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Author/s:

Chen, GQ;Wei, K;Hassanvand, A;Freeman, BD;Kentish, SE

Title:

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Date:

2020-05-15

Citation:

Chen, G. Q., Wei, K., Hassanvand, A., Freeman, B. D. & Kentish, S. E. (2020). Single and binary ion sorption equilibria of monovalent and divalent ions in commercial ion exchange membranes.. Water Research, 175, <https://doi.org/10.1016/j.watres.2020.115681>.

Persistent Link:

<https://hdl.handle.net/11343/237421>

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

G. Q. Chen¹, K. Wei², A. Hassanvand¹, B. D. Freeman³, S. E. Kentish^{1*}

¹ Department of Chemical Engineering, The University of Melbourne, Victoria 3010, Australia.

² State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, P. R. China

³ McKetta Department of Chemical Engineering, The University of Texas at Austin, 200 E, Dean Keeton St., Stop C0400, Austin, Texas 78712-1589, United States

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

*Corresponding Author

Prof S. Kentish

Tel: +61 3 8344 6682

Fax: +61 3 8344 4153

E-mail address: sandraek@unimelb.edu.au

1 **ABSTRACT**

2 The co-ion and counter-ion sorption of monovalent (Na^+ , K^+ , Cl^- and NO_3^-) and divalent ions
3 (Ca^{2+} and SO_4^{2-}) in commercial Neosepta ion exchange membranes were systemically
4 studied in both single and binary salt systems. The new generation of Neosepta cation
5 exchange membrane (CSE) showed a significant difference in water uptake and co-ion
6 sorption compared to the earlier generation CMX. Use of the Manning model confirmed
7 that there were significant differences between these membranes, with the estimated value
8 of the Manning parameter changing from 1.0 ± 0.1 for CMX to 2.8 ± 0.5 in CSE. There were
9 fewer differences between the two Neosepta anion exchange membranes, AMX and ASE. In
10 single salt solutions, potassium sorbed most strongly into the cation exchange membranes,
11 but in binary salt mixtures, calcium dominated due to Donnan exclusion at low
12 concentrations. While these trends were expected, the sorption behaviour in the anion
13 exchange membranes was more complex. The water uptake of both AMX and ASE was shown to
14 be the greatest in Na_2SO_4 solutions. This strong water uptake was reflected in strong sorption
15 of sulphate ions in a single salt solution. Conversely, in a binary salt mixture with NaCl,
16 sulphate sorption fell significantly at higher concentrations. This was possibly caused by ion
17 pairing within the solution, as well as the strongly hydrophobic nature of styrene in the
18 charged polymer. Water uptake was lowest in NaNO_3 solutions, even though sorption of the
19 nitrate ion was comparable to that of chloride in these single salt solutions. In the binary
20 mixture, nitrate was absorbed more strongly than chloride. These results could be due to the
21 low surface charge density of this ion allowing it to bond more strongly with the
22 hydrophobic polymeric backbone at the exclusion of water and other ions.

24 **1. Introduction**

25 The transport of ions through ion exchange membranes is a critical factor to maximise energy
26 efficiency and productivity in the electromembrane processes used in water treatment, such as
27 electrodialysis (Arola et al. 2019, Kim et al. 2012, Van der Bruggen et al. 2004, Van der Bruggen et al.
28 2003), Donnan dialysis (Durmaz et al. 2005), electrodialysis with bipolar membranes (Li et al. 2016),
29 reverse electrodialysis (Kim et al. 2019, Vermaas et al. 2013), and membrane capacitive deionisation
30 (Hassanvand et al. 2018, Ma et al. 2020). These processes involve the selective migration of ionic
31 species through charged polymeric membranes, often made from dense, non-porous polymers that
32 have anionic and/or cationic fixed charged groups (Sata 2004). These fixed charged groups are
33 typically sulfonic acid groups ($-\text{SO}_3^-$) for cation exchange membranes and amine groups ($-\text{NH}_3^+$,
34 $-\text{NRH}_2^+$, $-\text{NR}_2\text{H}^+$) for anion exchange membranes.

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

40 Ion transport through IEMs is governed by the absorption of the ionic species into the membrane
41 and their migration through the membrane phase (Sata et al. 2002). Hence, ion sorption, or ion
42 partitioning between the IEM and the surrounding electrolyte solution is an important transport
43 property of ion exchange membranes (Fan and Yip 2019, Geise et al. 2012). It has been reported that
44 ion mobility, affinity of the competing ions (Galama et al. 2014, Sata et al. 2002, Van der Bruggen et
45 al. 2004), the concentration of charged groups bound to the membrane matrix (i.e. ion exchange
46 capacity) (Kamcev et al. 2017b), and water uptake of the membrane (Geise et al. 2014, Ju et al.
47 2010) can affect the ultimate ion sorption. Direct measurements of sorption equilibria have been
48 performed in many studies in single electrolyte systems (Galizia et al. 2019, Kamcev et al. 2016b,

49 Kamcev et al. 2017a, 2018, Le et al. 2009, Martí-Calatayud et al. 2014, Pintauro and Bennion 1984).
50 However, it is of practical importance to quantify and obtain a better understanding of the
51 competitive absorption of a mixture of ions in commercial IEMs. This has been conducted by a
52 number of research groups who have used various cation exchange membranes (Bontha and
53 Pintauro 1994, Chapotot et al. 1994, Palomo and Pintauro 2003, Pintauro et al. 1995) and anion
54 exchange membranes (Guesmi et al. 2010, Hannachi et al. 2013, Malewitz et al. 2007), mostly by
55 varying the mixing ratios of the two divalent and monovalent ions at a fixed total concentration.

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

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

$$72 \quad a_+^m a_-^m = a_+^s a_-^s \quad (1)$$

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

$$79 \quad C_-^m = \sqrt{\frac{(C_{\text{fix}}^m)^2}{4} + \frac{(\gamma_{\pm}^s)^2}{\gamma_+^m \gamma_-^m} (C_s^s)^2} - \frac{C_{\text{fix}}^m}{2} \quad (2)$$

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

$$84 \quad \Gamma = \frac{(\gamma_{\pm}^s)^2}{\gamma_+^m \gamma_-^m} \quad (3)$$

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

$$89 \quad \gamma_+^m = \left(\frac{\frac{1}{\xi} \cdot \frac{C_{\text{fix}}^m}{C^m} + 1}{\frac{C_{\text{fix}}^m}{C^m} + 1} \right) \exp \left(- \frac{\frac{1}{2} \cdot \frac{C_{\text{fix}}^m}{C^m}}{\frac{C_{\text{fix}}^m}{C^m} + 2 \xi} \right) \quad (4)$$

$$90 \quad \gamma_-^m = \exp \left(- \frac{\frac{1}{2} \cdot \frac{C_{\text{fix}}^m}{C^m}}{\frac{C_{\text{fix}}^m}{C^m} + 2 \xi} \right) \quad (5)$$

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

$$93 \quad (C_-^m + C_{\text{fix}}^m)(C_-^m) \left(\frac{\frac{C_{\text{fix}}^m}{\xi} + 1}{\frac{C_-^m}{\xi} + 1} \right) \exp \left(- \frac{\frac{C_{\text{fix}}^m}{\xi}}{\frac{C_-^m}{\xi} + 2} \right) = (\gamma_{\pm}^s)^2 (C_s^s)^2 \quad (6)$$

94 It should be noted that in this framework the ion concentrations are expressed as moles of ions per
 95 unit volume of sorbed water. A similar expression can be found in the Supporting Information (Eq.
 96 S1) for when a cation exchange membrane is in equilibrium with an M-X₂ type salt solution (e.g.,
 97 CaCl₂), or when an anion exchange membrane is in equilibrium with an M₂-X type salt solution (e.g.,
 98 Na₂SO₄).

