Single and binary ion sorption equilibria of monovalent and divalent ions in commercial ion exchange membranes

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ABSTRACT

The co-ion and counter-ion sorption of monovalent (Na^+, K^+, Cl^- and NO^{3-}) and divalent ions (Ca^{2+} and SO_4^{2-}) in commercial Neosepta ion exchange membranes were systemically studied in both single and binary salt systems. The new generation of Neosepta cation exchange membrane (CSE) showed a significant difference in water uptake and co-ion sorption compared to the earlier generation CMX. Use of the Manning model confirmed that there were significant differences between these membranes, with the estimated value of the Manning parameter changing from 1.0 ± 0.1 for CMX to 2.8 ± 0.5 in CSE. There were fewer differences between the two Neosepta anion exchange membranes, AMX and ASE. In single salt solutions, potassium sorbed most strongly into the cation exchange membranes, but in binary salt mixtures, calcium dominated due to Donnan exclusion at low concentrations. While these trends were expected, the sorption behaviour in the anion exchange membranes was more complex. The water uptake of both AMX and ASE was shown to be the greatest in Na_2SO_4 solutions. This strong water uptake was reflected in strong sorption of sulphate ions in a single salt solution. Conversely, in a binary salt mixture with NaCl, sulphate sorption fell significantly at higher concentrations. This was possibly caused by ion pairing within the solution, as well as the strongly hydrophobic nature of styrene in the charged polymer. Water uptake was lowest in $NaNO_3$ solutions, even though sorption of the nitrate ion was comparable to that of chloride in these single salt solutions. In the binary mixture, nitrate was absorbed more strongly that chloride. These results could be due to the low surface charge density of this ion allowing it to bond more strongly with the hydrophobic polymeric backbone at the exclusion of water and other ions.

1. Introduction

The transport of ions through ion exchange membranes is a critical factor to maximise energy efficiency and productivity in the electromembrane processes used in water treatment, such as electrodialysis (Arola et al. 2019, Kim et al. 2012, Van der Bruggen et al. 2004, Van der Bruggen et al. 2003), Donnan dialysis (Durmaz et al. 2005), electrodialysis with bipolar membranes (Li et al. 2016), reverse electrodialysis (Kim et al. 2019, Vermaas et al. 2013), and membrane capacitive deionisation (Hassanvand et al. 2018, Ma et al. 2020). These processes involve the selective migration of ionic species through charged polymeric membranes, often made from dense, non-porous polymers that have anionic and/or cationic fixed charged groups (Sata 2004). These fixed charged groups are typically sulfonic acid groups ($-SO_3^-$) for cation exchange membranes and amine groups ($-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$) for anion exchange membranes.

Commercial applications of these electromembrane processes are often hindered by the limited ion selectivity, high electrical resistance and high manufacturing costs of the ion exchange membranes (IEMs) (Strathmann 2010). To overcome these hurdles, a fundamental understanding of the ion sorption, diffusion and transport properties in exchange membrane materials is required to advance the design and fabrication of high performance, cost effective membranes.

Ion transport through IEMs is governed by the absorption of the ionic species into the membrane and their migration through the membrane phase (Sata et al. 2002). Hence, ion sorption, or ion partitioning between the IEM and the surrounding electrolyte solution is an important transport property of ion exchange membranes (Fan and Yip 2019, Geise et al. 2012). It has been reported that ion mobility, affinity of the competing ions (Galama et al. 2014, Sata et al. 2002, Van der Bruggen et al. 2004), the concentration of charged groups bound to the membrane matrix (i.e. ion exchange capacity) (Kamcev et al. 2017b), and water uptake of the membrane (Geise et al. 2014, Ju et al. 2010) can affect the ultimate ion sorption. Direct measurements of sorption equilibria have been performed in many studies in single electrolyte systems (Galizia et al. 2019, Kamcev et al. 2016b, Kamcev et al. 2017a, 2018, Le et al. 2009, Martí-Calatayud et al. 2014, Pintauro and Bennion 1984). However, it is of practical importance to quantify and obtain a better understanding of the competitive absorption of a mixture of ions in commercial IEMs. This has been conducted by a number of research groups who have used various cation exchange membranes (Bontha and Pintauro 1994, Chapotot et al. 1994, Palomo and Pintauro 2003, Pintauro et al. 1995) and anion exchange membranes (Guesmi et al. 2010, Hannachi et al. 2013, Malewitz et al. 2007), mostly by varying the mixing ratios of the two divalent and monovalent ions at a fixed total concentration.

An equilibrium uptake model, based on a key assumption that membranes are considered as an array of cylindrical pores of identical radius with fixed charge groups uniformly distributed on the pore wall surface, was proposed by the Pintauro group in the 1990s and since then mainly applied to ion sorption in Nafion membranes (Bontha and Pintauro 1994, Palomo and Pintauro 2003, Pintauro et al. 1995). However, to quantitatively account for not only the properties of polymer chains but also the non-ideal behavior in the membranes, a thermodynamically-based framework was developed recently by Kamcev et al. (Kamcev et al. 2016a, Kamcev et al. 2015b), based on Manning's counter-ion condensation theory. The non-ideal behavior in the membrane is described by the electrostatic interactions between the fixed charged groups within the polymer matrix and the electrolyte ions present. Similar to an electrolyte solution where non-ideal behaviour is quantified by an activity coefficient, such non-ideality can be evaluated based on the concentration dependence of the counter and co-ion activity in the IEMs (Kamcev et al. 2015b).

In an ion exchange membrane, the ions of opposite charge to the fixed charge groups are called counter-ions, while those of the same charge are called co-ions. When equilibrium is established between a charged membrane and an electrolyte solution, for a monovalent electrolyte (e.g. NaCl), the thermodynamic condition is often given by (Sata 2004):

$$a_+^m a_-^m = a_+^s a_-^s \qquad (1)$$

where a is the activity, superscripts m and s refer to the membrane and external solution, respectively, and subscripts + and – denote counter-ion (e.g. Na^+ for CEMs and Cl^- for AEMs) and co-ion (e.g. Cl^- for CEMs and Na^+ for AEMs), respectively. The activity of an ion is the product of the concentration and the activity coefficient in the same phase. The thermodynamic condition for a co-ion within a monovalent electrolyte can be rewritten as Eq. (2) below. Full derivation of this expression can be found in the original paper published by Kamcev et al. (Kamcev et al. 2016b):

$$C_-^m = \sqrt{\frac{(C_{\text{fix}}^m)^2}{4} + \frac{(\gamma_\pm^s)^2}{\gamma_+^m \gamma_-^m}(C_s^s)^2} - \frac{C_{\text{fix}}^m}{2} \qquad (2)$$

where C_-^m, the co-ion concentration within the membrane, is a function of the fixed charge group concentration (C_{fix}^m), the concentration in the external salt solution (C_s^s), the external salt solution mean activity coefficient ($\gamma_\pm^s$) and the activity coefficient of co-ion and counter-ion in the membrane (γ_-^m and γ_+^m). The ratio of activity coefficients for a monovalent salt is defined in Donnan Theory as:

$$\Gamma = \frac{(\gamma_\pm^s)^2}{\gamma_+^m \gamma_-^m} \qquad (3)$$

While the activity coefficients of ions in the external salt solution can be estimated by the Pitzer Model, those in the membrane can be related to, a dimensionless linear charge density of the polymer chains (Manning's parameter, ξ), via Manning's counter-ion condensation theory for describing colligative properties in polyelectrolyte solutions (Kamcev et al. 2016b):

$$\gamma_+^m = \left(\frac{\frac{1}{\xi}\cdot\frac{C_{\text{fix}}^m}{C_-^m}+1}{\frac{C_{\text{fix}}^m}{C_-^m}+1}\right) exp\left(-\frac{\frac{1}{2}\cdot\frac{C_{\text{fix}}^m}{C_-^m}}{\frac{C_{\text{fix}}^m}{C_-^m}+2\,\xi}\right) \qquad (4)$$

$$\gamma_-^m = exp\left(-\frac{\frac{1}{2}\cdot\frac{C_{\text{fix}}^m}{C_-^m}}{\frac{C_{\text{fix}}^m}{C_-^m}+2\,\xi}\right) \qquad (5)$$

Combining Eq. (2), (4) and (5) yields the following expression that can be used to calculate the co-ion concentration:

$$(C_{-}^{m} + C_{\text{fix}}^{m})(C_{-}^{m})\left(\frac{\frac{C_{\text{fix}}^{m}}{\xi\, C_{-}^{m}}+1}{\frac{C_{\text{fix}}^{m}}{C_{-}^{m}}+1}\right) exp\left(-\frac{\frac{C_{\text{fix}}^{m}}{C_{-}^{m}}}{\frac{C_{\text{fix}}^{m}}{C_{-}^{m}}+2\,\xi}\right) = \left(\gamma_{\pm}^{s}\right)^{2}(C_{\text{s}}^{s})^{2} \tag{6}$$

It should be noted that in this framework the ion concentrations are expressed as moles of ions per unit volume of sorbed water. A similar expression can be found in the Supporting Information (Eq. S1) for when a cation exchange membrane is in equilibrium with an M-X_2 type salt solution (e.g., $CaCl_2$), or when an anion exchange membrane is in equilibrium with an M_2-X type salt solution (e.g., Na_2SO_4).

