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Partitioning of Mobile Ions Between Ion Exchange Polymers and Aqueous Salt Solutions: Importance of Counter-ion Condensation

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Supplementary Information

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S1. Expressions for membrane mobile salt concentrations

In this section, expressions for membrane mobile salt concentrations in negatively and positively charged membranes equilibrated with monovalent and divalent aqueous salt solutions are given. In the following expressions, C_+^m and C_-^m are the concentrations of cations and anions, respectively, in the membrane, C_A^m is the concentration of fixed charge groups, C_s^m is the mobile salt concentration in the membrane, C_+^s and C_-^s are the concentrations of cations and anions, respectively, in the external solution, C_s^s is the external salt concentration, γ_+^m and γ_-^m are the activity coefficients of cations and anions, respectively, in the membrane, $\gamma_\pm^s$ is the external salt solution mean activity coefficient, and ξ is the membrane fixed charge density from the Manning model.

For an MX-type salt and a negatively or positively charged membrane, the membrane mobile salt concentration is equal to the membrane co-ion concentration. For an MX_2-type salt, the membrane mobile salt concentration is one half the membrane co-ion concentration for a negatively charged membrane (i.e., CEM), and it is equal to the membrane co-ion concentration for a positively charged membrane (i.e., AEM). For an M_2X type salt, the membrane mobile salt concentration is one half the membrane co-ion concentration for a positively charged membrane (i.e., AEM), and it is equal to the membrane co-ion concentration for a negatively charged membrane (i.e., CEM).

For a negatively charged (i.e., cation exchange) membrane equilibrated with an MX-type electrolyte:

$$C_{+}^{s} = C_{-}^{s} = C_{s}^{s} \tag{1}$$

$$C_{-}^{m} = C_{s}^{m} \tag{2}$$

The thermodynamic condition for equilibrium is:

$$\left(C_{+}^{m} C_{-}^{m}\right)\left(\gamma_{+}^{m} \gamma_{-}^{m}\right) = \left(\gamma_{\pm}^{s}\right)^{2}\left(C_{s}^{s}\right)^{2} \tag{3}$$

A charge balance in the membrane gives:

$$C_{+}^{m} = C_{A}^{m} + C_{s}^{m} \tag{4}$$

The Manning expressions for membrane ion activity coefficients are:

$$\gamma_{+}^{m} = \left(\frac{\frac{C_{A}^{m}}{\xi C_{s}^{m}} + 1}{\frac{C_{A}^{m}}{C_{s}^{m}} + 1} \right) \exp\left[-\frac{\frac{1}{2}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}} + 2\xi} \right] \tag{5}$$

$$\gamma_{-}^{m} = \exp\left[-\frac{\frac{1}{2}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}} + 2\xi} \right] \tag{6}$$

The final expression for membrane mobile salt concentration, C_{s}^{m}, is obtained by combining Eqns. 1-6:

$$\left(C_A^m + C_s^m\right)\left(C_s^m\right)\left(\frac{\frac{C_A^m}{\xi C_s^m}+1}{\frac{C_A^m}{C_s^m}+1}\right)\exp\left[-\frac{\frac{C_A^m}{C_s^m}}{\frac{C_A^m}{C_s^m}+2\xi}\right]=\left(\gamma_\pm^s\right)^2\left(C_s^s\right)^2 \tag{7}$$

Once C_s^m is computed using Eqn. 7, the membrane counter-ion concentration, C_+^m, is calculated from Eqn. 4.

For a positively charged (i.e., anion exchange) membrane equilibrated with an MX-type electrolyte:

$$C_+^s = C_-^s = C_s^s \tag{8}$$

$$C_+^m = C_s^m \tag{9}$$

The thermodynamic condition for equilibrium is:

$$\left(C_+^m C_-^m\right)\left(\gamma_+^m \gamma_-^m\right)=\left(\gamma_\pm^s\right)^2\left(C_s^s\right)^2 \tag{10}$$

A charge balance in the membrane gives:

$$C_-^m = C_A^m + C_s^m \tag{11}$$

The Manning expressions for membrane ion activity coefficients are:

$$\gamma_-^m = \left(\frac{\frac{C_A^m}{\xi C_s^m}+1}{\frac{C_A^m}{C_s^m}+1}\right)\exp\left[-\frac{\frac{1}{2}\frac{C_A^m}{C_s^m}}{\frac{C_A^m}{C_s^m}+2\xi}\right] \tag{12}$$

$$\gamma_{+}^{m} = \exp\left[-\frac{\frac{1}{2}\frac{C_A^m}{C_s^m}}{\frac{C_A^m}{C_s^m} + 2\xi} \right] \tag{13}$$

The final expression for membrane mobile salt concentration, C_s^m, is obtained by combining Eqns. 8-13:

$$\left(C_A^m + C_s^m\right)\left(C_s^m\right)\left(\frac{\frac{C_A^m}{\xi C_s^m} + 1}{\frac{C_A^m}{C_s^m} + 1} \right) \exp\left[-\frac{\frac{C_A^m}{C_s^m}}{\frac{C_A^m}{C_s^m} + 2\xi} \right] = \left(\gamma_{\pm}^{s}\right)^2 \left(C_s^s\right)^2 \tag{14}$$

Once C_s^m is computed using Eqn. 14, the membrane counter-ion concentration, C_-^m, is calculated from Eqn. 11.

