Specific ion effects on membrane potential and the permselectivity of ion exchange membranes

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Membrane potential and permselectivity are critical parameters for a variety of electrochemically-driven separation and energy technologies. An electric potential is developed when a membrane separates electrolyte solutions of different concentrations, and a permselective membrane allows specific species to be transported while restricting the passage of other species. Ion exchange membranes are commonly used in applications that require advanced ionic electrolytes and span technologies such as alkaline batteries to ammonium bicarbonate reverse electrodialysis, but membranes are often only characterized in sodium chloride solutions. Our goal in this work was to better understand membrane behaviour in aqueous ammonium bicarbonate, which is of interest for closed-loop energy generation processes. Here we characterized the permselectivity of four commercial ion exchange membranes in aqueous solutions of sodium chloride, ammonium chloride, sodium bicarbonate, and ammonium bicarbonate. This stepwise approach, using four different ions in aqueous solution, was used to better understand how these specific ions affect ion transport in ion exchange membranes. Characterization of cation and anion exchange membrane permselectivity, using these ions, is discussed from the perspective of the difference in the physical chemistry of the hydrated ions, along with an accompanying re-derivation and examination of the basic equations that describe membrane potential. In general, permselectivity was highest in sodium chloride and lowest in ammonium bicarbonate solutions, and the nature of both the counter- and co-ions appeared to influence measured permselectivity. The counter-ion type influences the binding affinity between counter-ions and polymer fixed charge groups, and higher binding affinity between fixed charge sites and counter-ions within the membrane decreases the effective membrane charge density. As a result permselectivity decreases. The charge density and polarizability of the co-ions also appeared to influence permselectivity leading to ion-specific effects; co-ions that are charge dense and have low polarizability tended to result in high membrane permselectivity.

Introduction

Ion-selective synthetic polymer membranes are key components of several separation and energy technologies. In electrochemical separations, such as electrodialysis and membrane capacitive deionization, as well as energy technologies such as reverse electrodialysis and flow batteries, polymeric membranes are used as selective separators to allow passage of ionic current via certain ions while restricting transport of other, often oppositely charged, ions. Cation exchange membranes (CEMs) are used where cation transport is desired, and anion exchange membranes (AEMs) are used where anion transport is desired. While CEMs and AEMs have been used for some time in the fields of fuel cells, water purification, and food processing, new urgency in membrane development is being realized as the role of ion-containing membranes becomes more apparent in environmentally-friendly clean energy processes.

The efficiency of technologies that rely on CEMs and AEMs depends critically on the ability of the membrane to exclude co-ions (i.e., prevent their transport across the membrane) while simultaneously allowing transport of counter-ions. A membrane that permits transport of only counter-ions (e.g., cations for CEMs) while completely blocking transport of co-ions (e.g., anions for CEMs) is said to be perfectly permselective (Fig. 1). Co-ion transport could result from either diffusive (i.e., concentration-driven) transport from high to low concentration, or field-driven...
migration of co-ions, where the relative magnitude of each form of transport is sensitive to the concentration difference and the magnitude of the applied electric field. Co-ion transport through membranes reduces product purity in chemical separations, and it reduces efficiency and/or capacity in energy technologies. The fundamental underpinnings of these co-ion transport processes must be understood to further improve ion exchange membrane performance, particularly in unconventional electrolyte solutions.

Transport properties of ion exchange membranes are often characterized using sodium chloride as this salt is widely prevalent in nature and is often relevant, particularly in desalination technologies such as electrodialysis. Other electrolytes, however, are also of interest. Recently, the thermolytic salt, ammonium bicarbonate, has been considered for use in closed-loop energy technologies. Membrane properties determined using sodium chloride, however, are not necessarily representative of the properties that would be realized in applications where membranes come in contact with other ions. Much more is known about how transport of different ions occurs in aqueous solution compared to what is known about how transport of different ions occurs in polymeric membranes. Thus, there is a gap that needs to be closed in the community's understanding of the behaviour of membranes in the presence of ions other than sodium and chloride, or group 1 cations and group 17 anions, in general. Moreover, extending the knowledge of electrolytes in solution to their behaviour in membranes and predicting the properties of membranes in unconventional electrolytes from sodium chloride solution data would help guide new membrane design for advanced energy and environmental remediation applications.