99

100 In this work, the sorption equilibria of ions in two cation exchange membranes (CEMs, namely CMX
 101 and CSE) and two anion exchange membranes (AEMs, namely AMX and ASE) are studied over a total
 102 salt concentration range of 0.01 M to 1 M. These are commercially available IEMs manufactured by
 103 ASTOM Corporation, Japan and are categorised as standard grade with high mechanical strength.
 104 The investigation of co-ion and counter-ion solubility (i.e., partition coefficient) is carried out in
 105 solutions containing single cations (Na⁺, K⁺, Ca⁺) for CEMs and single anions (Cl⁻, NO₃⁻, SO₄²⁻) in AEMs,
 106 as well as their binary mixtures. The ion sorption framework based on Manning's counter-ion
 107 condensation theory, as described above, is employed to gain insight in the relationship between
 108 structural/material characteristics and ion sorption properties within these membranes. The
 109 quantification of single and binary ion sorption in IEMs presented in this work will improve the
 110 understanding of the principal phenomena governing ion transport and separation in
 111 electromembrane processes such as electrodialysis, reverse electrodialysis and capacitive de-
 112 ionisation. This is vital for future development of highly efficient ion exchange membranes to
 113 advance water purification processes.

114

115 **2. EXPERIMENTAL**

116 **2.1 Materials**

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

128

129 Sodium chloride (NaCl, 99.7%), potassium chloride (KCl, 99.0%), and calcium chloride anhydrous
130 (CaCl_2 , 98%), sodium nitrate (NaNO_3 , 99%) and sodium sulphate (Na_2SO_4 , 99%) were procured from
131 Chem-Supply Australia to prepare salt solutions at different concentrations. Caesium chloride (CsCl,
132 99.9%, Sigma Aldrich) and sodium iodide (NaI, 99.0%, Ajax FineChem) were used for desorbing the
133 absorbed ions in the membrane.

134 **2.2 Water Uptake**

135 Circular ion exchange membrane samples ($\varnothing = 45$ mm) were pre-soaked in water to remove residual
136 solvent not associated with the fixed charged groups. They were then dried in a vacuum oven at
137 room temperature for 48 h. Following this, the dry mass (m_d), thickness and diameter of the
138 membrane samples were obtained. The membranes were then immersed in salt solutions of desired

139 concentrations. These membranes were then wiped gently (Kimtech wipes) to obtain their wet mass
 140 (m_w), thickness and diameter. Water uptake can be calculated as:

$$141 \quad w_u = \frac{m_w - m_d}{m_d} \quad (7)$$

142 The thickness and diameter of the wet membranes were used to calculate the volume of the swollen
 143 membrane (V_m).

144

145 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%						

146 [^] Information provided by ASTOM, Japan.

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

149 ^{*} measured using 1 M NaCl solution.

150

151

152 2.3 Ion Sorption

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

162

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

168

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

$$171 C_+^m = C_-^m + C_{fix}^m \text{ for monovalent salts} \quad (8)$$

172 and

$$173 C_+^m = \frac{1}{2}C_-^m + \frac{1}{2}C_{fix}^m \text{ for divalent salts } MX_2 \text{ in CEMs and } M_2X \text{ in AEMs} \quad (9)$$

174 The factors of $\frac{1}{2}$ in Eq. (9) account for the valency of Ca²⁺ in CEMs and SO₄²⁻ in AEMs as counter-ions,
175 because (a) each mobile divalent ion is associated with two mobile co-ions and (b) each divalent
176 counter-ion is bound to two fixed charge groups in the ion exchange membrane. All concentrations

177 were expressed in eq/L swollen membrane, unless Eq. (1) to (5) were considered in which case eq/L
178 water sorbed was used. Ion exchange capacity (IEC) is defined as meq/g dry membrane
179 (milliequivalent per g of dry membrane).

180

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

$$183 \quad K_i = \frac{C_i^m}{C_i^s} \quad (10)$$

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

$$185 \quad S_j^i = \frac{K_i}{K_j} \quad (11)$$

186 The external solutions used for equilibrating the CEMs were NaCl, KCl and CaCl₂ solutions from 0.01
187 M to 1 M, and binary solutions of equimolar cation concentrations of NaCl + KCl and NaCl + CaCl₂.
188 Similarly, the AEMs were equilibrated in NaCl, NaNO₃ and Na₂SO₄ solutions from 0.01 M to 1 M, and
189 binary solutions of equimolar cation concentrations of NaCl + NaNO₃ and NaCl + Na₂SO₄. The
190 concentrations of cations (i.e., sodium, potassium and calcium) were determined using Inductively
191 Coupled Plasma Atomic Emission Spectroscopy (ICP-OES 720ES, Varian). The concentrations of
192 anions (i.e., chloride, nitrate and sulfate) were determined using Ion Chromatograph (IC-Dionex, ICS-
193 1000).

194

195

196 3. RESULTS AND DISCUSSION

197 3.1 Water uptake

198 The water uptake of the ion exchange membranes equilibrated in different salt solutions is
199 presented in Figure 1. As shown in Table 1, the fixed charges of these membranes are either strongly
200 negative (i.e., $-\text{SO}_3^-$ group) in CMX and CSE, or strongly positive in AMX and ASE. The water uptake
201 presented for all Neosepta IEMs studied in this work is within the typical range reported in the
202 literature (0.14 to 0.46 g $\text{H}_2\text{O}/\text{g}$ dry membrane) (Strathmann 2004).

203

204 Membrane swelling caused by water absorbed into the charged polymer has a direct influence on
205 the absorption and transport of ions with IEMs. Water enters the polymer matrix to hydrate both
206 the fixed charged groups and their counter-ions, stretching the polymer network. However, the
207 elastic forces that result from crosslinking resist the polymer stretching and thus the amount of
208 water than can enter the network. The water uptake is therefore a trade-off between these two
209 effects (Helfferich 1962, Kamcev 2016). Water uptake is affected by the concentration and type of
210 fixed charged groups and the degree of crosslinking. Water uptake is also related to the hydrated
211 radius of the counter-ions, the counter-ion valency and how it interacts with the fixed charge group
212 (Galizia et al. 2017, Strathmann 2004). The hydrated radius is similar between Na^+ and K^+ (3.58 Å and
213 3.31 Å) and is higher for Ca^{2+} (4.12 Å). However, for the cation exchange membranes (Figure 1(a)),
214 the water uptake of CMX and CSE is the highest in NaCl solutions, but is similar between KCl and
215 CaCl_2 (within experimental error). Similar trends have been reported by Bonner et al. (Bonner and
216 Smith 1957) for sulfonated polystyrene resins and Galizia et al. (Galizia et al. 2017) for cross-linked
217 poly (p -styrene sulfonate-co-divinylbenzene). For the anion exchange membranes (Figure 1(b)), the
218 water uptake of both AMX and ASE is shown to be the greatest in Na_2SO_4 solutions, and the lowest
219 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
220 Å, respectively. In binary solutions, the amount of water uptake mostly lies between the water

221 uptake values of the respective single salt solutions. This is the case for both CSE and ASE
222 membranes, as shown in Figure 1.