For a negatively charged membrane equilibrated with an MX_2-type electrolyte:

$$C_+^s = \frac{1}{2} C_-^s = C_s^s \tag{15}$$

$$C_-^m = 2C_s^m \tag{16}$$

The thermodynamic condition for equilibrium is:

$$\left(\gamma_+^m C_+^m\right)\left(\gamma_-^m C_-^m\right)^2 = \left(\gamma_+^s C_+^s\right)\left(\gamma_-^s C_-^s\right)^2 \tag{17}$$

A charge balance in the membrane gives:

$$C_+^m = \frac{1}{2} C_A^m + C_s^m \tag{18}$$

The Manning expressions for membrane ion activity coefficients are:

$$\gamma_{+}^{m}=\left(\frac{\frac{C_{A}^{m}}{2\xi C_{s}^{m}}+2}{\frac{C_{A}^{m}}{C_{s}^{m}}+2}\right)\exp\left[-\frac{\frac{1}{2}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}}+6\xi}\right] \tag{19}$$

$$\gamma_{-}^{m}=\exp\left[-\frac{\frac{1}{8}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}}+6\xi}\right] \tag{20}$$

The final expression for membrane mobile salt concentration, C_{s}^{m}, is obtained by combining Eqns. 15-20:

$$\left(\frac{1}{2}C_{A}^{m}+C_{s}^{m}\right)\left(C_{s}^{m}\right)^{2}\left(\frac{\frac{C_{A}^{m}}{2\xi C_{s}^{m}}+2}{\frac{C_{A}^{m}}{C_{s}^{m}}+2}\right)\exp\left[-\frac{\frac{3}{4}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}}+6\xi}\right]=\left(\gamma_{\pm}^{s}\right)^{3}\left(C_{s}^{s}\right)^{3} \tag{21}$$

Once C_{s}^{m} is computed using Eqn. 21, the membrane counter-ion concentration, C_{+}^{m}, is calculated from Eqn. 18.

For a positively charged membrane equilibrated with an MX_2-type electrolyte:

$$C_{+}^{s}=\frac{1}{2}C_{-}^{s}=C_{s}^{s} \tag{22}$$

$$C_{+}^{m}=C_{s}^{m} \tag{23}$$

The thermodynamic condition for equilibrium is:

$$\left(\gamma_{+}^{m}C_{+}^{m}\right)\left(\gamma_{-}^{m}C_{-}^{m}\right)^{2}=\left(\gamma_{+}^{s}C_{+}^{s}\right)\left(\gamma_{-}^{s}C_{-}^{s}\right)^{2} \tag{24}$$

A charge balance in the membrane gives:

$$C_{-}^{m} = C_{A}^{m} + 2C_{s}^{m} \tag{25}$$

The Manning expressions for membrane ion activity coefficients are:

$$\gamma_{-}^{m} = \left(\frac{\frac{C_{A}^{m}}{\xi C_{s}^{m}} + 2}{\frac{C_{A}^{m}}{C_{s}^{m}} + 2} \right) \exp\left[-\frac{\frac{1}{2}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}} + 6\xi} \right] \tag{26}$$

$$\gamma_{+}^{m} = \exp\left[-\frac{2\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}} + 6\xi} \right] \tag{27}$$

The final expression for membrane mobile salt concentration, C_{s}^{m}, is obtained by combining Eqns. 22-27:

$$\left(C_{A}^{m} + 2C_{s}^{m}\right)^{2}\left(C_{s}^{m}\right)\left(\frac{\frac{C_{A}^{m}}{\xi C_{s}^{m}} + 2}{\frac{C_{A}^{m}}{C_{s}^{m}} + 2} \right)^{2} \exp\left[-\frac{3\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}} + 6\xi} \right] = 4\left(\gamma_{\pm}^{s}\right)^{3}\left(C_{s}^{s}\right)^{3} \tag{28}$$

Once C_{s}^{m} is computed using Eqn. 28, the membrane counter-ion concentration, C_{-}^{m}, is calculated from Eqn. 25.