In this work, the sorption equilibria of ions in two cation exchange membranes (CEMs, namely CMX and CSE) and two anion exchange membranes (AEMs, namely AMX and ASE) are studied over a total salt concentration range of 0.01 M to 1 M. These are commercially available IEMs manufactured by ASTOM Corporation, Japan and are categorised as standard grade with high mechanical strength. The investigation of co-ion and counter-ion solubility (i.e., partition coefficient) is carried out in solutions containing single cations (Na^+, K^+, Ca^+) for CEMs and single anions (Cl^-, NO_3^-, SO_4^{2-}) in AEMs, as well as their binary mixtures. The ion sorption framework based on Manning's counter-ion condensation theory, as described above, is employed to gain insight in the relationship between structural/material characteristics and ion sorption properties within these membranes. The quantification of single and binary ion sorption in IEMs presented in this work will improve the understanding of the principal phenomena governing ion transport and separation in electromembrane processes such as electrodialysis, reverse electrodialysis and capacitive de-ionisation. This is vital for future development of highly efficient ion exchange membranes to advance water purification processes.

2. EXPERIMENTAL

2.1 Materials

Commercially available anion exchange membranes (Neosepta AMX and ASE) and cation exchange membranes (Neosepta CMX and CSE) were used in this study. These are standard grade, homogeneous membranes with high mechanical strength. As summarized in Table 1, the cation exchange membranes consist of a styrene based copolymer functionalized with negatively charged sulfonated groups, while the anion exchange membranes have a base polymer of styrene (crosslinked with divinyl-benzene) with strongly basic groups as the positive fixed charges. While the charged polymers are similar within the two CEMs and the AEMs, the backing fabric changes from polyvinyl chloride in CMX and AMX to mixtures of polyethylene and polypropylene in CSE and ASE. The proportions of polymer and reinforcement are also different between these membranes.This leads to differences in membrane characteristics such as thickness, electric resistance, burst strength, and ion exchange capacity (IEC) (Table 1).

Sodium chloride (NaCl, 99.7%), potassium chloride (KCl, 99.0%), and calcium chloride anhydrous ($CaCl_2$, 98%), sodium nitrate ($NaNO_3$, 99%) and sodium sulphate (Na_2SO_4, 99%) were procured from Chem-Supply Australia to prepare salt solutions at different concentrations. Caesium chloride (CsCl, 99.9%, Sigma Aldrich) and sodium iodide (NaI, 99.0%, Ajax FineChem) were used for desorbing the absorbed ions in the membrane.

2.2 Water Uptake

Circular ion exchange membrane samples (Ø = 45 mm) were pre-soaked in water to remove residual solvent not associated with the fixed charged groups. They were then dried in a vacuum oven at room temperature for 48 h, Following this, the dry mass (m_d), thickness and diameter of the membrane samples were obtained. The membranes were then immersed in salt solutions of desired concentrations. These membranes were then wiped gently (Kimtech wipes) to obtain their wet mass (m_W), thickness and diameter. Water uptake can be calculated as:

$$\boldsymbol{w_u} = \frac{\boldsymbol{m_w} - \boldsymbol{m_d}}{\boldsymbol{m_d}} \qquad (7)$$

The thickness and diameter of the wet membranes were used to calculate the volume of the swollen membrane ($\boldsymbol{V_m}$).

Table 1: General characteristics of the Neosepta cation and anion exchange membranes.

Description^		Content^		Electric Resistance^ (Ωcm^2)	Burst Strength^ (kg/cm^2)	Dry mass (g/m^2)	Membrane Thickness# (µm)	Swollen Membrane Volume# (ml)	Ion Exchange Capacity* (meq/g dry membrane)
Cation Ion Exchange Membranes									
CMX	Polymer	Styrene, divinyl benzene copolymer with sulfonic acid groups	45-60%	3.0	≥4	157 ± 1	168 ± 3	0.291 ± 0.011	1.68 ± 0.09
	Reinforcement	Polyvinyl chloride	40-55%						
CSE	Polymer	Styrene based copolymer with sodium sulfonic acid groups	40-60%	1.8	≥3.5	126 ± 1	148 ± 2	0.235 ± 0.014	2.07 ± 0.07
	Reinforcement	Mixture of polyethylene and polypropylene	40-60%						
Anion Ion Exchange Membranes									
AMX	Polymer	Styrene, divinyl benzene copolymer with strongly basic groups	30-50%	2.4	≥2.5	145 ± 1	137 ± 2	0.228 ± 0.014	1.73 ± 0.04
	Reinforcement	Polyvinyl chloride	50-70%						
ASE	Polymer	Styrene, divinyl benzene copolymer with strongly basic groups	40-60%	2.6	≥3.5	116 ± 1	146 ± 2	0.232 ± 0.014	2.36 ± 0.23
	Reinforcement	Mixture of polyethylene and polypropylene	40-60%						

^Information provided by ASTOM, Japan.

measured in swollen state after soaking a dry membrane of 45 mm in diameter in a 0.1 M NaCl solution for 48 hr.

* measured using 1 M NaCl solution.

2.3 Ion Sorption

Following water pre-soaking, the cation exchange membranes (i.e., CMX and CSE) were soaked in 1 M HCl to remove the previously sorbed ions and replace them with the H^+ form. Due to the limited pH tolerance of the anion exchange membranes (AMX and ASE), these membranes were used directly after water pre-soaking. The membranes were then immersed in 80 ml salt solutions of different concentrations (C_s^s) for 48 hours to reach equilibrium, after which the membranes were transferred to water of a known volume (80 ml) for a further 48 hours. During the second water soaking period, the adsorbed co-ions were released into the water. The concentration of co-ions in these water samples were later measured to determine the co-ion concentrations in the membranes (C_-^m).

The CEM membranes were then moved to a 0.1 M CsCl solution to release the absorbed counter-ion through uptake of the caesium ions. Similarly, the AEM membranes were placed in a 0.1 M NaI solution to exchange the adsorbed counter-ions with iodide. The concentrations of ions in these solutions were later measured to determine the fixed charge concentrations in the membranes ($\boldsymbol{C_{fix}^m}$).

The concentration of counter-ions (C_+^m) within the membrane is related to the fixed charge group concentration via:

$$C_+^m = C_-^m + C_{fix}^m \quad \text{for monovalent salts} \tag{8}$$

and

$$C_+^m = \frac{1}{2}C_-^m + \frac{1}{2}C_{fix}^m \quad \text{for divalent salts } MX_2 \text{ in CEMs and } M_2X \text{ in AEMs} \tag{9}$$

The factors of $\frac{1}{2}$ in Eq. (9) account for the valency of Ca^{2+} in CEMs and SO_4^{2-} in AEMs as counter-ions, because (a) each mobile divalent ion is associated with two mobile co-ions and (b) each divalent counter-ion is bound to two fixed charge groups in the ion exchange membrane. All concentrations were expressed in eq/L swollen membrane, unless Eq. (1) to (5) were considered in which case eq/L water sorbed was used. Ion exchange capacity (IEC) is defined as meq/g dry membrane (milliequivalent per g of dry membrane).