223 The backing fabric is changed from polyvinyl chloride for CMX to mixtures of polyethylene and
224 polypropylene for CSE which weighs less per unit area (Table 1). The percentage water uptake for
225 the cation exchange membranes also changes on a mass basis, declining from 37% - 44% for CMX to
226 28% - 35% for CSE (Figure 1(a)). The swollen CMX membranes are greater in both volume and
227 thickness, have a higher membrane resistance and lower IEC.

228

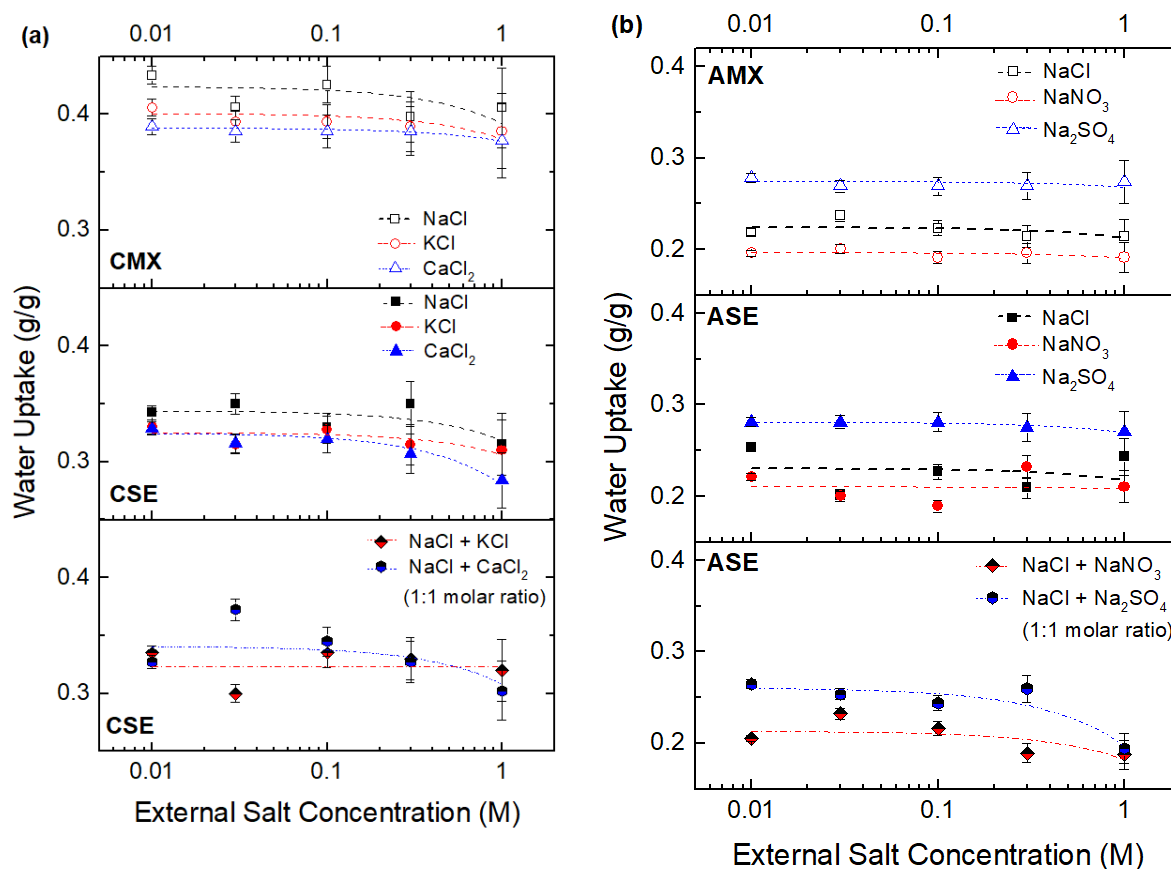
229 The water uptake, however, appears to be similar between AMX and ASE (18%-28%). As shown in
230 Table 1, the dry mass is lower for the ASE membranes than the AMX membranes, while the IEC is
231 higher. The swollen AMX membranes are thinner than the ASE membranes and the membrane
232 resistance reported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

239

240 Finally, it is known that water uptake also slightly decreases with increasing external salt
241 concentrations due to osmotic de-swelling (Kamcev 2016, Khare and Peppas 1995, Paul et al. 2008).

242 This decline at high salt concentrations is observed for most cases presented in Figure 1.

243



245

246 Figure 1. Water uptake of (a) cation exchange membranes (CMX and CSE) and (b) anion exchange
 247 membranes (AMX and ASE) after equilibration in different external salt solutions of concentrations
 248 ranging from 0.01 M to 1 M. Equimolar binary mixtures of NaCl + KCl and NaCl + CaCl₂ were used for
 249 CSE membranes (a), and those of NaCl + NaNO₃ and NaCl + Na₂SO₄ were used for ASE membranes
 250 (b). The dashed lines are drawn to guide the eye.

251

252 3.2 Co-ion concentration in membranes

253 Both the concentrations of counter-ion and co-ion within the IEMs were measured. Most of the
 254 counter-ions sorbed in the membrane are associated with the fixed charges within the polymer
 255 matrix, but a very small portion of counter-ions are required to neutralize any sorbed co-ions in the
 256 membrane. Therefore, this concentration of co-ion is also referred to as the mobile salt
 257 concentration within the membrane (Geise et al. 2012, Kamcev et al. 2015a). Since the co-ion

258 concentration in the desorption solution was very low for salt solutions of 0.01 M and 0.03 M, we
259 were not able to accurately determine these concentrations. Only co-ion concentrations for external
260 salt concentrations of greater than 0.1 M are reported.

261

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

271

272 Experimental data for these single salt experiments are fitted to Eq. (6) for monovalent counter ions
273 and Eq. (S1) for divalent counter ions. The fitting was performed using all three sets of data for each
274 membrane, treating the linear charge density of polymer, ξ as the only fitting parameter. This
275 approach assumes that ξ does not depend significantly on the type of salt used (Kamcev et al.
276 2016a). Within experimental error, the estimated values of linear charge density, reported in the
277 caption of Figure 2, are within the typical range (1 – 4) reported for polyelectrolyte systems (Kwak
278 1973, Manning 1969). The ratio of activity coefficients between the solution and the membrane, Γ ,
279 were also estimated by Eq. (3) for monovalent salts and Eq. (S5) for divalent salts, using the
280 modelled values of co-ion concentrations. This parameter is presented in Figure 3 (a) and (b) for
281 cation exchange membranes and anion exchange membranes, respectively. Γ decreases gradually
282 from low to high external salt concentrations for all membranes. Similar trends were also reported
283 by Kamcev et al. (Kamcev et al. 2015b) and Galizia et al. (Galizia et al. 2017). The activity coefficients

284 of the external salt solutions, in general, decrease with concentration. The decline in Γ as a function
285 of external salt concentration hence results from much lower activity coefficients in the membranes
286 when external salt concentration is low. As the concentration of external solution increases, the ion
287 concentration difference between the membrane phase and the external solution becomes smaller,
288 with Γ slowly approaching unity.