For a negatively charged membrane equilibrated with an M_2X-type electrolyte:

$$\frac{1}{2}C_{+}^{s} = C_{-}^{s} = C_{s}^{s} \tag{29}$$

$$C_{-}^{m} = C_{s}^{m} \tag{30}$$

The thermodynamic condition for equilibrium is:

$$\left(\gamma_+^m C_+^m\right)^2\left(\gamma_-^m C_-^m\right)=\left(\gamma_+^s C_+^s\right)^2\left(\gamma_-^s C_-^s\right) \tag{31}$$

A charge balance in the membrane gives:

$$C_+^m = C_A^m + 2C_s^m \tag{32}$$

The Manning expressions for membrane ion activity coefficients are:

$$\gamma_+^m = \left(\frac{\frac{C_A^m}{\xi C_s^m}+2}{\frac{C_A^m}{C_s^m}+2}\right)\exp\left[-\frac{\frac{1}{2}\frac{C_A^m}{C_s^m}}{\frac{C_A^m}{C_s^m}+6\xi}\right] \tag{33}$$

$$\gamma_-^m = \exp\left[-\frac{2\frac{C_A^m}{C_s^m}}{\frac{C_A^m}{C_s^m}+6\xi}\right] \tag{34}$$

The final expression for membrane mobile salt concentration, C_s^m, is obtained by combining Eqns. 29-34:

$$\left(C_A^m+2C_s^m\right)^2\left(C_s^m\right)\left(\frac{\frac{C_A^m}{\xi C_s^m}+2}{\frac{C_A^m}{C_s^m}+2}\right)^2\exp\left[-\frac{3\frac{C_A^m}{C_s^m}}{\frac{C_A^m}{C_s^m}+6\xi}\right]=4\left(\gamma_\pm^s\right)^3\left(C_s^s\right)^3 \tag{35}$$

Once C_s^m is computed using Eqn. 35, the membrane counter-ion concentration, C_+^m, is calculated from Eqn. 32.

For a positively charged membrane equilibrated with an M_2X-type electrolyte:

$$\frac{1}{2}C_+^s = C_-^s = C_s^s \tag{36}$$

$$C_{+}^{m} = 2C_{s}^{m} \tag{37}$$

The thermodynamic condition for equilibrium is:

$$\left(\gamma_{+}^{m}C_{+}^{m}\right)^{2}\left(\gamma_{-}^{m}C_{-}^{m}\right) = \left(\gamma_{+}^{s}C_{+}^{s}\right)^{2}\left(\gamma_{-}^{s}C_{-}^{s}\right) \tag{38}$$

A charge balance in the membrane gives:

$$C_{-}^{m} = \frac{1}{2}C_{A}^{m} + C_{s}^{m} \tag{39}$$

The Manning expressions for membrane ion activity coefficients are:

$$\gamma_{-}^{m} = \left(\frac{\frac{C_{A}^{m}}{2\xi C_{s}^{m}} + 2}{\frac{C_{A}^{m}}{C_{s}^{m}} + 2}\right)\exp\left[-\frac{\frac{1}{2}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}} + 6\xi}\right] \tag{40}$$

$$\gamma_{+}^{m} = \exp\left[-\frac{\frac{1}{8}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}} + 6\xi}\right] \tag{41}$$

The final expression for membrane mobile salt concentration, C_{s}^{m}, is obtained by combining Eqns. 29-34:

$$\left(\frac{1}{2}C_{A}^{m} + C_{s}^{m}\right)\left(C_{s}^{m}\right)^{2}\left(\frac{\frac{C_{A}^{m}}{2\xi C_{s}^{m}} + 2}{\frac{C_{A}^{m}}{C_{s}^{m}} + 2}\right)\exp\left[-\frac{\frac{3}{4}\frac{C_{A}^{m}}{C_{s}^{m}}}{\frac{C_{A}^{m}}{C_{s}^{m}} + 6\xi}\right] = \left(\gamma_{\pm}^{s}\right)^{3}\left(C_{s}^{s}\right)^{3} \tag{42}$$

Once C_{s}^{m} is computed using Eqn. 42, the membrane counter-ion concentration, C_{-}^{m}, is calculated from Eqn. 39.