The sorption coefficient, or partition coefficient of each ion was measured as the ratio of ion concentration in the swollen membrane (C_i^m) to that in external solution (C_i^s):

$$K_i = \frac{C_i^m}{C_i^s} \tag{10}$$

The selectivity of two co-absorbing ions (S_j^i) is defined as:

$$S_j^i = \frac{K_i}{K_j} \tag{11}$$

The external solutions used for equilibrating the CEMs were NaCl, KCl and $CaCl_2$ solutions from 0.01 M to 1 M, and binary solutions of equimolar cation concentrations of NaCl + KCl and NaCl + $CaCl_2$. Similarly, the AEMs were equilibrated in NaCl, $NaNO_3$ and Na_2SO_4 solutions from 0.01 M to 1 M, and binary solutions of equimolar cation concentrations of NaCl + $NaNO_3$ and NaCl + Na_2SO_4. The concentrations of cations (i.e., sodium, potassium and calcium) were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES 720ES, Varian). The concentrations of anions (i.e., chloride, nitrate and sulfate) were determined using Ion Chromatograph (IC-Dionex, ICS-1000).

3. RESULTS AND DISCUSSION

3.1 Water uptake

The water uptake of the ion exchange membranes equilibrated in different salt solutions is presented in Figure 1. As shown in Table 1, the fixed charges of these membranes are either strongly negative (i.e., -SO_3^- group) in CMX and CSE, or strongly positive in AMX and ASE. The water uptake presented for all Neosepta IEMs studied in this work is within the typical range reported in the literature (0.14 to 0.46 g H_2O/g dry membrane) (Strathmann 2004).

Membrane swelling caused by water absorbed into the charged polymer has a direct influence on the absorption and transport of ions with IEMs. Water enters the polymer matrix to hydrate both the fixed charged groups and their counter-ions, stretching the polymer network. However, the elastic forces that result from crosslinking resist the polymer stretching and thus the amount of water than can enter the network. The water uptake is therefore a trade-off between these two effects (Helfferich 1962, Kamcev 2016). Water uptake is affected by the concentration and type of fixed charged groups and the degree of crosslinking. Water uptake is also related to the hydrated radius of the counter-ions, the counter-ion valency and how it interacts with the fixed charge group (Galizia et al. 2017, Strathmann 2004). The hydrated radius is similar between Na^+ and K^+ (3.58 Å and 3.31 Å) and is higher for Ca^{2+} (4.12 Å). However, for the cation exchange membranes (Figure 1(a)), the water uptake of CMX and CSE is the highest in NaCl solutions, but is similar between KCl and $CaCl_2$ (within experimental error). Similar trends have been reported by Bonner et al. (Bonner and Smith 1957) for sulfonated polystyrene resins and Galizia et al. (Galizia et al. 2017) for cross-linked poly (p-styrene sulfonate-co-divinylbenzene). For the anion exchange membranes (Figure 1(b)), the water uptake of both AMX and ASE is shown to be the greatest in Na_2SO_4 solutions, and the lowest in $NaNO_3$ solutions. In this case, the hydrated radii of Cl^-, NO_3^- and SO_4^{2-} are 3.32 Å, 3.35 Å and 3.79 Å, respectively. In binary solutions, the amount of water uptake mostly lies between the water uptake values of the respective single salt solutions. This is the case for both CSE and ASE membranes, as shown in Figure 1.

The backing fabric is changed from polyvinyl chloride for CMX to mixtures of polyethylene and polypropylene for CSE which weighs less per unit area (Table 1). The percentage water uptake for the cation exchange membranes also changes on a mass basis, declining from 37% - 44% for CMX to 28% - 35% for CSE (Figure 1(a)). The swollen CMX membranes are greater in both volume and thickness, have a higher membrane resistance and lower IEC.

The water uptake, however, appears to be similar between AMX and ASE (18%-28%). As shown in Table 1, the dry mass is lower for the ASE membranes than the AMX membranes, while the IEC is higher. The swollen AMX membranes are thinner than the ASE membranes and the membrane resistance reported by the manufacturer is similar between AMX and ASE. However, these changes do not seem to affect greatly the percentage of water sorbed per dry mass of membrane or the swollen membrane volume. Although changes have been made to the content of the polymer and the backing fabric, no information is available as to whether the degree of crosslinking or the type of fixed charged group has been altered. Therefore, it is unclear how the changes in IEC and the content in polymer and fabric backing ultimately leads to a similar water uptake between AMX and ASE (Figure 1(b)).

Finally, it is known that water uptake also slightly decreases with increasing external salt concentrations due to osmotic de-swelling (Kamcev 2016, Khare and Peppas 1995, Paul et al. 2008). This decline at high salt concentrations is observed for most cases presented in Figure 1.

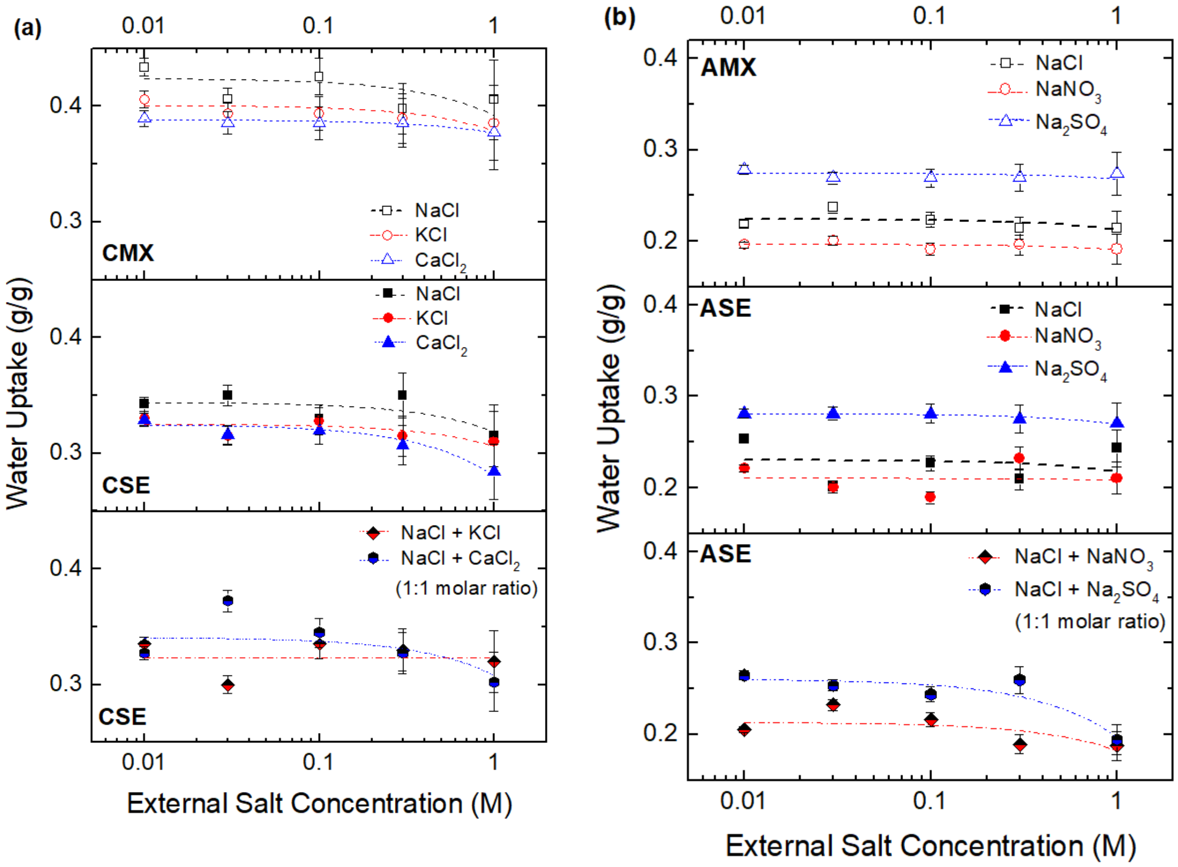

Figure 1. Water uptake of (a) cation exchange membranes (CMX and CSE) and (b) anion exchange membranes (AMX and ASE) after equilibration in different external salt solutions of concentrations ranging from 0.01 M to 1 M. Equimolar binary mixtures of NaCl + KCl and NaCl + $CaCl_2$ were used for CSE membranes (a), and those of NaCl + $NaNO_3$ and NaCl + Na_2SO_4 were used for ASE membranes (b). The dashed lines are drawn to guide the eye.