289

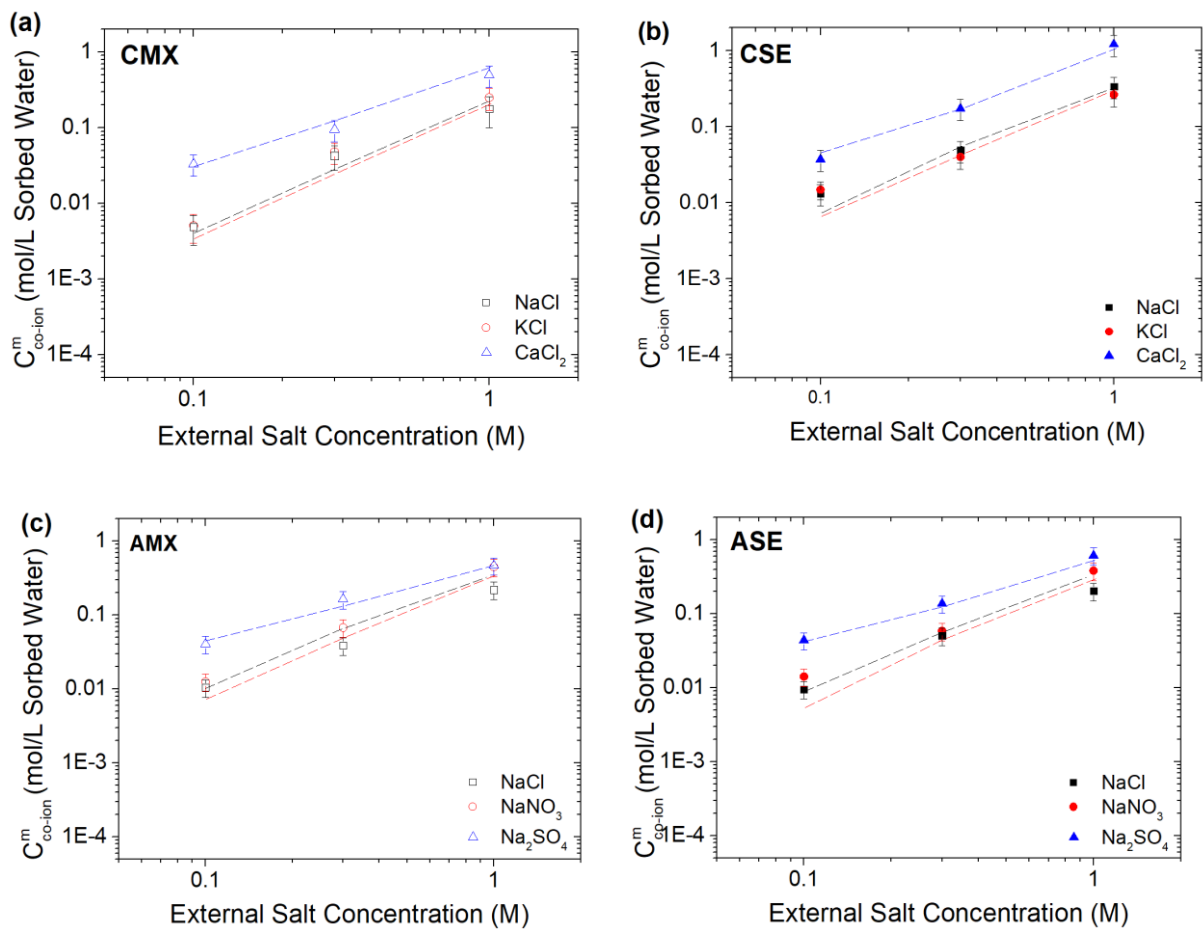
290 For single electrolyte system, the Cl^- concentrations in the CSE membrane are higher than that in
291 CMX in all solutions (Figure 2 (a) and (b)). However, the Na^+ concentrations do not appear
292 to vary between AMX and ASE when these anion exchange membranes are equilibrated with
293 different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

306

307 For binary electrolyte systems, it is also apparent that the co-ion concentration increases steadily
308 with external solution concentration (Figure 4). The concentration of co-ion for the monovalent salt
309 mixtures ($\text{NaCl} + \text{KCl}$ for CSE in Figure 4 (a) and $\text{NaCl} + \text{NaNO}_3$ for ASE in Figure 4 (b)) is lower than

310 that for the monovalent and divalent salt mixtures (NaCl + CaCl₂ for CSE in Figure 4 (a) and NaCl +
 311 Na₂SO₄ for ASE in Figure 4 (b)). This is expected as the presence of divalent ions again decreases the
 312 Donnan potential for co-ions. The concentrations of co-ion in the IEMs for monovalent salt mixtures
 313 are similar to the concentrations observed in single salt experiments. For monovalent and divalent
 314 mixtures, however, the co-ion concentration sits between the values for the single monovalent salt
 315 experiments and the single divalent salt experiments.

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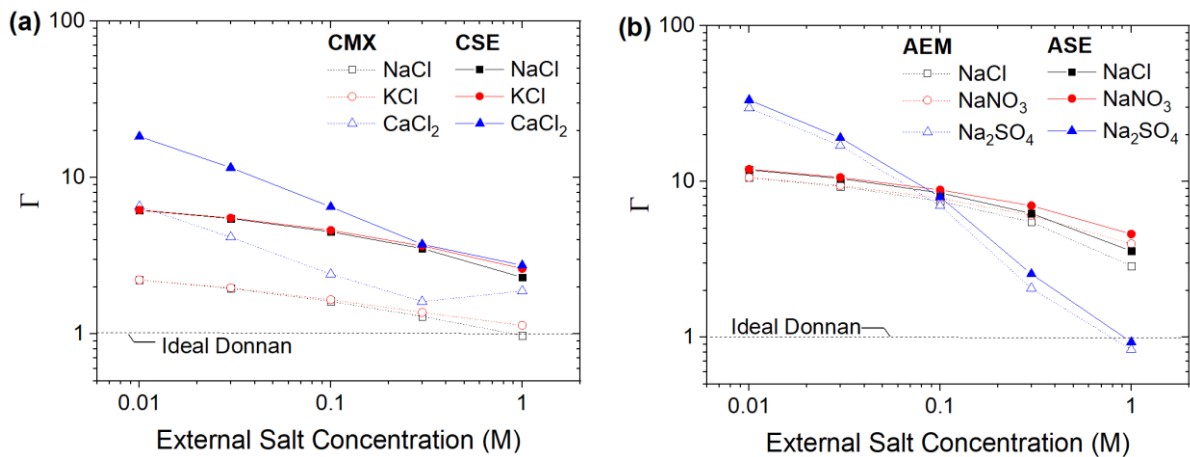


317

318

319 Figure 2. Concentration of co-ion (expressed in mol/L sorbed water)) in cation exchange membranes
 320 (i.e., [Cl⁻] in CEM (a) and CSE (b)) and anion exchange membranes (i.e., [Na⁺] in AMX (c) and ASE (d))
 321 as a function of external salt concentration. Data are shown for single salts experiments, and are
 322 fitted to Eq. (6) for MX salts in IEMs, and Eq. (S1) for CaCl₂ in CEMs and Na₂SO₄ in AEMs. The fitting
 323 was performed using all three sets of data for each membrane, treating ξ as the only fitting
 324 parameter ($\xi_{\text{CMX}} = 1.0 \pm 0.1$, $\xi_{\text{CSE}} = 2.8 \pm 0.5$, $\xi_{\text{AMX}} = 4.8 \pm 1.4$, and $\xi_{\text{ASE}} = 5.4 \pm 1.5$).