S2. Membrane chemical structures and properties

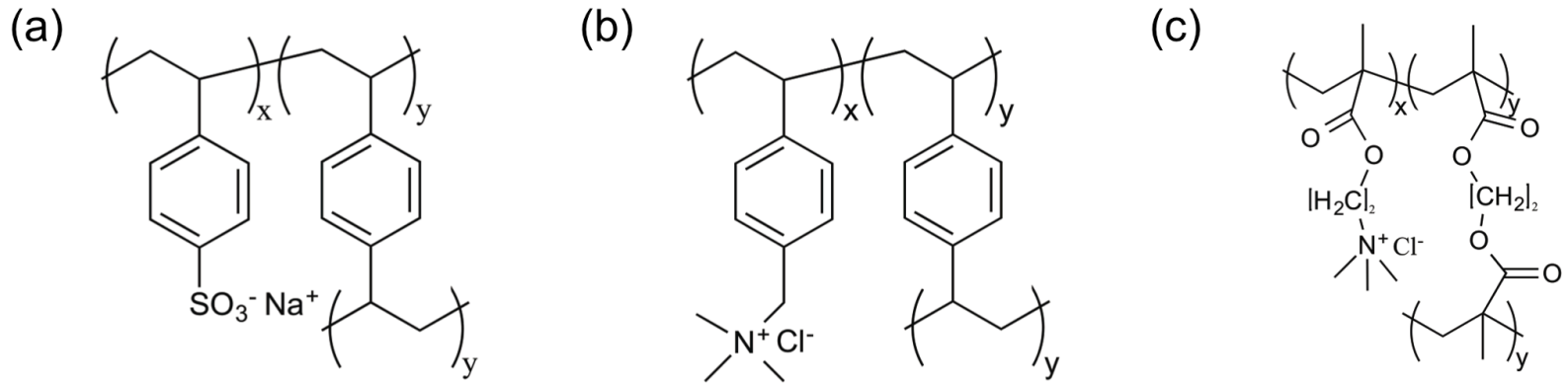

Figure S1. Chemical structures of the membranes considered in this study: (a) CR61, (b) AR103, and (c) AR204.

Table S1. Properties of the membranes considered in this study.

Membrane	Type [Functional Group]	Thickness [cm]	Reported IEC [meq/g (dry polymer)][a]	C_A^m [mol fixed charge groups/L (water sorbed)][b, 1]	Measured water uptake, w_u, [g (water)/g (dry polymer)][a, 1]
CR61-CMP	Styrenic [$-SO_3^- Na^+$]	0.06	2.2 (minimum)	3.21 ± 0.08	0.84 ± 0.01
AR103-QDP	Styrenic [$-N(CH_3)_3^+ Cl^-$]	0.06	2.2 (minimum)	3.58 ± 0.07	0.65 ± 0.01
AR204-SZRA	Acrylic [$-N(CH_3)_3^+ Cl^-$]	0.06	2.4 (minimum)	2.82 ± 0.04	0.96 ± 0.01

[a]The reported IEC and measured water uptake values are for the ion-containing polymer (i.e., contributions of backing are excluded). Reported IEC values were obtained from specification sheets provided directly by the manufacturer (GE Power and Water).

[b]Estimated as the counter-ion concentration in the ion exchange membrane at an external NaCl concentration of 0.01 M.

S3. Co-ion concentrations in anion-exchange membranes

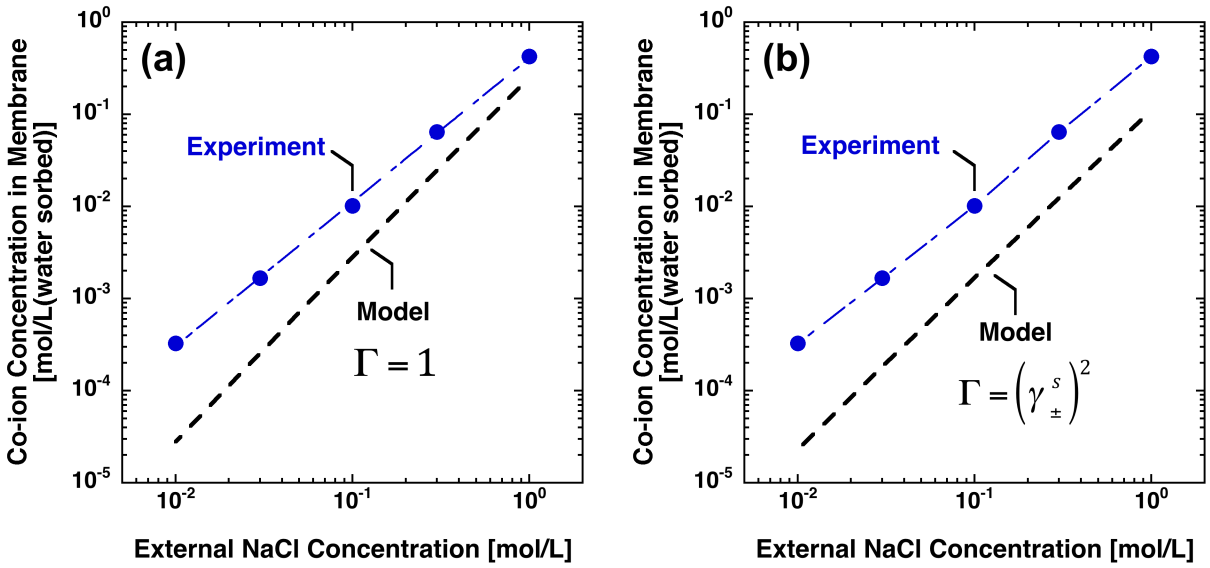

Figure S2. Membrane co-ion concentration as a function of external NaCl concentration for anion exchange membrane AR103. The filled circles represent experimental values, and the dashed line represents values predicted by Eqn. 5 in the main text. (a) Ion activity coefficients in membrane and solution phase were set to unity (i.e., ideal behavior), or ratio of ion activity coefficients set to unity. (b) Solution activity coefficients were calculated using the Pitzer model, membrane activity coefficients set to unity.