Here we report permselectivity data for a series of commercially available CEMs and AEMs measured using sodium chloride, ammonium bicarbonate, ammonium chloride, and sodium bicarbonate electrolytes in order to determine how membrane permselectivity depends on the properties of these different ions in aqueous solutions. The nature of the counter-ions influences the membrane water content, which is often linked to ion transport properties, and binding affinity between counter-ions and fixed charge groups within the membrane correlate with permselectivity. The nature of the co-ions also influences permselectivity, and these effects are not as widely recognized as the counter-ion effects. Both the charge density and the polarizability of the co-ions appear to influence permselectivity by presumably influencing co-ion exclusion.

### Materials and methods

#### Ion exchange membranes

Commercially available ion exchange membranes were used in this study. Two CEMs were used: Selemion CMV (Asahi Glass, Co., Tokyo, Japan) and PCCell PC-SK (Polymerchemie Altmeier GmbH, Heusweiler, Germany). The AEMs used in this study were Selemion AMV (Asahi Glass, Co., Tokyo, Japan) and PCCell PC-SA (Polymerchemie Altmeier GmbH, Heusweiler, Germany). The ion exchange capacity (IEC) of these membranes, which describes the extent of fixed charge group functionalization, is reported in Table 1. Membrane coupons were cut and stored in the hydrated state according to the manufacturers' instructions prior to experimental characterization. Before use, membrane samples were equilibrated in the electrolyte solution of interest for at least 24 hours prior to the measurement.

#### Water uptake

Water uptake was measured gravimetrically after membrane samples were equilibrated with 0.5 mol L⁻¹ aqueous solutions of sodium chloride, ammonium chloride, sodium bicarbonate, or ammonium bicarbonate at ambient temperature and pressure.

### Table 1: Properties of the commercial membranes used in this study

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Type</th>
<th>Ion exchange capacity (IEC) [meq g(dry polymer)⁻¹]</th>
<th>Water uptake [g(water) g(dry polymer)⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selemion CMV</td>
<td>CEM</td>
<td>2.08[16]</td>
<td>NaCl: 0.272 ± 0.006, NH₄Cl: 0.248 ± 0.007, NaHCO₃: 0.276 ± 0.003, NH₄HCO₃: 0.256 ± 0.009</td>
</tr>
<tr>
<td>PCCell PC-SK</td>
<td>CEM</td>
<td>1.2[4]</td>
<td>NaCl: 0.214 ± 0.013, NH₄Cl: 0.185 ± 0.005, NaHCO₃: 0.197 ± 0.013, NH₄HCO₃: 0.176 ± 0.009</td>
</tr>
<tr>
<td>Selemion AMV</td>
<td>AEM</td>
<td>1.85 ± 0.04[17]</td>
<td>NaCl: 0.245 ± 0.003, NH₄Cl: 0.264 ± 0.003, NaHCO₃: 0.272 ± 0.004, NH₄HCO₃: 0.252 ± 0.005</td>
</tr>
<tr>
<td>PCCell PC-SA</td>
<td>AEM</td>
<td>Weak: 0.4 Strong: 1.1[5]</td>
<td>NaCl: 0.428 ± 0.021, NH₄Cl: 0.391 ± 0.004, NaHCO₃: 0.419 ± 0.009, NH₄HCO₃: 0.451 ± 0.016</td>
</tr>
</tbody>
</table>

Hydrated membranes were removed from solution, residual solution on the surface of the membrane was quickly removed using a laboratory wipe, and the wet mass of the membrane, $m_w$, was recorded. Samples were then dried under vacuum in vented petri dishes at ambient temperature until the dry mass of the membrane, $m_d$, stabilized (typically 48 h). Water uptake, $w_u$, was calculated as:

$$w_u = \frac{m_w - m_d}{m_d}$$  

(1)

Water uptake data are reported as the average of at least four measurements, and the uncertainty is reported as one standard deviation from the average. The samples were discarded and not used further after the drying process.

