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Effect of ambient carbon dioxide on salt permeability and sorption measurements in ion-exchange membranes

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ABSTRACT

Characterizing ion sorption and transport properties in charged polymers is critical for developing fundamental understanding necessary to prepare high performance membranes. The presence of dissolved CO_2 from the atmosphere in aqueous solutions can interfere with measurements of salt permeability and sorption in ion-exchange membranes, frustrating characterization of ion transport properties. In water or aqueous saline solutions, CO_2 speciates to form ions such as H^+ and $HCO_3{}^-$. NaCl or other salt permeability experiments are often performed by exposing a membrane to two salt solutions of different concentrations in a conventional diffusion cell and monitoring the conductivity rise with time in the receiving chamber (i.e., the chamber containing the lower salt concentration). H^+ and $HCO_3{}^-$ ions in the external solutions on either side of the membrane undergo ion exchange with counter-ions in cation- and anion-exchange membranes, respectively. This CO_2-induced ion exchange interferes with conductivity measurements designed to measure receiver salt concentration change with time due to ion permeation through the polymer from the higher salt concentration chamber (i.e., the donor chamber). This phenomenon results in non-linear changes in downstream conductivity with time, which is most pronounced at low donor cell NaCl concentrations, especially for anion-exchange membranes. Furthermore, this effect is absent when an anion-exchange membrane in the $HCO_3{}^-$ form is tested using $NaHCO_3$ rather than NaCl for permeability measurements. The effect of CO_2 on NaCl permeability measurements can be significantly reduced when ultra-high purity N_2 gas is bubbled through the donor and receiver solutions in the diffusion cell during the experiment, making it possible to obtain true NaCl permeability values. During NaCl sorption experiments, when an ion-exchange membrane was equilibrated with a NaCl solution of 0.1 M or lower, the amount of desorbed mobile counter-ions was significantly greater than the amount of desorbed mobile co-ions. The desorption of unequal amounts of ions can also be attributed to ion exchange between the membrane and solution phase and has implications for determining the mobile NaCl sorption coefficient. Procedures for addressing these issues are described.

1. Introduction

Ion-exchange membranes (IEMs) play key roles in a variety of membrane-based technologies. IEMs are typically made from polymers containing ionizable functional groups covalently bound to a polymer backbone (i.e., fixed ions) [1–3]. Bound (i.e., fixed) groups in cation exchange membranes (CEMs) are negatively charged (e.g., sulfonic acid), and they are positively charged (e.g., quaternary amines) in anion-exchange membranes (AEMs). The fixed charge groups in IEMs allow selective permeation of cations in CEMs, or anions in AEMs, across the membrane, a property necessary for technologies such as electrodialysis and reverse electrodialysis [4–12]. This behavior stems largely from Donnan exclusion of co-ions, which are ions having the same charge as the fixed ions. In addition, IEMs have relatively high electrical conductivity, making them attractive for use in batteries and fuel cells [13–18]. Membranes with fixed charge groups are often hydrophilic and are water permeable. Thus, they have been explored for processes that do not necessarily require charged membranes, such as reverse osmosis, forward osmosis, dialysis, etc. but where ion selectivity is an advantage [1,19–25].

Technologies such as those described above rely on controlling the rate of water and/or ion transport across the membranes. Improvement of membrane performance is one avenue for

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increasing process efficiencies and decreasing operating costs. Improving membranes ultimately requires a deep understanding of the influence of membrane structure (chemical and physical) on water and ion transport properties [26]. To make useful connections between membrane structure and performance, fundamental structure/property relations must be developed by systematically characterizing water and ion transport properties in a variety of membranes having different structures.

Atmospheric CO_2 can substantially impact the performance of anion-exchange membrane fuel cells (AEMFCs) [27–31]. When CO_2 gas dissolves in water, it forms carbonic acid, which dissociates into H^+, HCO_3^-, and CO_3^{2-} ions [32]. The HCO_3^- and CO_3^{2-} ions can displace at least some of the OH^- counter-ions in an AEM, resulting in a sharp decrease in membrane conductivity due to the much lower mobility of HCO_3^- and CO_3^{2-} ions compared to that of OH^- ions [27,29]. Several studies have investigated the effect of dissolved CO_2 from the ambient atmosphere (currently ~400 ppm) on AEMFC fuel cell performance [27,29–31]. However, the effect of dissolved CO_2 on salt permeability and sorption measurements in ion-exchange membranes has not been reported. In this study, the effect of atmospheric CO_2 on NaCl permeability and ion sorption measurements in cation and anion exchange membranes is explored, and suggestions are provided to mitigate these effects, so that reliable sorption and transport results may be obtained.

