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## Specific ion effects on the permselectivity of sulfonated poly (ether sulfone) cation exchange membranes



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#### **ABSTRACT**

Water uptake and permselectivity were measured for five sulfonated poly(ether sulfone) cation exchange membranes with varying degrees of functionalization from 20% to 60%. Experiments were conducted in aqueous salt solutions of LiCl, NaCl, KCl, Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> to isolate the effect of counter-ions and co-ions on membrane permselectivity. Water uptake ranged from 0.13  $g_{water}/g_{polymer}$  to 0.76  $g_{water}/g_{polymer}$ depending on the degree of functionalization and salt used, but was not found to describe the permselectivity differences between salts as the counter-ion and co-ion were varied. This lack of correlation between water uptake and permselectivity is counter to expectations for swollen polymers. Counter-ion binding affinity, charge density and dilute solution mobility were identified as factors influencing membrane permselectivity. Specifically, counter-ions with higher binding affinities to the fixed charge group of the polymer showed lower permselectivities due to counter-ion condensation. Co-ion polarizability was identified as the primary factor for co-ion effects on permselectivity, with more polarizable co-ions resulting in lower membrane permselectivities.

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#### 1. Introduction

Ion exchange membranes are utilized for many clean energy processes, including energy storage via fuel cells [\[1\]](#page--1-0) or redox flow batteries [\[2\]](#page--1-0), and renewable power generation via reverse electrodialysis (RED) [\[3\].](#page--1-0) Additionally, ion exchange membranes have wide applications for ionic separations including desalination [\[4,5\]](#page--1-0) and the treatment of mine waste  $[6]$  via electrodialysis or diffusion dialysis. These processes rely on ion exchange membranes to form a permselective barrier, where ions of a given charge sign are blocked (co-ions), limiting ionic flux to ions of the opposing charge (counter-ions). An ion exchange membrane is classified as either an anion exchange membrane (AEM) or a cation exchange membrane (CEM), with AEMs ideally allowing only anions, and CEMs ideally allowing only cations to permeate through the material. Membrane permselectivity characterizes the degree to which an ion exchange membrane blocks co-ions, and is defined such that a perfect membrane has a permselectivity of unity, while a nonpermselective membrane has a permselectivity of zero. Energy recovery processes such as RED, redox flow batteries and fuel cells rely solely on concentration gradients for ion transport, making their efficiencies particularly sensitive to permselectivity [\[7,8\].](#page--1-0)

<http://dx.doi.org/10.1016/j.memsci.2016.02.048> 0376-7388/© 2016 Elsevier B.V. All rights reserved. With these processes employing a number of different salts, understanding how membrane permselectivity changes for salts other than sodium chloride (in which ion exchange membranes are typically characterized)  $[9,10]$  is crucial for the success of ionexchange based energy technologies.

For ammonium bicarbonate processes, Geise et al. [\[11\]](#page--1-0) found that both co- and counter-ion identity influence permselectivity for commercial cation and anion exchange membranes. For Selemion CMV commercial membranes, permselectivity was governed by the counter-ion binding affinity to the fixed ion group, with lower binding affinity resulting in a higher permselectivity. For both Selemion AMV and CMV membranes, co-ion charge density and polarizability was found to govern permselectivity, with coions with high charge densities and low polarizabilities having higher permselectivities. In general, previous studies have focused on commercial membranes for which the membrane properties are unknown and cannot be tuned, and salts that tend to have high levels of speciation [\[11](#page--1-0)–[13\].](#page--1-0)

In this work, we focused on sulfonated poly(ether sulfone) (SPES) cation exchange membranes with a wide range of functionalization equilibrated with lithium chloride, sodium chloride, potassium chloride, lithium sulfate, sodium sulfate and potassium sulfate. These model materials and salts were used to systemically investigate the co-ion and counter-ion effects on permselectivity in cation exchange membranes where no speciation effects were present in the salts studied. Membrane permselectivity and water

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uptake were measured to investigate the effect of changing electrolytes on membrane performance. Water uptake was not found to predict permselectivity for different co- or counter-ions, while the counter-ion binding affinity to the fixed charge group and coion polarizability have been identified as key parameters for describing membrane performance in different salt solutions.

#### 2. Materials and methods

#### 2.1. Ion exchange membranes

Cation exchange membranes were prepared by casting sulfonated poly(ether sulfone) (SPES) (Fig. 1) dissolved in dimethylacetamide (DMAc) with a polymer mass fraction of 4% into square glass molds with a target thickness of  $100 \mu m$ . The membranes were dried under atmospheric pressure at 80 °C for 24 h, and then placed under vacuum at 60 °C for another 24 h to ensure complete evaporation of DMAc. The SPES polymer used was the Aquafone SES01 Series (YANJIN Technology, Tianjin, China), and were purchased with five degrees of functionalization as summarized in [Table 1.](#page--1-0) Membranes were equilibrated in 0.5 M solutions of the test salt for at least 24 h, changing the solution at least three times.

#### 2.2. Water uptake

Water uptake  $(w_u)$  is defined as the mass of water absorbed by a polymer divided by the dry mass of the polymer:

$$
w_u = \frac{m_{\text{swollen}} - m_{\text{dry}}}{m_{\text{dry}}}
$$
\n(1)

Water uptake was found by measuring mass of a swollen membrane sample immediately after blotting off surface water. The membrane sample was then allowed to dry under vacuum at 60 °C before measuring the dry mass of the polymer.