325



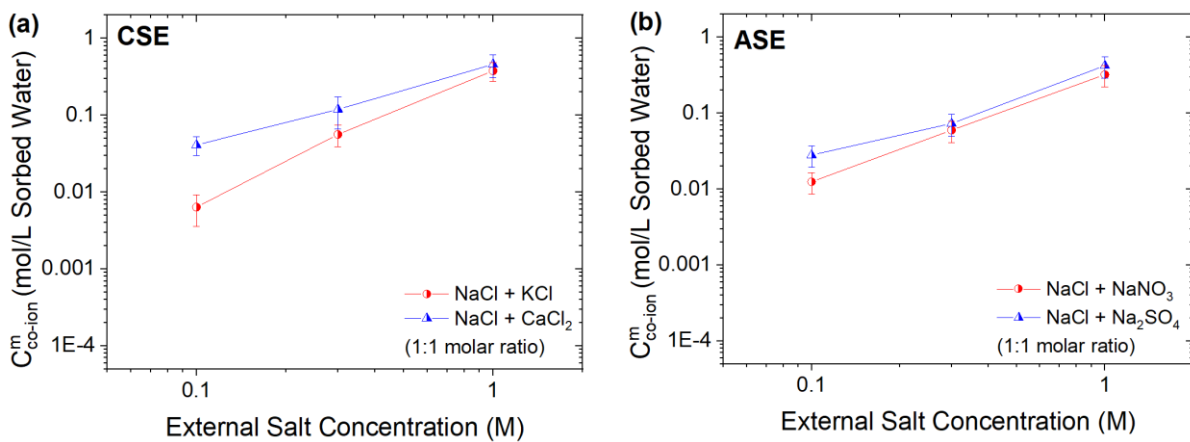
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327

328 Figure 3. The activity coefficient ratio for (a) cation exchange membranes and (b) anion exchange
329 membranes as a function of external salt concentration, modelled using Eq. (3) for monovalent salts
330 and Eq. (S4) for CaCl₂ in CEMs and Na₂SO₄ in AEMs.

331

332



333

334

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

339

340

341 3.3 Partition of Counter-ion in IEMs

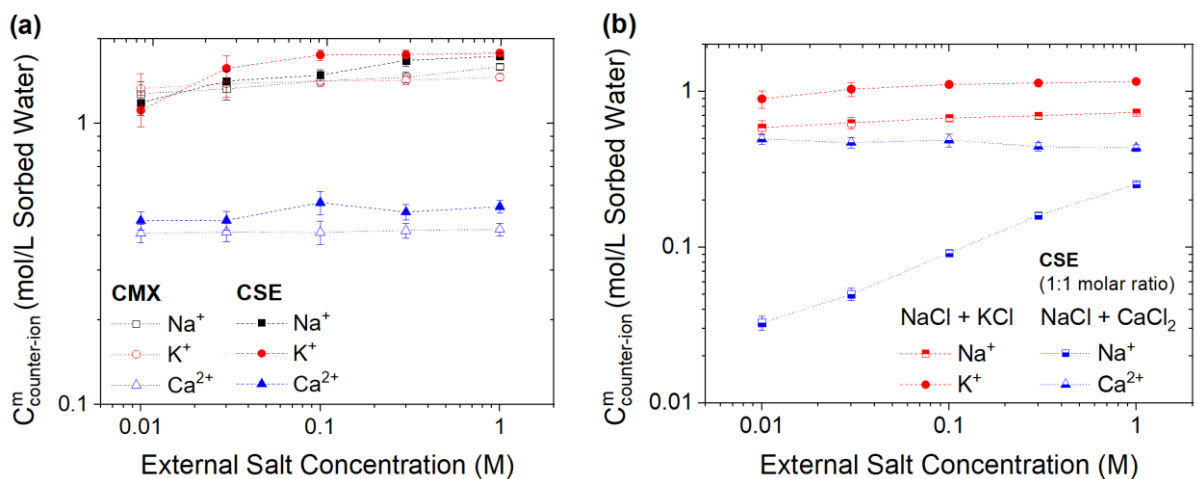
342 3.3.1 Cation Exchange Membranes

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

354

355 The distribution of Na^+ and K^+ within these Neosepta membranes in a mixture of equimolar NaCl and
356 KCl solutions is reported here for the first time. As presented in Figure 5(b), potassium is preferably
357 absorbed by CSE which is consistent with the results from the single-salt sorption experiments at low
358 salt concentrations (Figure 5(a)). A smaller hydrated radius of potassium and correspondingly a
359 higher charge density is probably the reason for such a trend. Figure 5(b) also presents the counter-
360 ion concentrations for a NaCl + $CaCl_2$ mixture is equimolar concentration, which reveal a strong
361 preference of the divalent ions over monovalent ions in the CSE membrane. The strong electrostatic
362 forces between divalent cations and the fixed charged group leads to the preferential divalent
363 counter-ion sorption (Strathmann 2004). This is the basis of Donnan Exclusion Theory (Donnan
364 1924). However, as total salt concentrations increase, the concentration of sodium in the membrane
365 approaches that of calcium. This is because the electrostatic forces are screened by the increasing

366 charge from the ions in the solution, reducing the extent of Donnan exclusion for monovalent ions.
 367 It should be noted that the calcium concentration in the binary system is very close to its
 368 concentration for the single salt case, although the calcium concentrations in the external solutions
 369 were halved. While the hydrated radii of Ca^{2+} is larger than that of Na^+ , in this case, the double
 370 charge of the former ion leads to stronger bonds with the fixed charged groups of the CSE.
 371

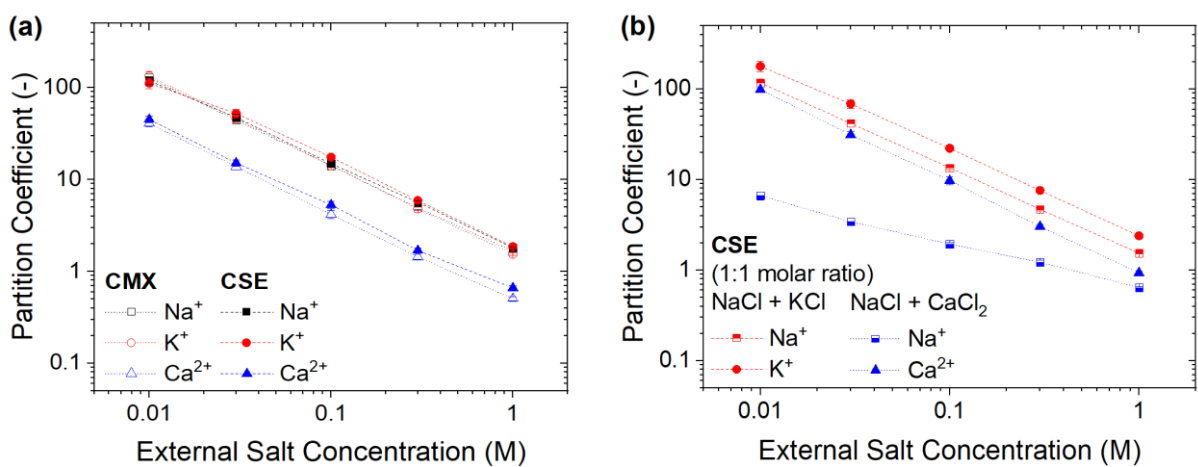


372
 373 Figure 5. Counter-ion concentration for (a) single salt experiments in cation exchange membranes
 374 CMX and CSE, where NaCl, KCl and CaCl_2 were used in external solutions, and for (b) binary salts
 375 experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + CaCl_2 were used in external
 376 solutions. Lines are drawn to guide the eye.