2. Background

Mass transfer across dense (i.e., nonporous) membranes is described by the solution–diffusion model [33–35]. According to this model, penetrants molecularly dissolve into the upstream (i.e., high concentration) face of the membrane, diffuse across the membrane due to a concentration (i.e., thermodynamic activity) gradient, and desorb from the downstream face of the membrane. At pseudo-steady state, the integral permeability coefficient of penetrant i, $\langle P_i \rangle$, defined as the steady state flux of i normalized by the membrane thickness and driving force, can be written in terms of a sorption coefficient, K_i, and an effective, concentration averaged diffusion coefficient, $\langle D_i \rangle$, as follows [33,34]:

$$\langle P_i \rangle = K_i \langle D_i \rangle \tag{1}$$

Experimentally determining steady state salt (e.g., NaCl) permeability and equilibrium ion sorption coefficients is important for developing fundamental structure/property relations in dense membranes for concentration gradient driven salt transport [36,37]. Once these values are determined, salt diffusion coefficients may be obtained within the framework of the solution–diffusion model, allowing for complete characterization of concentration gradient driven transport in membranes [26,37].

Typically, NaCl permeability coefficients are obtained using a diffusion cell. A simple schematic of such a device is shown in Fig. 1a. The membrane is placed between two chambers, where the upstream (i.e., donor) chamber contains a NaCl or other salt solution of known concentration, and the downstream (i.e., receiver) chamber initially contains DI water. As NaCl permeates across the membrane from the upstream chamber to the downstream chamber, the change in NaCl concentration in the downstream chamber with respect to time is recorded using a conductivity meter. The conductivity of the downstream chamber solution is converted to NaCl concentration via a calibration curve, and the NaCl permeability coefficient can be obtained from these data using well-known methods [25,35,37].

When NaCl transport across the membrane reaches pseudo-steady state and over timescales typically used in such experiments, the downstream conductivity should increase linearly with time, following an initial transient period, as illustrated in Fig. 1b. However, for IEMs such as those considered in this study, anomalous behavior is observed when the NaCl concentration in the upstream chamber is approximately 0.1 M or lower, in particular when an anion-exchange membrane is used. The conductivity in the downstream chamber increases non-linearly over time scales that are large relative to the characteristic time for diffusion across the membrane. This phenomenon is illustrated in Fig. 2. As the initial NaCl concentration in the upstream chamber decreases, the nonlinearity in the time dependence of the downstream chamber conductivity becomes more pronounced. This anomalous behavior makes it difficult to determine true NaCl permeability coefficients in the polymer and properly characterize the transport properties of NaCl in such anion-exchange membranes. Indeed, the apparent NaCl permeability values obtained from a standard analysis of data such as that shown in Fig. 2b and c can vary considerably depending on which portion of the data is analyzed, particularly for dilute upstream NaCl concentrations.

For comparison, Fig. 2 also illustrates the expected data in the absence of this anomalous behavior. Using the reported dependence of NaCl permeability on upstream NaCl concentration in other charged membrane systems having similar charge characteristics, the data labeled “Expected” in Fig. 2 were generated [25,26,37]. The NaCl permeability coefficient for various cation-exchange membranes increases linearly with increasing upstream NaCl concentration when the data are plotted on a log–log scale [25,26,37]. Such studies are not widely available for anion-exchange membranes, but initial evidence obtained in this study suggests a qualitatively similar trend. Fig. 3 presents the NaCl permeability dependence on upstream NaCl concentration for a CEM and an AEM used in this study. Considering the data for the AEM, where the anomalous behavior was not observed (i.e., at NaCl concentrations >0.1 M), the NaCl permeability dependence on upstream NaCl concentration is similar in both the CEM and AEM. This observation permits an estimation of the NaCl permeability coefficient in the NaCl concentration range where anomalous behavior is observed (see dashed line in Fig. 3), which can, in turn, be used to generate a plot of expected solution conductivity in the downstream chamber as a function of time. This methodology was used to generate the “Expected” data in Fig. 2. The difference between the expected and experimental data becomes larger as upstream NaCl concentration decreases, making it increasingly difficult to characterize the true NaCl transport properties of the membrane as upstream salt concentration decreases.

One shortcoming of the experimental technique described above is the use of conductivity to track changes in NaCl concentration in the downstream chamber. The conductivity measurement is not sensitive to the identity of the ions in solution, and every ion in the solution, regardless of its chemical structure, contributes to the measured conductivity. Therefore, the presence of ions other than those under study can contribute to the solution conductivity, potentially masking the true NaCl permeability value. The anomalous behavior observed when measuring NaCl permeability in AEMs is shown, in this study, to be caused by dissolved atmospheric CO_2 in the diffusion cell solutions.

3. Experimental

3.1. Polymers

One strong acid cation-exchange membrane, CR61-CMP (CR61), and two different strong base anion-exchange membranes, AR103-QDP (AR103) and AR204-SZRA (AR204), were used in this study. The chemical structures of the membranes are illustrated in Fig. 4. The cation-exchange membrane was received in its sodium counter-ion