3.2 Co-ion concentration in membranes

Both the concentrations of counter-ion and co-ion within the IEMs were measured. Most of the counter-ions sorbed in the membrane are associated with the fixed charges within the polymer matrix, but a very small portion of counter-ions are required to neutralize any sorbed co-ions in the membrane. Therefore, this concentration of co-ion is also referred to as the mobile salt concentration within the membrane (Geise et al. 2012, Kamcev et al. 2015a). Since the co-ion concentration in the desorption solution was very low for salt solutions of 0.01 M and 0.03 M, we were not able to accurately determine these concentrations. Only co-ion concentrations for external salt concentrations of greater than 0.1 M are reported.

Co-ions are restricted from entering the membrane due to repulsion by the fixed charge groups which generate an electrical potential, known as the Donnan potential, at the membrane/solution interface (Donnan 1924). As the external salt concentration increases, this electrical potential declines due to charge screening, allowing more co-ions to be absorbed. Thus as expected, the concentration of co-ion (i.e., the chloride concentration in CMX and CSE and the sodium concentration in AMX and ASE) increases with increasing external salt concentration (Figure 2). The Donnan potential is inversely proportional to the counter-ion valence (Galizia et al. 2019) and thus the presence of divalent counter-ions (i.e., calcium in CEMs and sulphate in AEMs) reduces the Donnan potential, which also results in a greater co-ion concentration within the membrane.

Experimental data for these single salt experiments are fitted to Eq. (6) for monovalent counter ions and Eq. (S1) for divalent counter ions. The fitting was performed using all three sets of data for each membrane, treating the linear charge density of polymer, $\boldsymbol{\xi}$ as the only fitting parameter. This approach assumes that $\boldsymbol{\xi}$ does not depend significantly on the type of salt used (Kamcev et al. 2016a). Within experimental error, the estimated values of linear charge density, reported in the caption of Figure 2, are within the typical range (1 – 4) reported for polyelectrolyte systems (Kwak 1973, Manning 1969). The ratio of activity coefficients between the solution and the membrane, $\boldsymbol{\Gamma}$, were also estimated by Eq. (3) for monovalent salts and Eq. (S5) for divalent salts, using the modelled values of co-ion concentrations. This parameter is presented in Figure 3 (a) and (b) for cation exchange membranes and anion exchange membranes, respectively. $\boldsymbol{\Gamma}$ decreases gradually from low to high external salt concentrations for all membranes. Similar trends were also reported by Kamcev et al. (Kamcev et al. 2015b) and Galzia et al. (Galizia et al. 2017). The activity coefficients of the external salt solutions, in general, decrease with concentration. The decline in $\boldsymbol{\Gamma}$ as a function of external salt concentration hence results from much lower activity coefficients in the membranes when external salt concentration is low. As the concentration of external solution increases, the ion concentration difference between the membrane phase and the external solution becomes smaller, with $\boldsymbol{\Gamma}$ slowly approaching unity.

For single electrolyte system, the Cl^- concentrations in the CSE membrane are higher than that in CMX in all solutions (Figure 2**Figure *2*** (a) and (b)). However, the Na^+ concentrations do not appear to vary between AMX and ASE when these anion exchange membranes are equilibrated with different counter-ions (i.e. Cl^-, NO_3^- and SO_4^{2-}) (Figure 2 (c) and (d)). The estimated value of $\boldsymbol{\xi}$ changes from 1.0 ± 0.1 for CMX to 2.8 ± 0.5 in CSE, while within experimental error, does not change between AMX and ASE (4.8 ± 1.4 and 5.4 ± 1.5, respectively). Similar to the water uptake results, the change from AMX to ASE appears to have little effects on the fixed charge group properties. It seems that the polymer itself was not changed, which is partly confirmed by the description provided by the manufacturer (Table 1). For the cation exchange membranes, the polymer changed from a styrene and divinyl benzene copolymer with sulfonic acid groups in CMX to a styrene-based copolymer with sodium sulfonic acid groups in CSE. This has resulted in some changes to the fixed charge group properties as indicated by the change in the value of $\boldsymbol{\xi}$. The amount of water uptake in the CMX membrane, as discussed previously, is hence higher than that in the CSE membrane. Due to the lack of information on the detailed chemistry of the polymers used and the exact relative portion of polymer to backing fabric in these commercial membranes, further interpretation of the $\boldsymbol{\xi}$ has not been carried out.

For binary electrolyte systems, it is also apparent that the co-ion concentration increases steadily with external solution concentration (Figure 4). The concentration of co-ion for the monovalent salt mixtures (NaCl + KCl for CSE in Figure 4 (a) and NaCl + $NaNO_3$ for ASE in Figure 4 (b)) is lower than that for the monovalent and divalent salt mixtures (NaCl + $CaCl_2$ for CSE in Figure 4 (a) and NaCl + Na_2SO_4 for ASE in Figure 4 (b)). This is expected as the presence of divalent ions again decreases the Donnan potential for co-ions. The concentrations of co-ion in the IEMs for monovalent salt mixtures are similar to the concentrations observed in single salt experiments. For monovalent and divalent mixtures, however, the co-ion concentration sits between the values for the single monovalent salt experiments and the single divalent salt experiments.

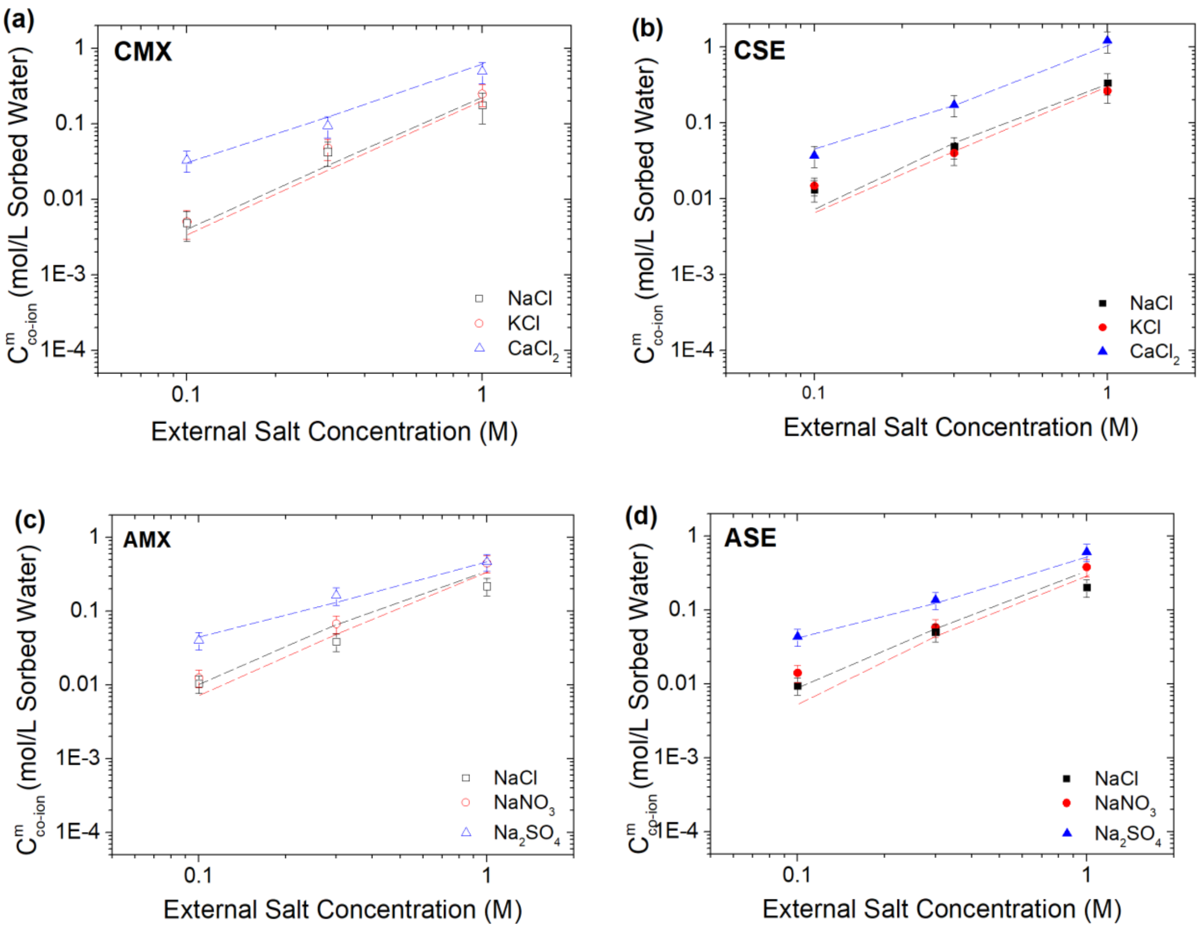

Figure 2. Concentration of co-ion (expressed in mol/L sorbed water)) in cation exchange membranes (i.e., $[Cl^-]$ in CEM (a) and CSE (b)) and anion exchange membranes (i.e., $[Na^+]$ in AMX (c) and ASE (d)) as a function of external salt concentration. Data are shown for single salts experiments, and are fitted to Eq. (6) for MX salts in IEMs, and Eq. (S1) for $CaCl_2$ in CEMs and Na_2SO_4 in AEMs. The fitting was performed using all three sets of data for each membrane, treating ξ as the only fitting parameter ($\xi_{CMX} = 1.0 \pm 0.1$, $\xi_{CSE} = 2.8 \pm 0.5$, $\xi_{AMX} = 4.8 \pm 1.4$, and $\xi_{ASE} = 5.4 \pm 1.5$).