**Membrane potential and permselectivity**

The permselectivity, $\alpha$, of an ion exchange membrane, which describes the tendency of the membrane to pass ionic current by counter-ions only, can be defined in terms of transport numbers:

$$\alpha = \frac{r_\text{M}}{r_X}$$  

(2)

where $r_i$ is the transport number of ion i, M refers to counter-ions and X refers to co-ions in phase j, m refers to the membrane phase, and s refers to the solution phase. When $r_M^s = 1$ in eqn (2), all ion transport through the membrane occurs via counter-ion transport, and the membrane is said to be perfectly permselective; alternatively, when $r_M^s = r_X^s$, ion transport through the membrane occurs in a manner analogous to that in solution, and the permselectivity is equal to zero.

Membrane potential measurements made across membranes that separated solutions of high and low electrolyte concentration were used to determine membrane counter-ion transport numbers. For many monovalent binary electrolytes, the membrane potential, $E_m$, can be used to determine the counter-ion transport number in a membrane so long as the transport number is assumed to be constant throughout the membrane:

$$r_M^s = \frac{E_m}{\left(\frac{RT}{F} \ln \frac{a_X^s}{a_X^M}\right) + 1}$$  

(3)

where $R$ is the ideal gas constant, $T$ is absolute temperature, $F$ is Faraday’s constant, and $a_x$ is the average electrolyte activity (i.e., $a_x = \sqrt{a_x^M a_x^N}$) in solution at either the high concentration solution side of the membrane ($k = 0$) or the low concentration solution side of the membrane ($k = 1$). Eqn (3) is often used to relate membrane potential to the counter-ion/membrane transport number, but this relationship relies on assumptions that are detailed in Appendix A and discussed throughout this work. Eqn (3) can be combined with eqn (2) to calculate the apparent permselectivity, $\alpha_{AP}$, of the membrane:

$$\alpha_{AP} = \frac{E_m}{\left(\frac{RT}{F} \ln \frac{a_X^s}{a_X^M}\right) + 1 - \frac{2r_M}{2r_X}}$$  

(4)

where this apparent permselectivity neglects osmotic transport of water through the membrane.

Membrane potential was determined by placing a membrane sample between 0.1 and 0.5 mol L$^{-1}$ electrolyte solutions (Fig. 2) and measuring the electric potential difference across Ag/AgCl double junction reference electrodes (RREF 0024, Pine Instrument Company, Grove City, PA). The concentrations of the solutions in each chamber were maintained by continuous flow of fresh solution at 5 mL min$^{-1}$. The solutions were well-mixed by overhead stirring at 800 rpm. The potential across the reference electrodes was measured using a digital multimeter (Model 2000, Keithley, Cleveland, OH) as a function of time using LabView (National Instruments, Austin, TX). The experimental steady state potential, $E_x$, was determined by averaging the measured potential for at least 20 min after the potential versus time curve stabilized (typically 20–30 minutes to stabilization). Following the measurement, the offset potential of the electrodes, $E_{\text{offset}}$, was determined in 0.5 mol L$^{-1}$ electrolyte. This offset potential, which results from asymmetry between the two reference electrodes, was subtracted from $E_x$ to determine the membrane potential, $E_m$:

$$E_m = E_x - E_{\text{offset}}$$  

(5)

The molar electrolyte activities were determined using the OLI Analyzer 9.0 (MSE databank) electrolyte software package, and were: $a_{NaCl}^s = 0.0778, 0.0767, 0.0760$, and 0.0665 for 0.1 mol L$^{-1}$ NaCl, NH$_4$Cl, NaHCO$_3$, and NH$_4$HCO$_3$, respectively, and $a_{NH_4}^s = 0.3430, 0.3223, 0.3164$, and 0.2684 for 0.5 mol L$^{-1}$ NaCl, NH$_4$Cl, NaHCO$_3$, and NH$_4$HCO$_3$, respectively.

For each membrane and electrolyte, at least 3 measurements were performed and the results averaged. The uncertainty in $E_m$ was taken as one standard deviation from the average as this value was greater than the uncertainty calculated based on the electric potential fluctuations (typically on the order of 10$^{-2}$ mV) that were observed during the measurement of $E_x$.