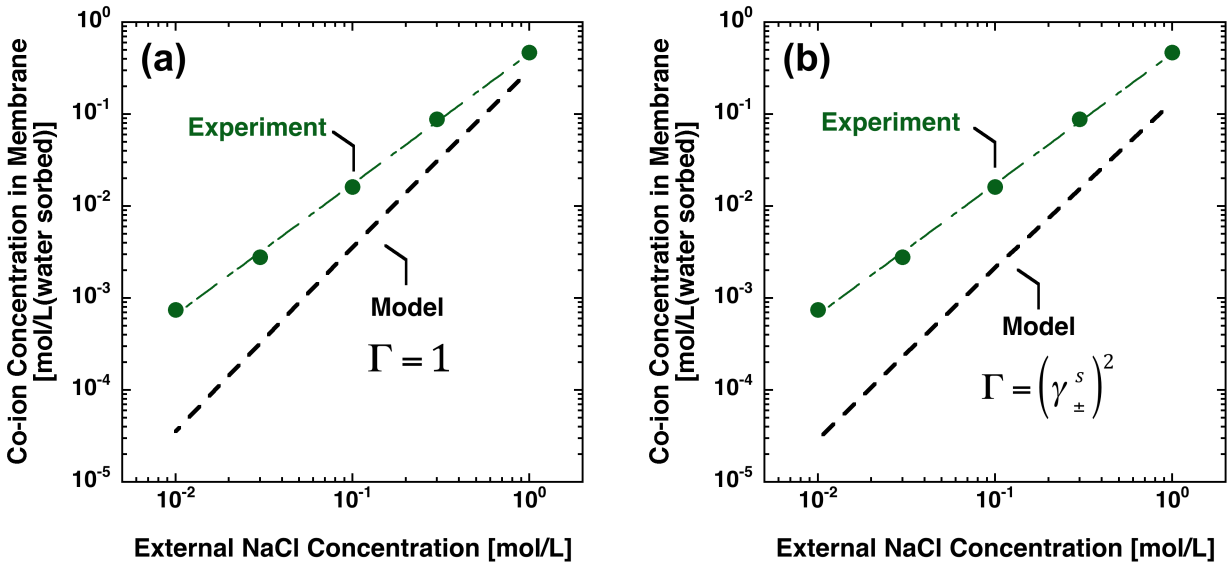

Figure S3. Membrane co-ion concentration as a function of external NaCl concentration for anion exchange membrane AR204. The filled circles represent experimental values, and the dashed line represents values predicted by Eqn. 5 in the main text. (a) Ion activity coefficients in membrane and solution phase were set to unity (i.e., ideal behavior), or ratio of ion activity coefficients set to unity. (b) Solution activity coefficients were calculated using the Pitzer model, membrane activity coefficients set to unity.

S4. $MgCl_2$ and $CaCl_2$ sorption in CR61 and AR103.

CEM counter-ion form conversion. The cation exchange membranes were supplied in the Na^+ counter-ion form and the anion exchange membranes were supplied in the Cl^- counter-ion form. Before measuring membrane ion concentrations of salts containing cations other than sodium, the cation exchange membranes were converted to the Mg^{2+} or Ca^{2+} counter-ion forms. Water equilibrated membrane samples, in the form of circular disks, were soaked in a 0.01 M $CaCl_2$ or $MgCl_2$ solution for 2 hours.

The salt solution was replaced several times to ensure adequate driving force for ion exchange. Single membrane samples were removed from the salt solution at regular time intervals, and dried under vacuum for at least 24 h. Each dry membrane was placed in a porcelain crucible for ashing.[2] Crucibles were placed in a furnace (Fisher Scientific Isotemp, Dubuque, IA) and the temperature was increased to 700°C, with a heating rate of 10°C /min. Ashed membranes were dissolved in 15 mL of 2% vol. nitric acid solution, and the resulting solutions were analyzed for Na^+ using Flame Atomic Absorption Spectrophotometry (Varian AA240, Victoria, Australia). The concentration of sodium was negligible after few hours of soaking in the salt solution, indicating complete conversion to the divalent cation form.

Following the conversion step, membranes were soaked in DI water to desorb mobile salt. The desorption of mobile salt was complete after 48 h of soaking in DI water.[3] The converted membranes were then used for subsequent ion sorption analysis. The anion exchange membranes were used as is since the counter-ion was the same for all electrolytes considered.