377
 378 The partition coefficient of the counter-ion for CMX and CSE, determined using Eq. (10) is presented
 379 in Figure 6 for the single salt and binary salts experiments. Ion partitioning between ion exchange
 380 membranes and the surrounding salt solutions is governed by the concentration of charged groups
 381 bound to the membrane matrix (Geise et al. 2012, Lonsdale et al. 1965, Paul 2004). Similar to
 382 counter-ion concentration in mol/L swollen membrane, the partition coefficients are slightly higher
 383 for CSE than CMX, but both showing a declining trend with increasing external salt concentration for
 384 all three cations. The partition of the counter-ion is higher for a monovalent salt in comparison with
 385 a divalent one, reflecting the changes in membrane concentration, due to the double charge on the

386 divalent ion and to Donnan exclusion, shown in Figure 5. The selectivity between the ion pairs,
 387 calculated by Eq. (11) is shown in Figure 7. As expected, the selectivity of Na^+ to K^+ is around 1, due
 388 to the similarities between these two ions. In a binary mixture, CSE selectively absorbed K^+ , as seen
 389 in Figure 5 (b), probably due to the smaller hydrated radius of potassium. A higher selectivity of Ca^{2+}
 390 in the membrane for a binary salt solution is in agreement with data reported by Sata (Sata 2004) for
 391 a typical ion exchange membrane with sulfonate groups.

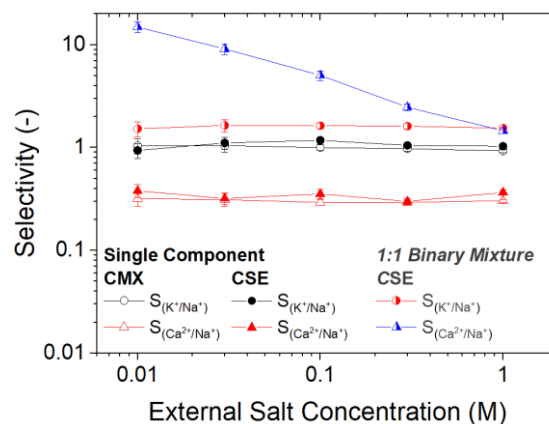
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394

395 Figure 6. Partition coefficient of counter-ions in cation exchange membranes for (a) single salt
 396 experiments in CMX and CSE where NaCl , KCl and CaCl_2 were used in external solutions and for (b)
 397 binary salts experiments in CSE where equimolar mixtures of $\text{NaCl} + \text{KCl}$ and $\text{NaCl} + \text{CaCl}_2$ were used
 398 in external solutions.



399

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

402 experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + CaCl₂ were used in external
403 solutions.

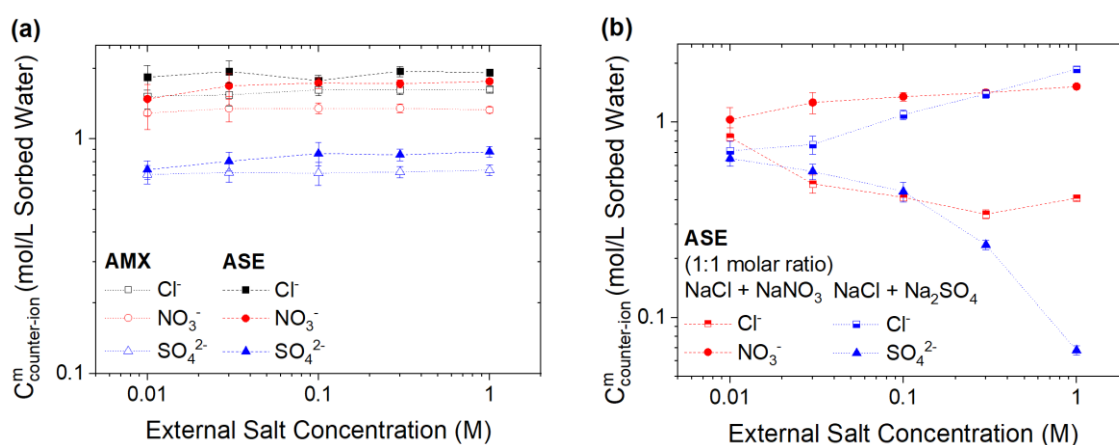
404

405 **3.3.2 Anion Exchange Membranes**

406 Similar experiments were conducted with different salts (NaCl, NaNO₃ and Na₂SO₄) to obtain the
407 concentration of various counter-ions within the Neosepta anion exchange membranes. The
408 concentration of nitrate in both the AMX and ASE (Figure 8 (a)) is lower than that of chloride,
409 expressed in mol/L swollen membrane. This trend is reversed when the amount of water uptake is
410 taken into consideration (Figure S1) so that this concentration is expressed in mol/L solution. The
411 water uptake is noticeably lower when the AEMs are equilibrated in NaNO₃ solutions in comparison
412 with NaCl solutions (Figure 1). It is also more apparent that NO₃⁻ is preferably absorbed when the
413 membrane was equilibrated in binary salt solutions of NaCl and NaNO₃ (Figure 8 (b)). Unlike Na⁺ and
414 K⁺ in the CMX and CSE membranes where the hydrated radii are noticeably different, those of NO₃⁻
415 and Cl⁻ are much closer (3.35 Å and 3.32 Å, respectively). Some researchers have reported that AMX
416 (Malewitz et al. 2007) and Nafion (Bontha and Pintauro 1994, Pintauro et al. 1995) membranes
417 selectively absorb the monovalent counter-ion with a larger hard sphere radius (Cl⁻: 1.81 Å, NO₃⁻,
418 2.64 Å) and hence lower surface charge density. This lower charge density may allow the NO₃⁻ to
419 bond more strongly with the hydrophobic polymeric backbone (Table 1) and may also explain the
420 lower water uptake. Similar behaviour has been previously observed where hydrophobic resins
421 demonstrated affinity towards perchlorate (Wang 2010, Xiong et al. 2007). Sata (Sata 2000, 2004)
422 also showed a higher transport number for NO₃⁻ over Cl⁻ at different concentrations (transport
423 number ratio >1). Luo et al. (Luo et al. 2018) also note that the permselectivity for NO₃⁻ over Cl⁻ is
424 consistent with the Hofmeister series (Hofmeister and Hofmeister 1888) and the Gibbs hydration
425 energy.