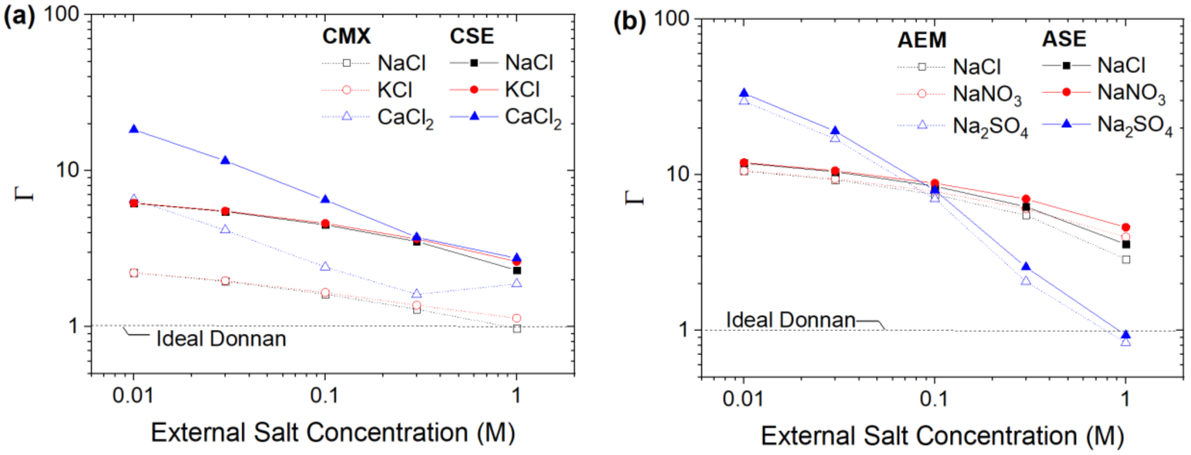

Figure 3. The activity coefficient ratio for (a) cation exchange membranes and (b) anion exchange membranes as a function of external salt concentration, modelled using Eq. (3) for monovalent salts and Eq. (S4) for $CaCl_2$ in CEMs and Na_2SO_4 in AEMs.

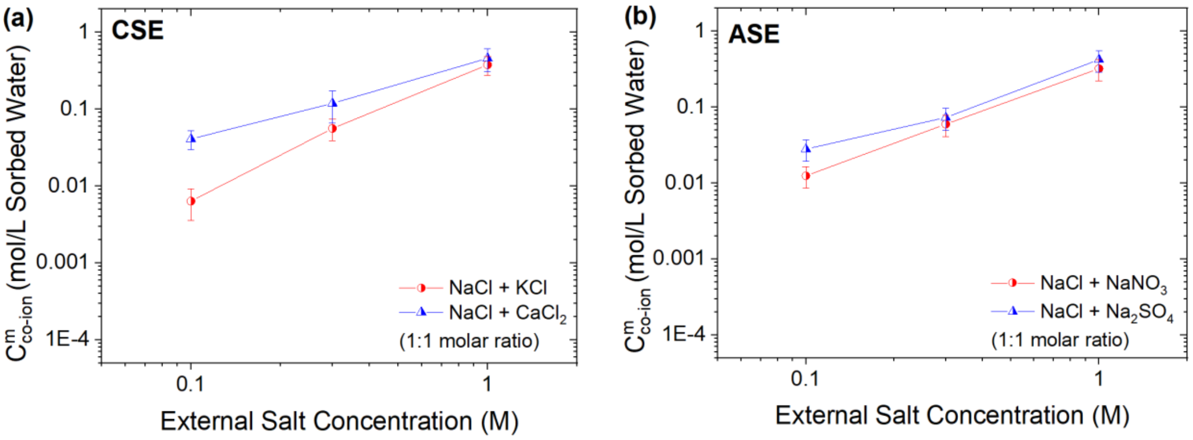

Figure 4. Concentration of co-ion (expressed in mol/L sorbed water)) in (a) cation exchange membranes (i.e. $[Cl^-]$ in CSE) and (b) anion exchange membranes (i.e. $[Na^+]$ in ASE) as a function of external salt concentration. Data are shown for binary salts experiments. The solid lines are drawn to guide the eye.

3.3 Partition of Counter-ion in IEMs

3.3.1 Cation Exchange Membranes

The counter-ion concentration in the cation exchange membranes, expressed in moles per L of swollen membrane, is presented in Figure 5. The concentration of the counter-ion in the IEMs is more sensitive to external salt concentration at values below 0.1 M, after which the concentration begins to plateau. The cation exchange membranes are initially in an H^+ form as they were pre-soaked in 1M HCl solution (Section 2.3). At low concentrations of the external solution, not all H^+ ions bound to the fixed charges can be replaced by Na^+ ions. However, as the external concentration increases, provision of more counter-ions in the external solution results in little further change as all fixed charge groups are occupied. Only slightly more counter-ions are sorbed in CSE than in CMX, resulting from a greater IEC but a smaller swollen membrane volume for CSE. The calcium concentration is around half of that of Na^+ and K^+ due to its double charge, showing a steady trend over the range of external salt concentrations.

The distribution of Na^+ and K^+ within these Neosepta membranes in a mixture of equimolar NaCl and KCl solutions is reported here for the first time. As presented in Figure 5(b), potassium is preferably absorbed by CSE which is consistent with the results from the single-salt sorption experiments at low salt concentrations (Figure 5(a)). A smaller hydrated radius of potassium and correspondingly a higher charge density is probably the reason for such a trend. Figure 5(b) also presents the counter-ion concentrations for a NaCl + $CaCl_2$ mixture is equimolar concentration, which reveal a strong preference of the divalent ions over monovalent ions in the CSE membrane. The strong electrostatic forces between divalent cations and the fixed charged group leads to the preferential divalent counter-ion sorption (Strathmann 2004). This is the basis of Donnan Exclusion Theory (Donnan 1924). However, as total salt concentrations increase, the concentration of sodium in the membrane approaches that of calcium. This is because the electrostatic forces are screened by the increasing charge from the ions in the solution, reducing the extent of Donnan exclusion for monovalent ions. It should be noted that the calcium concentration in the binary system is very close to its concentration for the single salt case, although the calcium concentrations in the external solutions were halved. While the hydrated radii of Ca^{2+} is larger than that of Na^{+}, in this case, the double charge of the former ion leads to stronger bonds with the fixed charged groups of the CSE.

