charge groups incorporated into the polymer matrix [1–7]. Anion exchange membranes (AEMs) contain positively charged groups and preferentially transport anions (i.e., counter-ions) while excluding cations (i.e., co-ions). In contrast, cation exchange membranes (CEMs) contain negatively charged groups and preferentially transport cations (i.e., counter-ions) while excluding anions (i.e., co-ions). The ability of these IEMs to selectively transport counter-ions over co-ions is critical to their function in electromembrane processes.

The permselectivity of an ion exchange membrane describes the extent to which a membrane selectively transports counter-ions and excludes co-ions [2,3], and it is linked to the efficiency of many electromembrane-based separation (e.g., electrodialysis (ED) [6–9]), energy generation (e.g., reverse electrodialysis (RED) [10–16]), and energy storage (e.g., redox flow batteries (RFB) [17–22]) technologies. Highly permselective IEMs enable efficient ED separation processes,

efficient energy recovery in RED, and high coulombic efficiency and low capacity fade in redox flow batteries [8,9,14,22]. Therefore, it is critical to maximize the permselectivity properties of ion exchange membranes for these applications.

Traditionally, ion exchange membrane permselectivity has been characterized and studied using sodium chloride. Emerging separation challenges and electro-membrane applications, however, require membranes optimized for solutions containing electrolytes that are different from sodium chloride [7,17,18,20–31]. Perhaps one of the more pronounced examples of this situation is the application of membranes as separators in RFB applications. The development of flow batteries has involved the identification of a wide range of battery chemistry options, and vanadium-based ions, bromide, zinc ions, cerium, or organic redox shuttles are a few examples of the types of molecules that could be exposed to the membrane separator in RFB systems [17–19,26,31]. Additionally, many membrane-based energy recovery technologies could expose ion exchange membranes to complex ionic solutions, such as ammonium bicarbonate [16], lithium chlorate [12], or copper and ammonia-based solutions [27,28].

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Furthermore, deionization via ED could be challenged with increasingly contaminated waters containing, for example, chromium [32], cadmium [33,34], fluoride [35], nitrate [8], perchlorate [36–38], and sulfate [8]. Since IEMs are required in these technologies, membrane permselectivity properties must be understood for electrolytes other than sodium chloride.

Membranes that selectively transport ions via differences in ion valence (e.g., di-valent versus mono-valent ions) are available [39–50], but fewer studies have addressed the problem of engineering selective ion transport between ions of similar valence (e.g., selectivity between different mono-valent ions) [29,30,51,52]. Li et al. measured the permselectivity properties of three poly(phenylene oxide)-based anion exchange membranes using sodium electrolytes with fluoride, chloride, bromide, iodide, hydroxyl, nitrate, and nitrite counter-ions; membrane permselectivity was correlated with the Gibbs free energy of anion hydration and the Stokes radii of the anions [51]. Geise et al. measured the permselectivity properties of four commercial ion exchange membranes using sodium chloride and bicarbonate as well as ammonium chloride and bicarbonate [29]. Cassidy et al. subsequently measured the permselectivity properties of a sulfonated poly(ether sulfone) membrane using lithium, sodium, and potassium salts with chloride and sulfate [30]. In the latter two studies, ion specific effects were discussed within the framework of counter-ion binding affinity and co-ion polarizability. Imteyaz et al. measured the permselectivity of a zirconium aluminophosphate-poly(vinyl chloride) composite cation exchange membrane using lithium, sodium, potassium salts with chloride and nitrate, and ascribed differences in permselectivity to counter-ion binding affinity, and the hydrated radii of the co-ions [52].

In general, membrane permselectivity has been observed to decrease as the binding affinity between the counter-ion and fixed charge group increases [29,53]. The relationship between co-ion properties and membrane permselectivity is less clear compared to the situation for the counter-ions. Studies suggest that co-ion specific membrane permselectivity properties may be related to the Gibbs free energy of hydration [51], co-ion Stokes radius [51], co-ion polarizability [29,30], and co-ion hydrated radius [52], but few general conclusions exist. These preliminary studies highlight the need for a deeper understanding of the fundamental interactions that drive co-ion specific permselectivity properties in ion exchange membranes.