426

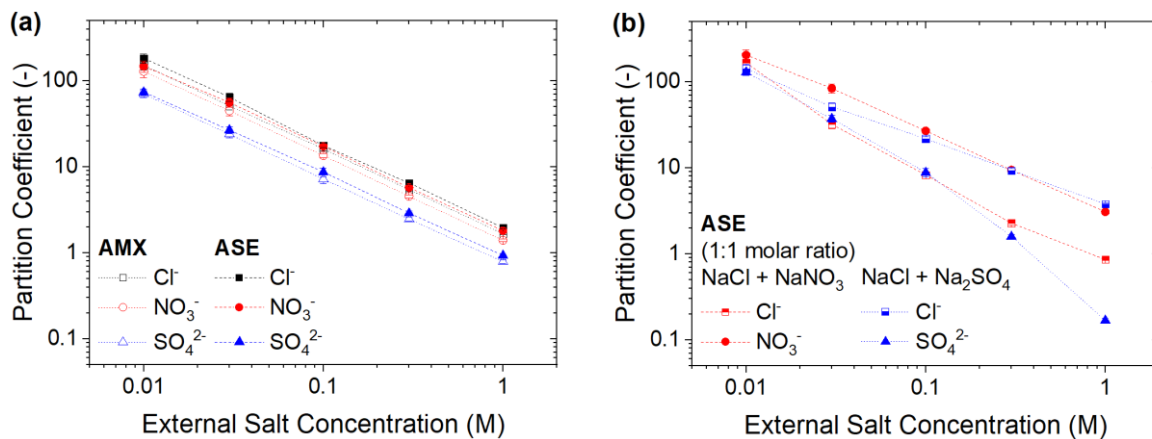
427 For an equimolar binary mixture of NaCl and Na₂SO₄, the concentration of SO₄²⁻ decreases with
 428 external solution concentration while that of Cl⁻ increases (Figure 8 Figure 8 (b)). These trends are
 429 different to what is observed for the monovalent and divalent counter-ion mixture in cation
 430 exchange membranes. The transport number of SO₄²⁻ relative to Cl⁻ ions for different types of anion
 431 exchange membranes was also reported to be less than one, in contrast to the relative ratio
 432 between NO₃⁻ and Cl⁻ (Sata 2000). The hydrophobic nature of styrene in AEMs could partly inhibit the
 433 absorption of sulphate ions which are strongly hydrated (Sata et al. 1998), as the Gibbs hydration
 434 energy of SO₄²⁻ is the highest among the three anions studied (Cl⁻: 370 kJ/mol, NO₃⁻: 270 kJ/mol, SO₄²⁻
 435 : 1000 kJ/mol). Another reason is likely to be the formation of [NaSO₄]⁻ (i.e., ion pairing) within the
 436 solution at higher concentrations. Ion pairing has been identified as the cause of very low activity
 437 coefficients for sulfate in aqueous solutions (Buchner et al. 1999, Marcus and Hefter 2006). As a
 438 monovalent ion, [NaSO₄]⁻ would compete less effectively with Cl⁻ within the anion exchange
 439 membrane. However, its full impact upon the activity and the ion partitioning in ion exchange
 440 membranes is still unknown and requires further study.
 441



442 Figure 8. Counter-ion concentration in anion exchange membranes for (a) single salt experiments in
 443 AMX and ASE where NaCl, NaNO₃ and Na₂SO₄ were used in external solutions and for (b) binary salts
 444 experiments in ASE where equimolar mixtures of NaCl + NaNO₃ and NaCl + Na₂SO₄ were used in
 445 external solutions.
 446
 447

448 The partition coefficient of these counter-ions determined using Eq. (10) are presented in Figure 9
 449 for the single salt and binary salts experiments. Similar to counter-ion concentration in mol/L
 450 swollen membrane, the partition coefficients are similar between AMX and ASE, but both showing a
 451 declining trend with increasing external salt concentration for all three anions. The partition of the
 452 monovalent anions is higher than that of divalent anions in the case of single salt experiments. This
 453 trend can again be justified both by the lower concentration in the membrane (Figure 8); and by the
 454 lower activity coefficient of the divalent ions in the bulk solution in comparison with that of
 455 monovalent ions. The selectivity between the anion pairs, determined by Eq. (11) is shown in Figure
 456 10. When considering single salt data, the selectivity of NO_3^- to Cl^- is close to 1. But in a binary
 457 mixture, ASE selectively absorbs NO_3^- , as seen in Figure 8 (b), with a ratio of partition coefficients of
 458 ~ 3.5 . This is in a similar range of values reported for anion exchange membranes with benzyl
 459 trimethylammonium groups (Sata et al. 1998). A very low selectivity of SO_4^{2-} in the membrane for a
 460 binary salt solution is observed, in agreement with the trends shown in Figure 8 (b) for counter-ion
 461 concentration.

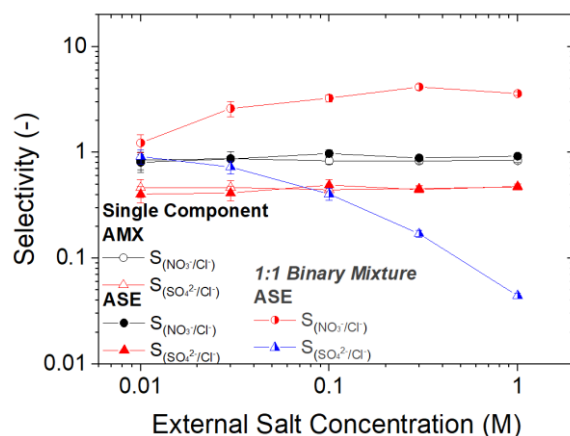
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463

464

465 Figure 9. Partition coefficient of counter-ions in anion exchange membranes for (a) single salt
 466 experiments in AMX and ASE where NaCl , NaNO_3 and Na_2SO_4 were used in external solutions and for
 467 (b) binary salts experiments in ASE where equimolar mixtures of $\text{NaCl} + \text{NaNO}_3$ and $\text{NaCl} + \text{Na}_2\text{SO}_4$
 468 were used in external solutions.



469

470 Figure 10. Selectivity of NO_3^- and SO_4^{2-} to Cl^- for single salt experiments in AMX and ASE where NaCl,
 471 $NaNO_3$ and Na_2SO_4 were used in external solutions; and for binary salts experiments in ASE where
 472 equimolar mixtures of $NaCl + NaNO_3$ and $NaCl + Na_2SO_4$ were used in external solutions.

473

474 4. CONCLUSIONS

475 We have reported the sorption equilibria of ions in commercial Neosepta ion exchange membranes,
 476 including CMX and CSE cation exchange membranes and AMX and ASE ion exchange membranes.

477 Calcium has little impact at the water uptake in the CEMs, while the presence of sulphate results in
 478 the highest water uptake among all anions. The Manning/Donnan model was employed to

479 investigate the structural characteristics of these membranes, as co-ion concentration is determined
 480 by the Donnan equilibrium between the membrane and the external solution. The change in

481 polymer composition from CMX to CSE leads to a change in the Manning's parameter. This is
 482 consistent with the differences in sorption properties between CMX and CSE. The ion sorption

483 characteristics, however, were found to be similar between AMX and ASE, which was also confirmed
 484 from the similar Manning's parameter obtained. Sorption of counter-ion in the binary mixtures of

485 these ions revealed very different trends of monovalent and divalent ion sorption between CSE and
 486 ASE. While calcium dominates the fixed charge groups in CSE, the concentration of sodium in the

487 membrane increases significantly with increasing external salt concentrations. However, the
 488 concentration of sulphate in the anion exchange membrane (ASE) declines with external salt

489 concentration, while the concentration of chloride in the binary system increases. This leads to very

490 low selectivities between sulphate and chloride. This unusual behavior could be due to the strong
491 hydration of the sulfate anion and its interaction with the hydrophobic styrene in the charged
492 polymer. It may also relate to the formation of the ion pair $[\text{NaSO}_4]^-$ as external concentrations
493 increase. Nitrate ions also show unusual behavior. In single salt solutions, they absorb as strongly as
494 chloride ions, but with less water accompanying the uptake. In binary mixtures, the nitrate is able to
495 exclude chloride. This behavior may be related to the low surface charge density of the nitrate ion
496 allowing it to interact more readily with the polymeric backbone. The characterisation of ion
497 sorption behavior in single and binary mixtures provides useful information for their future
498 applications for these commercial membranes.