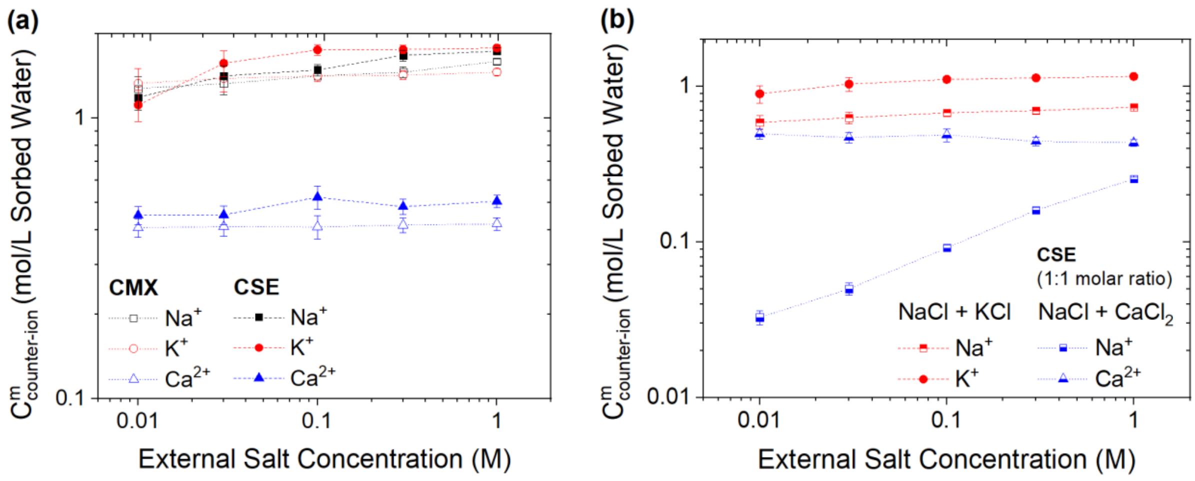

Figure 5. Counter-ion concentration for (a) single salt experiments in cation exchange membranes CMX and CSE, where NaCl, KCl and $CaCl_2$ were used in external solutions, and for (b) binary salts experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + $CaCl_2$ were used in external solutions. Lines are drawn to guide the eye.

The partition coefficient of the counter-ion for CMX and CSE, determined using Eq. (10) is presented in Figure 6 for the single salt and binary salts experiments. Ion partitioning between ion exchange membranes and the surrounding salt solutions is governed by the concentration of charged groups bound to the membrane matrix (Geise et al. 2012, Lonsdale et al. 1965, Paul 2004). Similar to counter-ion concentration in mol/L swollen membrane, the partition coefficients are slightly higher for CSE than CMX, but both showing a declining trend with increasing external salt concentration for all three cations. The partition of the counter-ion is higher for a monovalent salt in comparison with a divalent one, reflecting the changes in membrane concentration, due to the double charge on the divalent ion and to Donnan exclusion, shown in Figure 5. The selectivity between the ion pairs, calculated by Eq. (11) is shown in Figure 7. As expected, the selectivity of Na^+ to K^+ is around 1, due to the similarities between these two ions. In a binary mixture, CSE selectively absorbed K^+, as seen in Figure 5 (b), probably due to the smaller hydrated radius of potassium. A higher selectivity of Ca^{2+} in the membrane for a binary salt solution is in agreement with data reported by Sata (Sata 2004) for a typical ion exchange membrane with sulfonate groups.

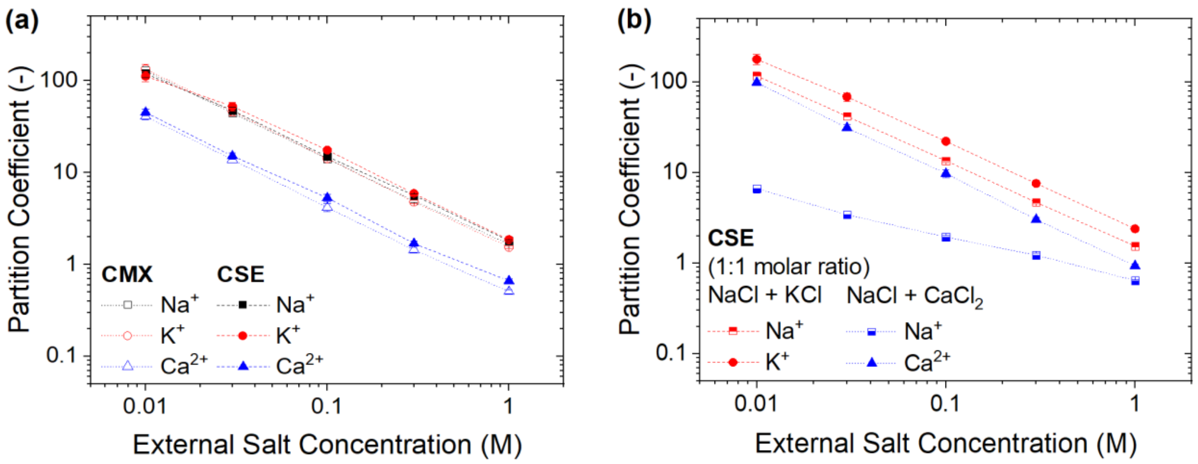

Figure 6. Partition coefficient of counter-ions in cation exchange membranes for (a) single salt experiments in CMX and CSE where NaCl, KCl and $CaCl_2$ were used in external solutions and for (b) binary salts experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + $CaCl_2$ were used in external solutions.

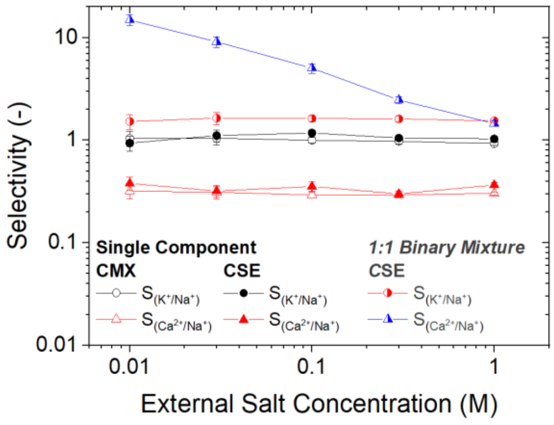

Figure 7. Selectivity of K^+ and Ca^{2+} to Na^+ in cation exchange membranes for single salt experiments in CMX and CSE where NaCl, KCl and $CaCl_2$ were used in external solutions; and for binary salts

experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + $CaCl_2$ were used in external solutions.

3.3.2 Anion Exchange Membranes

Similar experiments were conducted with different salts (NaCl, $NaNO_3$ and Na_2SO_4) to obtain the concentration of various counter-ions within the Neosepta anion exchange membranes. The concentration of nitrate in both the AMX and ASE (Figure 8 (a)) is lower than that of chloride, expressed in mol/L swollen membrane. This trend is reversed when the amount of water uptake is taken into consideration (Figure S1) so that this concentration is expressed in mol/L solution. The water uptake is noticeably lower when the AEMs are equilibrated in $NaNO_3$ solutions in comparison with NaCl solutions (Figure 1). It is also more apparent that NO_3^- is preferably absorbed when the membrane was equilibrated in binary salt solutions of NaCl and $NaNO_3$ (Figure 8 (b)). Unlike Na^+ and K^+ in the CMX and CSE membranes where the hydrated radii are noticeably different, those of NO_3^- and Cl^- are much closer (3.35 Å and 3.32 Å, respectively). Some researchers have reported that AMX (Malewitz et al. 2007) and Nafion (Bontha and Pintauro 1994, Pintauro et al. 1995) membranes selectively absorb the monovalent counter-ion with a larger hard sphere radius (Cl^-: 1.81 Å, NO_3^-, 2.64 Å) and hence lower surface charge density. This lower charge density may allow the NO_3^- to bond more strongly with the hydrophobic polymeric backbone (Table 1) and may also explain the lower water uptake. Similar behaviour has been previously observed where hydrophobic resins demonstrated affinity towards perchlorate (Wang 2010, Xiong et al. 2007). Sata (Sata 2000, 2004) also showed a higher transport number for NO_3^- over Cl^- at different concentrations (transport number ratio >1). Luo et al. (Luo et al. 2018) also note that the permselectivity for NO_3^- over Cl^- is consistent with the Hofmeister series (Hofmeister and Hofmeister 1888) and the Gibbs hydration energy.

For an equimolar binary mixture of NaCl and Na_2SO_4, the concentration of SO_4^{2-} decreases with external solution concentration while that of Cl^- increases (Figure 8 Figure *8* (b)). These trends are different to what is observed for the monovalent and divalent counter-ion mixture in cation exchange membranes. The transport number of SO_4^{2-} relative to Cl^- ions for different types of anion exchange membranes was also reported to be less than one, in contrast to the relative ratio between NO_3^- and Cl^- (Sata 2000). The hydrophobic nature of styrene in AEMs could partly inhibit the absorption of sulphate ions which are strongly hydrated (Sata et al. 1998), as the Gibbs hydration energy of SO_4^{2-} is the highest among the three anions studied (Cl^-: 370 kJ/mol, NO_3^-: 270 kJ/mol, SO_4^{2-}: 1000 kJ/mol). Another reason is likely to be the formation of $[NaSO_4]^-$ (i.e., ion pairing) within the solution at higher concentrations. Ion pairing has been identified as the cause of very low activity coefficients for sulfate in aqueous solutions (Buchner et al. 1999, Marcus and Hefter 2006). As a monovalent ion, $[NaSO_4]^-$ would compete less effectively with Cl^- within the anion exchange membrane. However, its full impact upon the activity and the ion partitioning in ion exchange membranes is still unknown and requires further study.