Membrane permselectivity, α , is defined using cation and anion transport numbers:

$$\alpha \equiv \frac{t_M^m - t_M^s}{t_X^s} = 1 - \frac{t_X^m}{t_X^s} \quad (1)$$

where t_i^j is the transport number of ion i in phase j [2]. Superscripts m and s represent the membrane and solution phases, respectively, and subscripts M and X represent counter-ion and co-ion species, respectively. The ion transport number is defined as the fraction of current that is carried by ion i relative to the other charge carriers, k [54]:

$$t_i^j = \frac{|z_i|c_i^jD_i^j}{\sum_k |z_k|c_k^jD_k^j} \quad (2)$$

where z_i is the ion valence, c_i^j is the concentration of ion i in phase j , and D_i^j is the diffusion coefficient of ion i in phase j .

Increases in the membrane-phase co-ion transport number drive a decrease in permselectivity (Eq. (1)). A perfectly permselective membrane ($\alpha = 1$) passes current via only counter-ions and completely prevents co-ion transport (i.e., $t_X^m = 0$) [2,55]. In the other limiting case, a non-permselective membrane, relative rates of ion transport are not affected by the membrane (i.e., $t_X^m = t_X^s$ and $\alpha = 0$) [2,55]. The permselectivity, therefore, varies between zero and unity as the co-ion transport number varies between zero and the value in bulk solution.

The definition of the membrane phase transport numbers, t_i^m , include both the ion concentration and diffusivity in the membrane phase. As a result, permselectivity is expected to increase as either the

co-ion concentration or mobility in the membrane phase is suppressed (see [Supplementary Material Section S1](#) for additional discussion). Therefore, attempts to understand or model co-ion specific permselectivity properties should recognize the contribution of co-ion specific sorption (or partitioning) and diffusion effects.

In this study, the apparent permselectivity properties of three CEMs were measured using four monovalent electrolytes, sodium chloride (NaCl), sodium bromide (NaBr), sodium nitrate (NaNO₃), and sodium perchlorate (NaClO₄). These electrolytes all dissociate completely in water and avoid aqueous speciation challenges recognized in other studies [56–59]. The co-ion sorption and diffusion coefficients of a crosslinked sulfonated polymer membrane (a CEM) were measured using the four electrolytes to quantify specific co-ion sorption and diffusion properties. To determine the underlying phenomena that drive co-ion specific sorption (and, thus, permselectivity) properties, co-ion sorption was modeled using Donnan exclusion theory [6,60] coupled with three models to describe the mean ionic activity coefficients in the polymer: Manning's counter-ion condensation theory [61], electrostatics (i.e., the Born model) [62,63], and a model combining electrostatic and dispersion forces [64]. Ion diffusion coefficients were modeled using a combination of the Mackie and Meares hindered diffusion model [65] and Manning's counter-ion condensation theory [66,67]. Co-ion properties, including polarizability and size, affect co-ion specific sorption and diffusion properties and, thus, permselectivity. Additionally, complexation between sodium perchlorate and the polymer affected permselectivity via both co-ion sorption and diffusion properties.

2. Theory

Several models have been proposed to describe ion sorption and diffusion in charged, swollen polymer membranes. The starting point for modeling ion sorption in charged polymers is to use Donnan exclusion theory to describe co-ion exclusion from the polymer that results from the combination of the thermodynamic equilibrium criterion and electroneutrality [4,6,68,69]. Donnan theory, however, includes mean ionic activity coefficient terms for the membrane and solution phases that must be evaluated [6,70].

The solution phase mean ionic activity coefficients were evaluated using the Pitzer model [71]. The mean ionic activity coefficients in the membrane phase, however, are more difficult to model. The Manning counter-ion condensation model [61,66] does not consider ion specific properties that make a given ion different from another ion of the same valence. As such, we have considered electrostatic and dispersion force-based approaches to calculate the mean ionic activity coefficients. The co-ion sorption coefficients, calculated using these models, are discussed and compared to experimentally measured co-ion sorption coefficients.

Ion diffusion properties were analyzed using the Mackie and Meares model, which describes hindered diffusion in hydrated polymers relative to diffusion in bulk solution [65,67]. Additionally, the Manning counter-ion condensation model can be combined with the Mackie and Meares model to describe ion diffusion in charged, hydrated polymer membranes [66,67]. This approach accounts for electrostatic interactions between fixed charge groups and ions that influence diffusivity [66,67].

2.1. Co-ion sorption

The co-ion sorption coefficient, K_X^m , is defined as the ratio of the concentration of co-ions in the membrane phase, c_X^m , relative to that in the external solution, c_X^s [72]:

$$K_X^m \equiv \frac{c_X^m}{c_X^s} \quad (3)$$

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