The apparent permselectivity was calculated using eqn (4) from the membrane potential and solution phase transport numbers, and the uncertainty in $\alpha_{AP}$ was determined from the
Table 2  Solution transport numbers for the electrolytes considered in this study calculated using eqn (6).21 The counter-ion and co-ion definitions are for CEMs, and they would simply be reversed for AEMs

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(t_i)</th>
<th>(t_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.396</td>
<td>0.604</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>0.494</td>
<td>0.506</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.540</td>
<td>0.460</td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>0.643</td>
<td>0.357</td>
</tr>
</tbody>
</table>

\(^{21}\) Sum of transport numbers for HCO₃\(^-\) and CO₃\(^{2-}\).

uncertainty in \(E_m\) by standard propagation of error methods.\(^{19}\) The solution phase transport number was defined as:\(^{20}\)

\[
\sum_{i} t_i = \frac{|z_i| c_i^s D_i}{\sum_j |z_j| c_j^s D_j}
\]

(6)

where \(z_i\) is the charge, \(c_i^s\) is the concentration in solution, and \(D_i\) is the self-diffusion coefficient of ion \(i\). Solution transport numbers for the ions in this study were calculated (Table 2) using eqn (6), ion concentration data determined using the OLI Analyzer 9.0 (MSE databank) electrolyte software package, and self-diffusion coefficients.\(^{21}\) For CEMs, the cation transport numbers are counter-ion transport numbers, and the anion transport numbers are co-ion transport numbers. The definitions are reversed for AEMs.

Membrane potentials were measured for the AEMs considered in this study, but apparent permselectivity values could only be calculated for AEMs characterized using NaCl or NH₄Cl because eqn (3) is derived based on the assumption that the electrolyte is a monovalent binary salt (see Appendix A). The NaHCO₃ and NH₄HCO₃ salts contain both bicarbonate and carbonate ions in aqueous solution. As these ions are counter-ions for AEMs, eqn (3) cannot be used to calculate the membrane counter-ion transport number, and insufficient information is presently available to develop and evaluate an expression for the AEM counter-ion transport numbers for these electrolytes.

Apparent permselectivity values for the CEMs were evaluated for membranes characterized using bicarbonate-containing salts because the divalent carbonate ion, which is a co-ion in CEMs, is both present in low concentration in solution (at the electrolyte concentrations used in this study, the concentration of carbonate in solution was at least 1 order of magnitude lower than that of bicarbonate) and highly excluded from the CEMs via Donnan exclusion (divalent co-ions are highly excluded from ion exchange membranes via Donnan exclusion\(^7\)). Therefore, for CEMs, the carbonate transport number in the membrane phase was assumed to be negligible compared to the bicarbonate transport number in the membrane phase due much greater Donnan exclusion of carbonate compared to bicarbonate. With this assumption, eqn (3) was applied to CEMs where the membrane potential was measured for membranes exposed to NaHCO₃ and NH₄HCO₃ solutions.

Polarizability calculations

The polarizability of the ions of interest in this study was quantified using density functional theory electronic structure calculations (DMol\(^3\), Materials Studio version 7.0).\(^{22,23}\) Energy optimization was performed using the PBE functional method using the TS method for DFT-D correction. The integration accuracy and SCF tolerances were set to fine, and the DNP version 4.4 basis set was used. The COSMO solvent model was used for water (with the default relative dielectric constant of 78.54) to simulate the ion in the presence of water.

Results and discussion

Apparent permselectivity values were measured for the commercial CEMs using four different electrolytes (Fig. 3). In general, the apparent permselectivity values for the Selemion CMV membranes were greater than those for the PCCell PC-SK membranes. The membrane permselectivity was highest in sodium chloride and lowest in ammonium bicarbonate solutions. To analyse the results further, the values were compared by holding either the counter-ion or co-ion constant, as illustrated by the rows and columns in Table 3.

Influence of counter-ion form on permselectivity

If the co-ion used in the experiment is held constant, the influence of counter-ion form on permselectivity can be determined. For the CEMs considered and for both chloride and bicarbonate co-ions, permselectivity was greater in the sodium...
counter-ion form compared to the ammonium counter-ion form (Fig. 3). Greater permselectivity values are characteristic of membranes where co-ion transport does not occur to as large an extent as in membranes that have lower permselectivity. As the co-ions are held constant here, these results suggest that the counter-ion form of the membrane influences the tendency of the membrane to exclude co-ions and therefore inhibit co-ion transport.