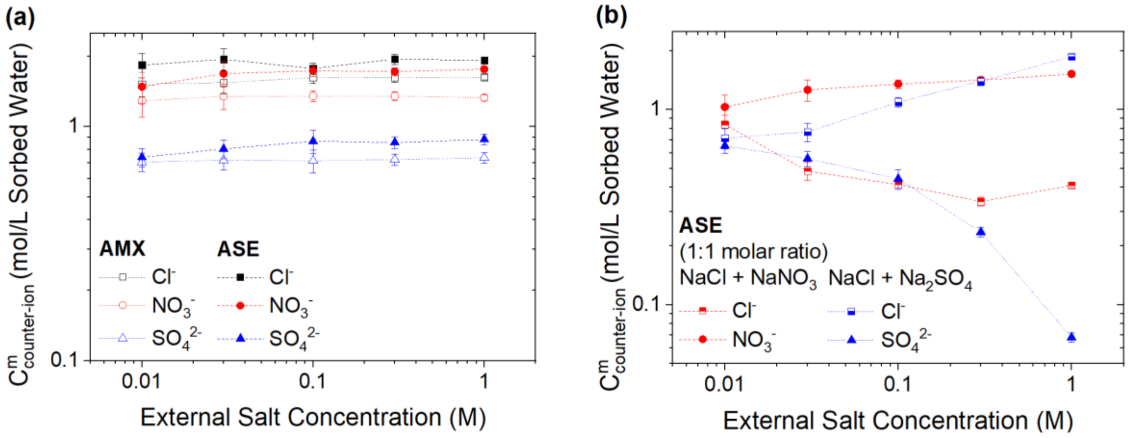

Figure 8. Counter-ion concentration in anion exchange membranes for (a) single salt experiments in AMX and ASE where NaCl, $NaNO_3$ and Na_2SO_4 were used in external solutions and for (b) binary salts experiments in ASE where equimolar mixtures of NaCl + $NaNO_3$ and NaCl + Na_2SO_4 were used in external solutions.

The partition coefficient of these counter-ions determined using Eq. (10) are presented in Figure 9 for the single salt and binary salts experiments. Similar to counter-ion concentration in mol/L swollen membrane, the partition coefficients are similar between AMX and ASE, but both showing a declining trend with increasing external salt concentration for all three anions. The partition of the monovalent anions is higher than that of divalent anions in the case of single salt experiments. This trend can again be justified both by the lower concentration in the membrane (Figure 8); and by the lower activity coefficient of the divalent ions in the bulk solution in comparison with that of monovalent ions. The selectivity between the anion pairs, determined by Eq. (11) is shown in Figure 10. When considering single salt data, the selectivity of NO_3^- to Cl^- is close to 1. But in a binary mixture, ASE selectively absorbs NO_3^-, as seen in Figure 8 (b), with a ratio of partition coefficients of ~3.5. This is in a similar range of values reported for anion exchange membranes with benzyl trimethylammonium groups (Sata et al. 1998). A very low selectivity of SO_4^{2-} in the membrane for a binary salt solution is observed, in agreement with the trends shown in Figure 8 (b) for counter-ion concentration.

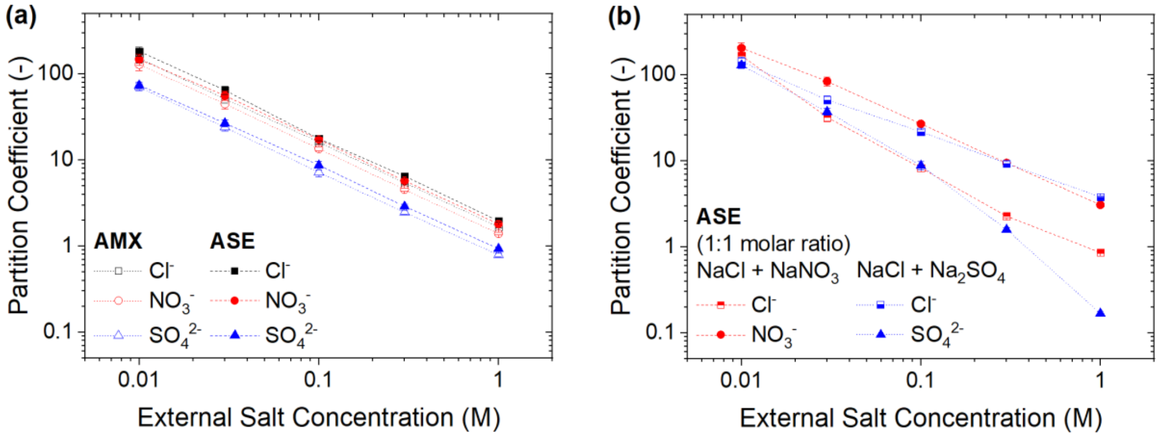

Figure 9. Partition coefficient of counter-ions in anion exchange membranes for (a) single salt experiments in AMX and ASE where NaCl, $NaNO_3$ and Na_2SO_4 were used in external solutions and for (b) binary salts experiments in ASE where equimolar mixtures of NaCl + $NaNO_3$ and NaCl + Na_2SO_4 were used in external solutions.

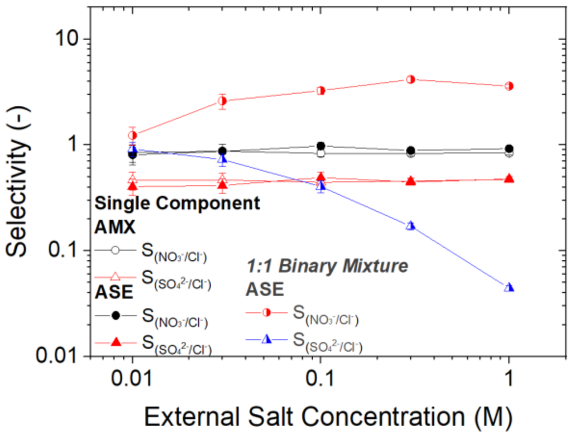

Figure 10. Selectivity of NO_3^- and SO_4^{2-} to Cl^- for single salt experiments in AMX and ASE where NaCl, $NaNO_3$ and Na_2SO_4 were used in external solutions; and for binary salts experiments in ASE where equimolar mixtures of NaCl + $NaNO_3$ and NaCl + Na_2SO_4 were used in external solutions.

4. CONCLUSIONS

We have reported the sorption equilibria of ions in commercial Neosepta ion exchange membranes, including CMX and CSE cation exchange membranes and AMX and ASE ion exchange membranes. Calcium has little impact at the water uptake in the CEMs, while the presence of sulphate results in the highest water uptake among all anions. The Manning/Donnan model was employed to investigate the structural characteristics of these membranes, as co-ion concentration is determined by the Donnan equilibrium between the membrane and the external solution. The change in polymer composition from CMX to CSE leads to a change in the Manning's parameter. This is consistent with the differences in sorption properties between CMX and CSE. The ion sorption characteristics, however, were found to be similar between AMX and ASE, which was also confirmed from the similar Manning's parameter obtained. Sorption of counter-ion in the binary mixtures of these ions revealed very different trends of monovalent and divalent ion sorption between CSE and ASE. While calcium dominates the fixed charge groups in CSE, the concentration of sodium in the membrane increases significantly with increasing external salt concentrations. However, the concentration of sulphate in the anion exchange membrane (ASE) declines with external salt concentration, while the concentration of chloride in the binary system increases. This leads to very low selectivities between sulphate and chloride. This unusual behavior could be due to the strong hydration of the sulfate anion and its interaction with the hydrophobic styrene in the charged polymer. It may also relate to the formation of the ion pair $[NaSO_4]^-$ as external concentrations increase. Nitrate ions also show unusual behavior. In single salt solutions, they absorb as strongly as chloride ions, but with less water accompanying the uptake. In binary mixtures, the nitrate is able to exclude chloride. This behavior may be related to the low surface charge density of the nitrate ion allowing it to interact more readily with the polymeric backbone. The characterisation of ion sorption behavior in single and binary mixtures provides useful information for their future applications for these commercial membranes.