#### 2.3. Permselectivity

#### 2.3.1. Theory

An electric diffusion potential develops to balance the entropic force driving ions from the ionomer to the solution. The general Nernst equation for a membrane concentration potential describes this diffusion potential [\[14\]:](#page--1-0)

$$
E_{\text{diff}} = -\frac{\text{RT}}{F} \int \sum \frac{t_i}{z_i} \, \text{d} \ln a_i \tag{2}
$$

where  $R$  is the ideal gas constant,  $T$  is the absolute temperature,  $F$ is Faraday's constant,  $z_i$  is the charge number of ion  $i$ ,  $t_i$  is the transport number (the fraction of current carried by a species) of ion *i*, and  $a_i$  is the effective concentration (activity) of ion *i*.

A similar equation describes the electric potential across the interface of a charged polymer when exposed to an ionic solution. This Donnan potential is described by:

$$
E_{\text{don}} = \bar{\psi} - \psi = \frac{1}{z_i F} [\text{RT} \ln \frac{a_i}{\bar{a_i}} - \left(\bar{P} - P\right) V_i]
$$
\n(3)

where  $V_i$  represents the partial molar volume of ion i, and a bar over a variable represents a membrane phase property and the absence of one represents a solution phase property. Eq.  $(3)$  is equivalent for all ions in the system.

For a single salt with negligible swelling pressure, applying the condition of electroneutrality to Eq. (3) results in the Donnan membrane equilibrium equation:

$$
\bar{a}_{\rm m}{}^{\nu_{\rm m}}\bar{a}_x{}^{\nu_x} = a_{\rm m}{}^{\nu_{\rm m}}a_x{}^{\nu_x} \tag{4}
$$

where  $\nu_{\rm m}$  and  $\nu_{\rm x}$  are the stoichiometric coefficients of the co- and counter-ion, respectively. Since the right-hand side of Eq. (4) is set for a given salt solution, the high membrane phase counter-ion activity  $(\bar{a}_x)$  needed to balance the large number of fixed ion groups results in a low membrane phase co-ion activity  $(\bar{a}_{\rm m})$ . This reduction in membrane phase co-ion activity is the mechanism behind the permselective properties for an ion exchange polymer.

Membrane permselectivity describes the degree to which ion exchange membrane excludes co-ions:

$$
\Psi = 1 - \frac{\bar{t}_{\rm m}}{t_{\rm m}} \tag{5}
$$

A perfect membrane has no co-ion transport and hence a permselectivity of one, while a membrane with no ionic selectivity transports co-ions at the same rate as the solution and has a permselectivity of zero.

Ion transport numbers can be determined by measuring the potential of a membrane separating solutions of different concentrations and using Eqs.  $(2)$  and  $(3)$ . These transport numbers can be inserted into Eq. (5) to give membrane permselectivity.

To determine ion transport numbers using Eq.  $(2)$ , one must know the activities of each ion in solution, which are not typically known; usually only the mean salt activity is reported. For instance, the activity coefficient of NaCl in a  $1.1$  mol  $L^{-1}$  aqueous solution is 0.650, but the activity coefficient of the Na<sup>+</sup> cation is 0.747 and the activity coefficient of the Cl-anion is 0.564 [\[15\]](#page--1-0). For a membrane separating two solutions of the same salt with different mean activities ( $a'_{+} > a''_{+}$ ), the ratio of mean activities can be related to the ratio of individual anion and cation activities by:

$$
\frac{a_{+}^{''}}{a_{+}^{'}} = \frac{a_{-}^{''}}{a_{-}^{'} } = \frac{a_{+}^{''}}{a_{+}^{'} }
$$
\n(6)

for a 1:1 salt  $[16]$ . This relation causes the individual ion activities to simplify to mean salt activities, resulting in the permselectivity equations most often reported. To determine permselectivity for membranes in salts that are not 1:1, a different method for relating individual ion activities to mean salt activities must be employed.

To relax the 1:1 salt requirement, a method developed by Harper [\[17\]](#page--1-0) for relating the activity coefficient of an individual ion ( $\gamma$ <sub>+</sub> or  $\gamma$ <sub>-</sub>) to the activity coefficient of its neutral salt ( $\gamma$ <sub>±</sub>) can be used. By convention, the mean activity coefficient of a salt is defined as:

$$
\gamma_{\pm} = \gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}} \tag{7}
$$

Harper  $[17]$  provides several substitutions that allow Eq.  $(7)$  to be rearranged to give:

$$
\gamma_{+} = \gamma_{+}^{\frac{z_{+}^{2}}{z_{+}z_{-1}}}
$$
 and  $\gamma_{-} = \gamma_{+}^{\frac{z_{-}^{2}}{z_{+}z_{-1}}}$  (8)

The membrane potential  $(\varphi_m)$  of a membrane separating two solutions of different concentration  $(a' > a'')$  is the sum of the



Fig. 1. Chemical structure of sulfonated poly(ether sulfone) used in this research. The ratio of functionalized to unfunctionalized repeat units represents the degree of functionalization:  $d.f. = m/(n+m)$ .

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