Membrane water content is often considered when discussing membrane transport properties, and typically, membranes that absorb more water tend to have lower selectivity compared to membranes that absorb less water. Here, the membranes that were characterized in the Na\(^+\) counter-ion form (i.e., those membranes characterized using sodium containing electrolytes) absorbed more water than the membranes that were characterized in the NH\(_4\)\(^+\) counter-ion form (Table 1). This result indicates that water content alone cannot explain the permselectivity results. The water content of these membranes suggest that the permselectivity of the Na\(^+\) counter-ion form membranes should be lower than that of the NH\(_4\)\(^+\) counter-ion form membranes as a result of greater water uptake in the Na\(^+\) compared to NH\(_4\)\(^+\) counter-ion forms.

The strength of the ionic interactions between the counter-ions and the fixed charge groups in the membrane may also influence permselectivity. Ammonium ions have a greater binding affinity for cation exchange resins compared to sodium ions. As such, in the NH\(_4\)\(^+\) counter-ion form membranes, the fixed charge of the polymer may be screened or neutralized (via counter-ion condensation) resulting in a fixed charge concentration within the membrane that is effectively lower than what it would be in the Na\(^+\) counter-ion form. This phenomenon is similar to that reported for aluminium-neutralized cation exchange materials where strong interactions between aluminium and the fixed charge group on the polymer result in a material that behaves more like an uncharged polymer than a CEM with fixed negative charges.

Donnan theory predicts that co-ion sorption in the membrane decreases as fixed charge concentration increases. Since co-ion sorption is related to co-ion transport, reduced fixed charge concentration in the membrane is expected to reduce permselectivity. In the NH\(_4\)\(^+\) counter-ion form, NH\(_4\)\(^+\) associates more strongly with the fixed charge groups in the membrane compared to Na\(^+\), and the membrane is, thus, less able to exclude co-ions compared to that in the Na\(^+\) form. The permselectivity of the membranes characterized in the NH\(_4\)\(^+\) counter-ion form, therefore, had lower permselectivity values compared to the Na\(^+\) counter-ion form membranes.

### Influence of co-ion type on permselectivity

Counter-ion form has long been recognized to influence ion exchange material properties (largely thanks to the ion exchange field), but the influence of co-ion type on ion exchange materials is less well understood compared to that of counter-ions. When a CEM in either the Na\(^+\) or NH\(_4\)\(^+\) counter-ion form is characterized with chloride as the co-ion, permselectivity is greater compared to characterizing the membrane using bicarbonate as the co-ion (Fig. 3 and Table 3). The water uptake of the CEMs was statistically insensitive to the nature of the co-ion (Table 1), suggesting that the water content of the membrane does not significantly influence the permselectivity of the membrane compared to the influence of the co-ion type on permselectivity.

Donnan theory, which to a first approximation can be used to describe co-ion sorption in ion exchange materials, distinguishes between different co-ions via the electrolyte activity coefficients that are present in the model. The necessary electrolyte activity coefficient data for the water-swollen polymer membranes used in this study are not available. The lack of information regarding co-ion activity coefficients in water-swollen polymer membranes combined with a limited theoretical framework provides little guidance to understand how the nature of the co-ion might influence ion sorption and transport, and thus, permselectivity in ion exchange materials.

Aside from Donnan exclusion, ions can also be excluded from polymers via dielectric effects. This so-called dielectric exclusion has been described as the tendency of ions to prefer to partition into high dielectric constant media (e.g., water) compared to lower dielectric constant media (e.g., a polar hydrocarbon solvent or water-swollen polymer). While such a discussion relies on a mean field approximation of nanoscopically heterogeneous ion exchange membranes, the difference in the solubility of chloride and bicarbonate salts (Table 4) in water compared to methanol, which has a lower dielectric constant than water, is qualitatively consistent with the permselectivity results reported in Fig. 3 and Table 3 when the influence of ion sorption on permselectivity is considered.

Sodium bicarbonate and ammonium bicarbonate are more soluble in methanol (\(\nu_r = 80.1\)) than their chloride-containing counterparts (Table 4). The enhanced solubility of bicarbonate-containing salts in low dielectric constant media relative to that in water (\(\nu_r = 80.1\)) appears to be consistent with the permselectivity results. Chloride-containing electrolytes are less soluble in methanol compared to water. By extension, chloride ions may be less soluble in swollen polymer membranes, which will likely have a static dielectric constant lower than that of water, compared to bicarbonate ions. In that case, greater dielectric exclusion of chloride ions from the membrane would be expected to result in higher permselectivity compared to that of the bicarbonate containing salts.