499

500 **ACKNOWLEDGEMENTS**

501 This research was supported under Australian Research Council's Industrial Transformation Research
502 Program (ITRP) funding scheme (project number IH120100005). The ARC Dairy Innovation Hub is a
503 collaboration between The University of Melbourne, The University of Queensland and Dairy
504 Innovation Australia Ltd. George Chen acknowledges support from an Early Career Researcher (ECR)
505 Grant awarded by the Melbourne School of Engineering, The University of Melbourne. BDF's
506 contribution to preparation of this manuscript was supported as part of the Center for Materials for
507 Water and Energy Systems (M-WET), an Energy Frontier Research Center funded by the U.S.
508 Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0019272.

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647 **Figure Captions**

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649 Figure 1. Water uptake of (a) cation exchange membranes (CMX and CSE) and (b) anion exchange
650 membranes (AMX and ASE) after equilibration in different external salt solutions of concentrations
651 ranging from 0.01 M to 1 M. Equimolar binary mixtures of NaCl + KCl and NaCl + CaCl₂ were used for
652 CSE membranes (a), and those of NaCl + NaNO₃ and NaCl + Na₂SO₄ were used for ASE membranes
653 (b). The dashed lines are drawn to guide the eye.

654 Figure 2. Concentration of co-ion (expressed in mol/L sorbed water) in cation exchange membranes
655 (i.e., [Cl⁻] in CEM (a) and CSE (b)) and anion exchange membranes (i.e., [Na⁺] in AMX (c) and ASE (d))
656 as a function of external salt concentration. Data are shown for single salts experiments, and are
657 fitted to Eq. (6) for MX salts in IEMs, and Eq. (S1) for CaCl₂ in CEMs and Na₂SO₄ in AEMs. The fitting
658 was performed using all three sets of data for each membrane, treating ξ as the only fitting
659 parameter ($\xi_{\text{CMX}} = 1.0 \pm 0.1$, $\xi_{\text{CSE}} = 2.8 \pm 0.5$, $\xi_{\text{AMX}} = 4.8 \pm 1.4$, and $\xi_{\text{ASE}} = 5.4 \pm 1.5$).

660 Figure 3. The activity coefficient ratio for (a) cation exchange membranes and (b) anion exchange
661 membranes as a function of external salt concentration, modelled using Eq. (3) for monovalent salts
662 and Eq. (S4) for CaCl₂ in CEMs and Na₂SO₄ in AEMs.

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

667 Figure 5. Counter-ion concentration for (a) single salt experiments in cation exchange membranes
668 CMX and CSE, where NaCl, KCl and CaCl₂ were used in external solutions, and for (b) binary salts
669 experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + CaCl₂ were used in external
670 solutions. Lines are drawn to guide the eye.

671 Figure 6. Partition coefficient of counter-ions in cation exchange membranes for (a) single salt
672 experiments in CMX and CSE where NaCl, KCl and CaCl₂ were used in external solutions and for (b)
673 binary salts experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + CaCl₂ were used
674 in external solutions.

675 Figure 7. Selectivity of K⁺ and Ca²⁺ to Na⁺ in cation exchange membranes for single salt experiments
676 in CMX and CSE where NaCl, KCl and CaCl₂ were used in external solutions; and for binary salts
677 experiments in CSE where equimolar mixtures of NaCl + KCl and NaCl + CaCl₂ were used in external
678 solutions.

679 Figure 8. Counter-ion concentration in anion exchange membranes for (a) single salt experiments in
680 AMX and ASE where NaCl, NaNO₃ and Na₂SO₄ were used in external solutions and for (b) binary salts
681 experiments in ASE where equimolar mixtures of NaCl + NaNO₃ and NaCl + Na₂SO₄ were used in
682 external solutions.

683 Figure 9. Partition coefficient of counter-ions in anion exchange membranes for (a) single salt
684 experiments in AMX and ASE where NaCl, NaNO₃ and Na₂SO₄ were used in external solutions and for
685 (b) binary salts experiments in ASE where equimolar mixtures of NaCl + NaNO₃ and NaCl + Na₂SO₄
686 were used in external solutions.

687 Figure 10. Selectivity of NO_3^- and SO_4^{2-} to Cl^- for single salt experiments in AMX and ASE where NaCl,
688 NaNO_3 and Na_2SO_4 were used in external solutions; and for binary salts experiments in ASE where
689 equimolar mixtures of $\text{NaCl} + \text{NaNO}_3$ and $\text{NaCl} + \text{Na}_2\text{SO}_4$ were used in external solutions.

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Supporting Information

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

George Q. Chen¹, Kajia Wei², Armineh Hassanvand¹, Benny Freeman³, Sandra E. Kentish^{1*}

¹ Department of Chemical Engineering, The University of Melbourne, Victoria 3010, Australia.

² State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, P. R. China

³ McKetta Department of Chemical Engineering, The University of Texas at Austin, 200 E, Dean Keeton St., Stop C0400, Austin, Texas 78712-1589, United States

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

*Corresponding Author

Prof Sandra Kentish

Tel: +61 3 8344 6682

Fax: +61 3 8344 4153

E-mail address: sandraek@unimelb.edu.au

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

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

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

6 Equation S1 is applicable when a cation exchange membrane is in equilibrium with an M-X₂ type salt
 7 solution (e.g., CaCl₂) and when an anion exchange membrane is in equilibrium with an M₂-X type salt
 8 solution (e.g., Na₂SO₄), where

$$9 \gamma_+^m (\gamma_-^m)^2 = \left(\frac{\frac{C_{\text{fix}}^m}{2\xi C_s^m} + 2}{\frac{C_{\text{fix}}^m}{C_s^m} + 2} \right) \exp \left(-\frac{\frac{3C_{\text{fix}}^m}{4C_s^m}}{\frac{C_{\text{fix}}^m}{C_s^m} + 6\xi} \right) \quad (\text{S2})$$

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

$$11 C_s^m = \frac{1}{2} C_-^m \quad (\text{S3})$$

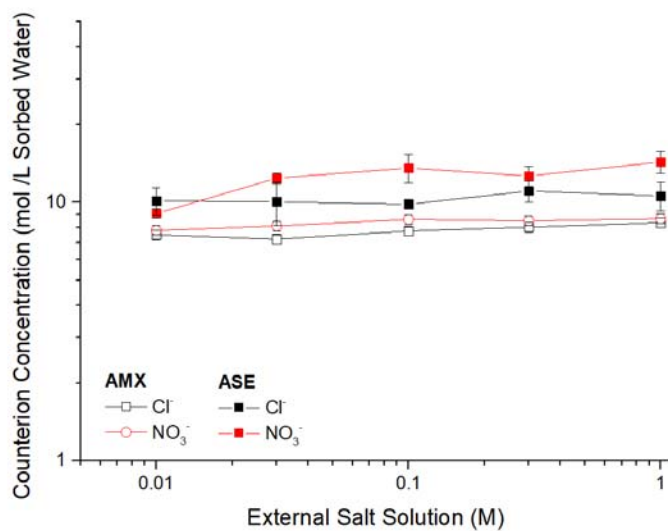
12 Note that for monovalent salts, $C_s^m = C_-^m$.

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

$$16 \Gamma = \frac{4(\gamma_{\pm}^s)^3}{\gamma_+^m (\gamma_-^m)^2} \quad (\text{S4})$$

$$17 = \frac{4(\gamma_{\pm}^s)^3}{\left(\frac{\frac{C_{\text{fix}}^m}{2\xi C_s^m} + 2}{\frac{C_{\text{fix}}^m}{C_s^m} + 2} \right) \exp \left(-\frac{\frac{3C_{\text{fix}}^m}{4C_s^m}}{\frac{C_{\text{fix}}^m}{C_s^m} + 6\xi} \right)} \quad (\text{S5})$$

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

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