Co-ion sorption. Membrane co-ion concentrations were measured using a desorption technique.[1, 2] Pre-swollen circular membranes in the appropriate counter-ion form were placed in aqueous salt solutions with concentrations ranging from 0.01 M to 1 M. The salt solution was replaced several times for a period of at least 48 hours to guarantee adequate driving force for ion sorption.

After 48 hours, the membranes were removed from the salt solutions and blotted with Kimwipes to remove excess solution from their surface. Following this step, the membranes were placed in a known volume of DI water for at least 24 hours. During this time, mobile salt desorbed from the membrane into the solution. Ion Chromatography (Dionex Corp. ICS-2100, Sunnyvale, CA) was used to analyze the desorption solution for chloride ions when CEMs were studied and Flame Atomic Absorption (flame AA) Spectrophotometry (Varian AA240, Victoria, Australia) was used to analyze the desorption solution for Mg^{2+} ions when AEMs were studied. Details regarding the experimental procedure are provided elsewhere.[1, 2]

The mobile salt concentration in the swollen composite polymer was calculated from:

$$C_i^{m,c} = \frac{C_d V_d}{V_m} \tag{43}$$

where C_d is the ion concentration in the desorption solution, measured via ion chromatography or flame AA, V_d is the volume of de-ionized water used for mobile salt desorption, and V_m is the volume of swollen composite membrane. For sorption of monovalent salts in CEMs with monovalent fixed ions, the mobile salt concentration is equal to the co-ion concentration. In the case of $CaCl_2$ and $MgCl_2$ sorption in CEMs, the mobile salt concentration is one half that of the co-ion concentration. For sorption of $MgCl_2$ in AEMs, the mobile salt concentration is equal to the co-ion concentration.

To express sorption data as mols of ions sorbed per volume of swollen ion exchange polymer alone, the volume of the backing was subtracted from the total volume of the swollen composite membrane. Details regarding the procedure to adjust sorption data for the effects of the fabric support are reported elsewhere.[3]

Counter-ion Sorption. The procedure used to measure membrane co-ion concentrations cannot be used to measure counter-ion concentrations. A majority of the counter-ions in the membrane are present to balance the fixed charge groups, so they will not desorb in water without being replaced by another counter-ion.[4] Therefore, a different procedure was used to measure membrane counter-ion concentration. Water swollen membranes were equilibrated in salt solutions, as described for anion sorption.

For CEMs, the samples were removed from the salt solutions after reaching equilibrium, blotted with Kimwipes to remove the excess solution from their surface, and dried under vacuum at room temperature. Each dry membrane was placed in a clean porcelain crucible for ashing.[2] The ashing procedure was the same as that used for the conversion tests described above. Ashed membranes were dissolved in 15 mL of 2 vol. % nitric acid solution. The resulting solutions were analyzed for each counter-ion using Flame Atomic Absorption Spectrophotometry (Varian AA240, Victoria, Australia).

For AEMs, the samples were removed from the salt solutions after reaching equilibrium, blotted with Kimwipes to remove the excess solution from their surface, and placed in a 0.03 M solution of NaI (≥99.5 % purity, Sigma-Aldrich, St. Louis, MO). The counter-ions in the external salt solution (i.e., I^-) ion exchanged with the counter-ions in the AEM (Cl^-) since strong base AEMs, such as those used in this study, typically have higher selectivity for I^- ions than for Cl^-

ions. The desorption solution was then analyzed for Cl^- ions using ion chromatography. Full details regarding this procedure are given elsewhere.[1]

Membrane ion concentrations were calculated using Eqn. 43. Finally, counter-ion concentrations, expressed as mols of ions per L of swollen membrane, were adjusted for the effects of the backing using the same procedure described above for co-ion sorption.

The model developed in the main body of this manuscript requires membrane ion concentrations expressed as mols of cations per L of sorbed water. The following relation was used to compute membrane ion concentrations on a basis of sorbed water volume, $C_i^{m,w}$,:

$$C_i^{m,w} = \frac{C_i^{m,p}}{\phi_w} \tag{44}$$

where $C_i^{m,p}$ is the membrane ion concentration expressed on a volume basis of swollen membrane and ϕ_w is the volume fraction of water in the membrane. The water volume fraction was determined according to previously reported techniques.[1]