Ion polarizability also can be considered as this property may influence the tendency of ions to absorb into the membrane.

### Table 4: Electrolyte solubility in water (relative dielectric constant, \(\nu_r = 80.1\)) and methanol (\(\nu_r = 33.0\)) and permselectivity values for the cation exchange membranes considered in this study

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Solubility in water (^a) (%)</th>
<th>Solubility in methanol (^a) (%)</th>
<th>Permselectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>26.5</td>
<td>1.4(^{20})</td>
<td>0.975 ± 0.001</td>
</tr>
<tr>
<td>NaHCO(_3)</td>
<td>9.3</td>
<td>2.1(^{21})</td>
<td>0.886 ± 0.007</td>
</tr>
<tr>
<td>NH(_4)Cl</td>
<td>28.3</td>
<td>3.5(^{20})</td>
<td>0.925 ± 0.001</td>
</tr>
<tr>
<td>NH(_4)HCO(_3)</td>
<td>19.9</td>
<td>10–11(^{19})</td>
<td>0.789 ± 0.004</td>
</tr>
</tbody>
</table>

\(^a\) Reported as mass%.
The co-ion polarizability can be calculated using DMol3 (Table 5). Polarizability characterizes the ability of the electrons within the ion to polarize in the presence of an electric field.33 The greater polarizability of bicarbonate compared to chloride suggests that bicarbonate may be more energetically stable in the polymer matrix compared to chloride. As a result, this difference in polarizability between bicarbonate and chloride may contribute to greater sorption of bicarbonate in the membrane compared to chloride, and this physical situation is consistent with the lower permselectivity values measured using bicarbonate compared to chloride containing electrolytes.

Bicarbonate ions are known to be more hydrated compared to chloride ions,36 and because both carry one negative charge, the charge density of bicarbonate is lower than that of chloride (Table 5). This difference in charge density may further facilitate sorption of bicarbonate into the membrane compared to chloride. The permselectivity of membranes characterized using bicarbonate containing electrolytes may be lower compared to that measured with chloride containing electrolytes as a result of greater chloride exclusion that could result from interactions between the charge dense chloride ion and the polymer matrix of the membrane.

Membrane potentials of anion exchange membranes

The permselectivity of AEMs can be examined using the same approach discussed above for CEMs. In AEMs, the counter-ions are negatively charged, and the co-ions are positively charged. In the bicarbonate containing electrolytes, however, the presence of multiple counter-ions in solution and the unknown partitioning of those counter-ions into the polymer frustrate determination of the counter-ion transport number and permselectivity due to speciation and determining the physical quantities, such as mobility, of all ions in the membrane.

Membrane potential can be measured for AEMs. This measurement allows quantitative comparison of different AEMs measured under identical experimental conditions. Additionally, membrane potential is useful for connecting membrane properties to electrochemical device performance as the measured membrane potential is ultimately linked to power output, for example, in a reverse electrodialysis system.37

Similar to the CEMs considered in this study, the membrane potential of the Selemion AMV membrane was greater than that of the PCCell PC-SA membrane for all of the electrolytes considered (Fig. 4). The uncertainty in the membrane potentials of the PC-SA membranes measured using the bicarbonate containing electrolytes was greater than that measured for the other electrolytes. This result suggests that speciation of the bicarbonate salts into multiple counter-ions may further complicate the measurement of AEM membrane potentials.

Permselectivity values were determined for AEMs characterized using NaCl and NH4Cl (Table 6) as both of these electrolytes have one dominant counter-ion (i.e., neglecting the carbonate system species present in solution as a result of solution equilibration with CO2 present in the atmosphere). The permselectivity of the AMV membrane measured using NH4Cl is statistically greater than that measured using NaCl, but the two values are statistically indistinguishable for the PC-SA membrane. This result may be due to the higher charge density of NH4+ compared to Na+ (Table 5), as discussed below.

