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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, Li₂SO₄, Na₂SO₄ and K₂SO₄ 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] or redox flow batteries [2], and renewable power generation via reverse electrodialysis (RED) [3]. Additionally, ion exchange membranes have wide applications for ionic separations including desalination [4,5] 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 non-permselective 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].

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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 ion-exchange based energy technologies.

For ammonium bicarbonate processes, Geise et al. [11] 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 co-ions 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 [11–13].

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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