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Figure Captions

Figure 1. Water uptake of (a) cation exchange membranes (CMX and CSE) and (b) anion exchange membranes (AMX and ASE) after equilibration in different external salt solutions of concentrations ranging from 0.01 M to 1 M. Equimolar binary mixtures of NaCl + KCl and NaCl + $CaCl_2$ were used for CSE membranes (a), and those of NaCl + $NaNO_3$ and NaCl + Na_2SO_4 were used for ASE membranes (b). The dashed lines are drawn to guide the eye.

Figure 2. Concentration of co-ion (expressed in mol/L sorbed water)) in cation exchange membranes (i.e., [Cl^-] in CEM (a) and CSE (b)) and anion exchange membranes (i.e., [Na^+] in AMX (c) and ASE (d)) as a function of external salt concentration. Data are shown for single salts experiments, and are fitted to Eq. (6) for MX salts in IEMs, and Eq. (S1) for $CaCl_2$ in CEMs and Na_2SO_4 in AEMs. The fitting was performed using all three sets of data for each membrane, treating ξ as the only fitting parameter ($\xi_{CMX} = 1.0 \pm 0.1$, $\xi_{CSE} = 2.8 \pm 0.5$, $\xi_{AMX} = 4.8 \pm 1.4$, and $\xi_{ASE} = 5.4 \pm 1.5$).

Figure 3. The activity coefficient ratio for (a) cation exchange membranes and (b) anion exchange membranes as a function of external salt concentration, modelled using Eq. (3) for monovalent salts and Eq. (S4) for $CaCl_2$ in CEMs and Na_2SO_4 in AEMs.

Figure 4. Concentration of co-ion (expressed in mol/L sorbed water)) in (a) cation exchange membranes (i.e. [Cl^-] in CSE) and (b) anion exchange membranes (i.e. [Na^+] in ASE) as a function of external salt concentration. Data are shown for binary salts experiments. The solid lines are drawn to guide the eye.

Figure 5. Counter-ion concentration for (a) single salt experiments in cation exchange membranes CMX and CSE, where NaCl, KCl and $CaCl_2$ were used in external solutions, and for (b) binary salts experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + $CaCl_2$ were used in external solutions. Lines are drawn to guide the eye.

Figure 6. Partition coefficient of counter-ions in cation exchange membranes for (a) single salt experiments in CMX and CSE where NaCl, KCl and $CaCl_2$ were used in external solutions and for (b) binary salts experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + $CaCl_2$ were used in external solutions.

Figure 7. Selectivity of K^+ and Ca^{2+} to Na^+ in cation exchange membranes for single salt experiments in CMX and CSE where NaCl, KCl and $CaCl_2$ were used in external solutions; and for binary salts experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + $CaCl_2$ were used in external solutions.

Figure 8. Counter-ion concentration in anion exchange membranes for (a) single salt experiments in AMX and ASE where NaCl, $NaNO_3$ and Na_2SO_4 were used in external solutions and for (b) binary salts experiments in ASE where equimolar mixtures of NaCl + $NaNO_3$ and NaCl + Na_2SO_4 were used in external solutions.

Figure 9. Partition coefficient of counter-ions in anion exchange membranes for (a) single salt experiments in AMX and ASE where NaCl, $NaNO_3$ and Na_2SO_4 were used in external solutions and for (b) binary salts experiments in ASE where equimolar mixtures of NaCl + $NaNO_3$ and NaCl + Na_2SO_4 were used in external solutions.

Figure 10. Selectivity of NO_3^- and SO_4^{2-} to Cl^- for single salt experiments in AMX and ASE where NaCl, $NaNO_3$ and Na_2SO_4 were used in external solutions; and for binary salts experiments in ASE where equimolar mixtures of NaCl + $NaNO_3$ and NaCl + Na_2SO_4 were used in external solutions.

Supporting Information

Single and binary ion sorption equilibria of monovalent and divalent ions in commercial ion exchange membranes

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Keywords: Ion exchange membrane; sorption; binary; calcium; nitrate; sulphate.

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The following expressions, derived in detail by Kamcev [1], can be used to relate the co-ion concentration in the membrane and the Manning expressions for membrane ion activity coefficients, after accounting for the charge balance in the membrane and the valency of salt ions:

$$\left(C_s^m + \frac{1}{2}C_{\text{fix}}^m\right)(C_s^m)^2\left(\frac{\frac{C_{\text{fix}}^m}{2\xi C_s^m}+2}{\frac{C_{\text{fix}}^m}{C_s^m}+2}\right)exp\left(-\frac{\frac{3C_{\text{fix}}^m}{4C_s^m}}{\frac{C_{\text{fix}}^m}{C_s^m}+6\xi}\right) = \left(\gamma_\pm^s\right)^3 (C_s^s)^3 \tag{S1}$$

where C_s^m is the mobile salt concentration in the membrane.

Equation S1 is applicable when a cation exchange membrane is in equilibrium with an M-X$_2$ type salt solution (e.g., CaCl$_2$) and when an anion exchange membrane is in equilibrium with an M$_2$-X type salt solution (e.g., Na$_2$SO$_4$), where

$$\gamma_+^m\,(\gamma_-^m)^2 = \left(\frac{\frac{C_{\text{fix}}^m}{2\xi C_s^m}+2}{\frac{C_{\text{fix}}^m}{C_s^m}+2}\right)exp\left(-\frac{\frac{3C_{\text{fix}}^m}{4C_s^m}}{\frac{C_{\text{fix}}^m}{C_s^m}+6\xi}\right) \tag{S2}$$

In both cases, C_s^m is related to co-ion concentration in the membrane as

$$C_s^m = \frac{1}{2}C_-^m \tag{S3}$$

Note that for monovalent salts, $C_s^m = C_-^m$.

Since the activity coefficients in the membrane phase are coincidentally identical, the ratio of activities coefficients of the solution phase to the membrane phase, as defined in Donnan Theory, for both divalent salts used in this work, is given by:

$$\Gamma = \frac{4\left(\gamma_\pm^s\right)^3}{\gamma_+^m\,(\gamma_-^m)^2} \tag{S4}$$

$$= \frac{4\left(\gamma_\pm^s\right)^3}{\left(\frac{\frac{C_{\text{fix}}^m}{2\xi C_s^m}+2}{\frac{C_{\text{fix}}^m}{C_s^m}+2}\right)exp\left(-\frac{\frac{3C_{\text{fix}}^m}{4C_s^m}}{\frac{C_{\text{fix}}^m}{C_s^m}+6\xi}\right)} \tag{S5}$$

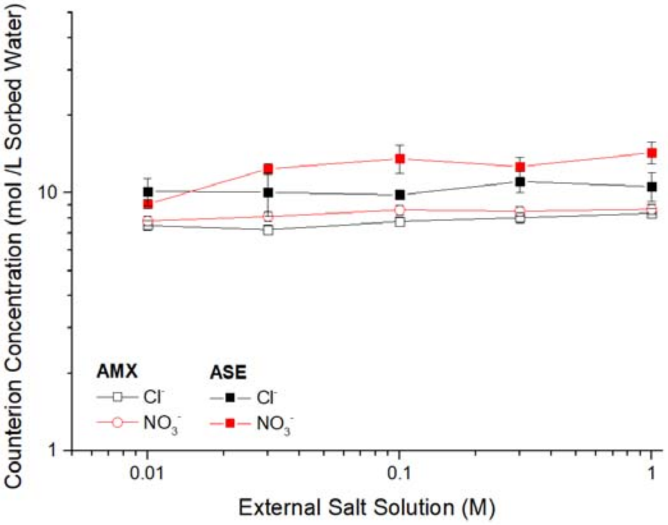

Figure S1 Counter-ion concentration (mol/L sorbed water) of chloride and nitrate in AMX and ASE, equilibrated in single salt solutions with sodium as the co-ion.

REFERENCES

[1] J. Kamcev, M. Galizia, F.M. Benedetti, E.-S. Jang, D.R. Paul, B.D. Freeman, G.S. Manning, Partitioning of mobile ions between ion exchange polymers and aqueous salt solutions: importance of counter-ion condensation, PCCP, 18 (2016) 6021-6031.