The AMV membrane is more swollen in NH4Cl compared to NaCl while the PC-SA membrane is more swollen in NaCl compared to NH4Cl (Table 1), so phenomena other than water content are likely responsible for the increased permselectivity of the AMV membrane in NH4Cl compared to NaCl. While the polarizability and methanol/water solubility discussion for the CEMs does not explain the AEM permselectivity results, the higher charge density of NH4+ compared to Na+ (Table 5) can be used to justify the AEM permselectivity data in a manner similar to that discussed above for the CEM permselectivity data. In this case, the charge dense NH4+ co-ion may be more excluded from the membrane compared to Na+ resulting in...
higher permselectivity values for membranes characterized using \( \text{NH}_4\text{Cl} \) versus \( \text{NaCl} \). This similarity between the CEM and AEM permselectivity data suggests that co-ion charge density may primarily influence co-ion sorption and, thus, permselectivity in ion exchange membranes.

These ion-specific effects and the physical chemistry of ions in aqueous solution compared to ions in condensed phases is reminiscent of what has been recently discussed in the context of ion adsorption in small carbon pores.\(^{38}\) The observations in the present work point to the importance of considering the influence of ion hydration, polarizability, and dielectric exclusion on the performance of ion exchange membranes. Additionally, we recognize the need to measure ion sorption, which influences the membrane transport numbers (Appendix A), of all of the principle ionic species in these membranes. Sorption or partitioning of sodium and chloride was measured previously for similar ion exchange membrane materials,\(^{9}\) but further work is needed on robust ion sorption measurements for a wide variety of electrolytes to better evaluate membrane transport numbers and the permselectivity of AEMs in bicarbonate-containing electrolytes.

**Conclusions**

Membrane potential and permselectivity were measured for four commercially available ion exchange membranes using aqueous solutions of sodium chloride, ammonium chloride, sodium bicarbonate, and ammonium bicarbonate in order to better understand the permselectivity of membranes in unconventional electrolytes. Permselectivity in the CEMs was highest in sodium chloride and lowest in ammonium bicarbonate. The binding affinity between counter-ions (cations) in CEMs and fixed charge groups on the polymer influenced permselectivity. The presence of \( \text{NH}_4^+ \) resulted in a reduction in permselectivity compared to \( \text{Na}^+\)-form CEMs likely because \( \text{NH}_4^+ \) is known to have a higher affinity for the sulfonate groups in the polymer compared to \( \text{Na}^+ \), and high binding affinity can reduce the effective fixed charge of the membrane thereby reducing Donnan exclusion and permselectivity. Also for the CEMs, the bicarbonate co-ion, with lower charge density and higher polarizability than the chloride co-ion, correlated with lower permselectivity of membranes. The presence of bicarbonate salts compared to chloride salts changes membrane permselectivity because low charge density and high polarizability of ions in solution may favour co-ion sorption in the membrane thereby reducing permselectivity.

Membrane potential was measured for the AEMs, and permselectivity was determined for membranes in sodium chloride and ammonium chloride solutions. Higher permselectivity of AEMs characterized using ammonium chloride compared to sodium chloride was consistent with greater exclusion of the charge dense \( \text{NH}_4^+ \) co-ion compared to the \( \text{Na}^+ \) co-ion.

The results of this study suggest that counter-ion binding affinity with polymer fixed charge groups and co-ion charge density may play an important role in determining the permselectivity of a membrane, and in some cases, these phenomena may be more significant than changes in water content that occur when membranes are equilibrated in different electrolytes. The results further highlight ion-specific effects that can influence ion transport in charged polymers when electrolytes other than commonly studied sodium chloride are used.

**Appendix A: derivation of eqn (3)**

The derivation of eqn (3) for, in this example, a CEM (the charges of counter- and co-ions can simply be reversed for AEMs) begins with an expression for the membrane potential, \( E_m \), in terms of the Donnan potentials (which describe the membrane-solution interfaces at the high concentration side, \( E_{\text{Don}} \) and the low concentration side, \( E_{\text{Don}} \)) and the diffusion potential, \( E_{\text{Diff}} \), which describes ion transport through the membrane phase:\(^{1,20}\)

\[
E_m = E_{\text{Don}} + E_{\text{Diff}} - E_{\text{Don}}
\]