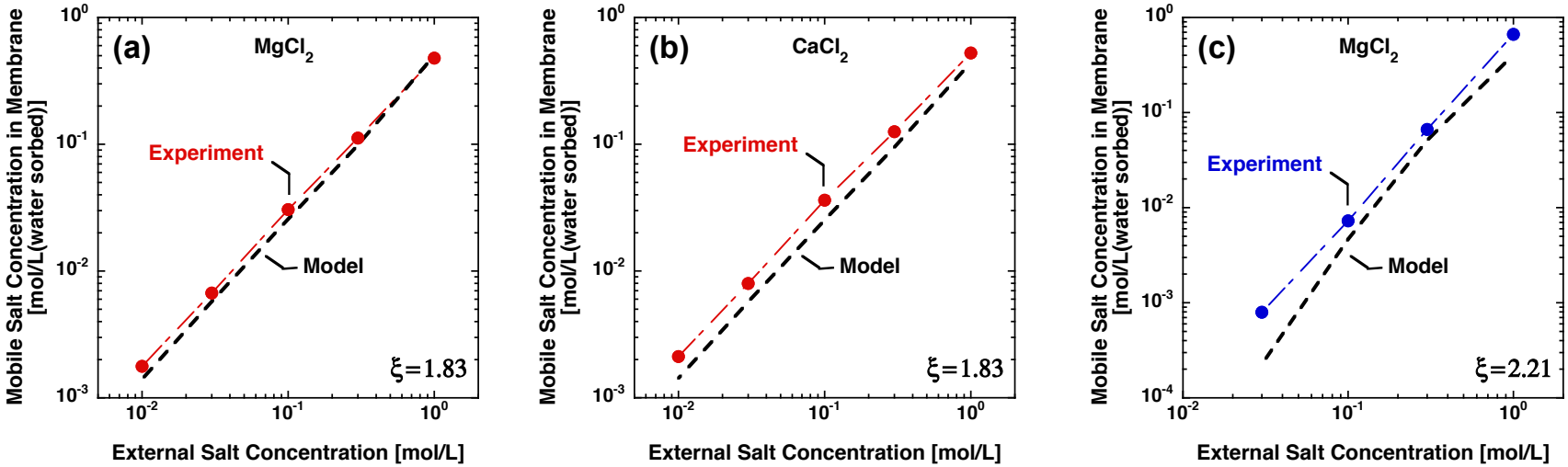

Figure S4. Membrane mobile salt concentration as a function of external salt concentration. The filled circles represent experimental values, and the dashed line represents values predicted by the Manning/Donnan model. (a) $MgCl_2$ sorption in cation exchange membrane CR61 (b) $CaCl_2$ sorption in cation exchange membrane CR61. (c) $MgCl_2$ sorption in anion exchange membrane AR103. The ξ values were the same as those for NaCl sorption, which were predicted a priori according to procedures given in the main text.

S5. Literature ion sorption equilibrium studies

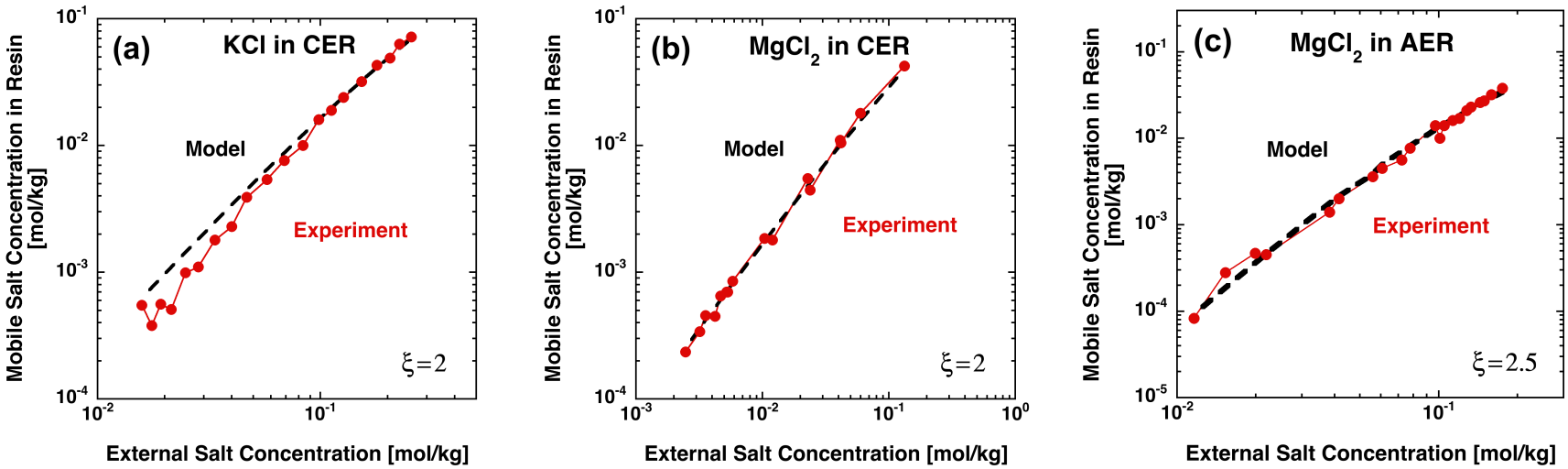

Figure S6. Mobile salt concentration in ion exchange resins as a function of external salt concentration. The Filled circles represent experimental values, and the dashed line represents model values. (a) KCl sorption in AG50wx2 cation exchange resin. (b) $MgCl_2$ sorption in AG50wx2 cation exchange resin. (c) $MgCl_2$ sorption in AG1x2 anion exchange resin (CER). The experimental data point at ~0.1 M KCl was used to calculate a value of 2 for ξ in the cation exchange resin and the experimental data point at ~0.08 M $MgCl_2$ was used to calculate a value of 2.5 for ξ in the anion exchange resin. The experimental data points used to estimate ξ were chosen randomly. This study was performed by Freeman *et al.*[5]