The Donnan potential is determined by the ratio of the thermodynamic ion activity in the membrane phase to that in the solution phase, and while thermodynamic equilibrium stipulates that the equations can be written in terms of either counter-ions or co-ions, the counter-ion form of the Donnan potential equations is used here:\(^{39}\)

\[
E_{\text{Don}}^M = \frac{RT}{F} \ln \frac{a^M_M}{a^M_M} \quad (A.2)
\]

\[
E_{\text{Don}}^L = -\frac{RT}{F} \ln \frac{a^L_M}{a^L_M} \quad (A.3)
\]

where \( R \) is the ideal gas constant, \( T \) is the absolute temperature, \( F \) is Faraday’s constant, and \( a^M_M \) is the counter-ion activity in the membrane or solution face (superscripts \( M \) or \( L \), respectively). The diffusion potential is defined entirely within the membrane phase:\(^{39}\)

\[
E_{\text{Diff}} = -\frac{RT}{F} \left( \sum_j t^j_\text{m} \ln a^j_m - \sum_k t^k_\text{s} \ln a^k_s \right) \quad (A.4)
\]

where \( t^j_\text{m} \) is the transport number, \( z_j \) is the valence, and \( a^j_m \) is the activity of ion \( j \) in the membrane.

By assuming that the electrolyte on either side of the membrane is a monovalent binary salt (containing ions \( M^+ \) and \( X^- \)), and the membrane transport numbers are constant throughout the membrane phase, eqn (A.4) simplifies to:

\[
E_{\text{Diff}} = -\frac{RT}{F} \left( t^M_\text{m} \ln a^M_M - t^X_\text{s} \ln a^X_X \right) \quad (A.5)
\]

Combining eqn (A.1)–(A.3) and (A.5) with the requirement that, for a binary electrolyte:

\[
t^M_\text{m} + t^X_\text{s} = 1 \quad (A.6)
\]

Eqn (A.1) simplifies to:

\[
\frac{E_m F}{RT} = t^M_\text{s} \ln a^M_M a^X_X - \ln a^M_M a^X_X \quad (A.7)
\]
The definition of the average electrolyte activity, \( a^{\text{av}}_e = \sqrt{a^m_e a^k_e} \), allows for further simplification of eqn (A.7):

\[
-\frac{E_m F}{RT} = 2k_0 \ln \frac{a^{\text{av}}_M}{a^m_M} - \ln \frac{a^{\text{av}}_M}{a^0_M}
\]

(A.8)

For many binary electrolytes such as NaCl and KCl, the thermodynamic activities of the cations and anions in solution are equivalent (determined using the OLI Analyzer 9.0 (MSE databank) electrolyte software package), so the assumption is made for the solution activity values that (also using the definition of the average electrolyte activity):

\[
a^k_M - a^k_e - a^k_k
\]

(A.9)

and combining eqn (A.8) and (A.9) gives:

\[
-\frac{E_m F}{RT} = 2k_0 \ln \frac{a^0_e}{a^m_M} - \ln \frac{a^0_e}{a^m_k}
\]

(A.10)

Thermodynamics stipulates that, at equilibrium, the electrochemical potential in solution is equal to the electrochemical potential in the membrane, and this relationship can be applied at both membrane surfaces and simplified to:7

\[
a^0_e - a^0_k - a^0_k
\]

(A.11)

Combining eqn (A.10) and (A.11), simplifies eqn (A.10) to:

\[
-\frac{E_m F}{RT} = (2k_0 - 1) \ln \frac{a^0_e}{a^m_k}
\]

(A.12)

which is equivalent to eqn (3) and the result presented by Strathmann.1 It is important to note that eqn (A.12) relies on an assumption that ion transport numbers are constant throughout the thickness of the membrane. This assumption improves as the salt concentrations on either side of the membrane become similar, but when the membrane is placed between solutions with very different concentrations, the transport number will not be constant throughout the thickness of the film due, at least in part, to the sensitivity of the transport number to the ion concentration within the membrane [eqn (6)] and the tendency of those ion concentrations to depend sensitively on external salt concentration.5 An alternate approach to integrating eqn (A.4) is to assume that the ratio of the counter- and co-ion mobilities in the membrane is constant (as opposed to assuming the membrane transport number is constant) and that activity coefficients are constant across the membrane. This approach leads to a result equivalent to the well-known Henderson equation.20,39–41

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**Notes and references**