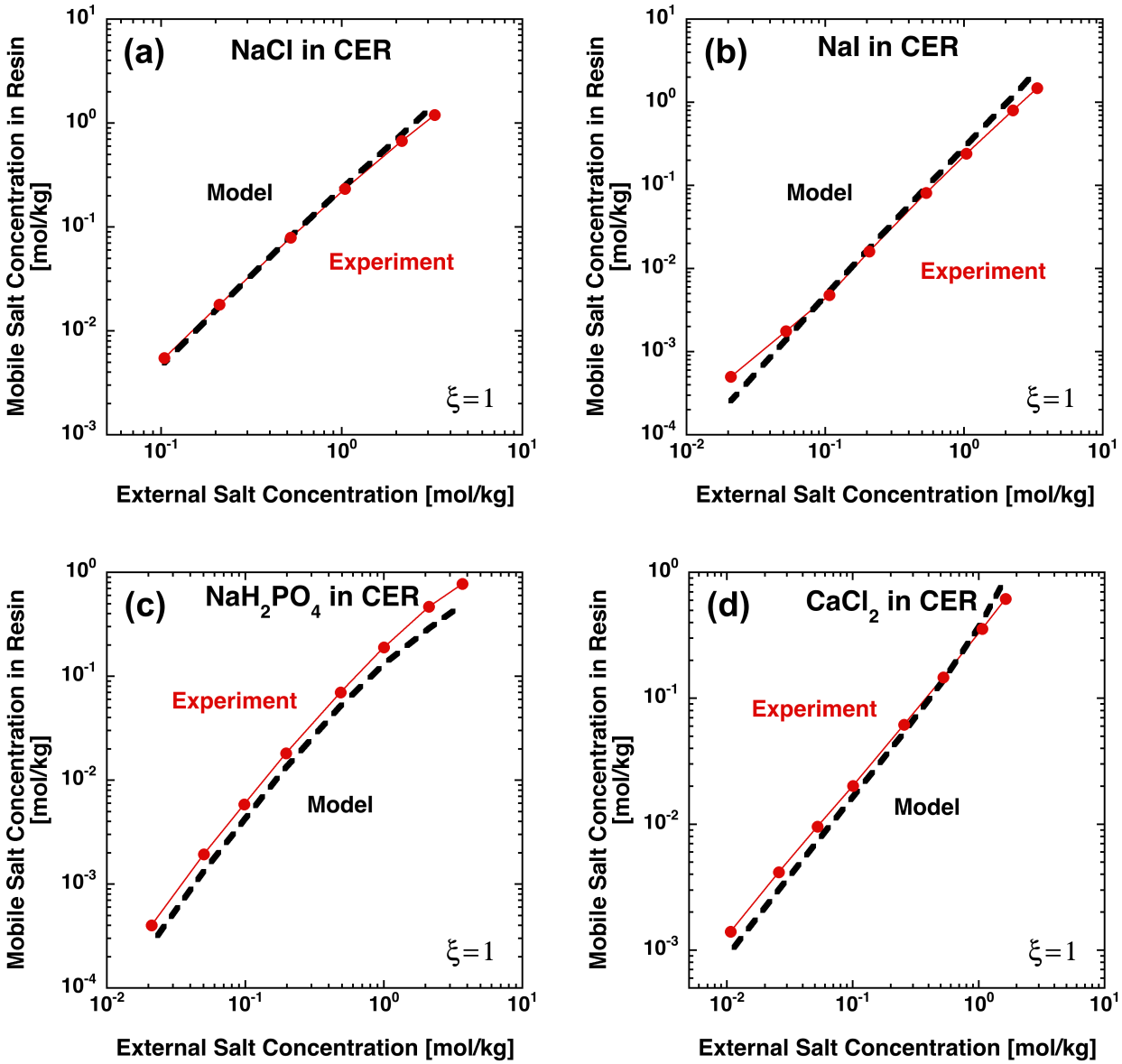

Figure S7. Mobile salt concentration in Amberlite XE-100 cation exchange resins as a function of external salt concentration for (a) NaCl, (b) NaI, (c) NaH_2PO_4, and (d) $CaCl_2$. The filled circles represent experimental values, and the dashed line represents model values. The experimental data point at ~0.5 M NaCl was used to calculate a value of 1 for ξ in the cation exchange resin. The same value was used to predict the sorption of the other electrolyte in the cation exchange resin. This study was performed by Gustafson.[6]

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