A Limiting Case of Constant Counterion Electrochemical Potentials in the Membrane for Examining Concentration Polarization at Ion-exchange Membranes and Patches

Andriy Yaroshchuk,[a,b]* Mykola Bondarenko,[c] Chao Tang,[d], and Merlin L. Bruening[d,e]*

[a]ICREA, pg.L.Companys 23, 08010 Barcelona, Spain

[b]Department of Chemical Engineering, Polytechnic University of Catalonia, av. Diagonal 647,08028 Barcelona, Spain

[c]Institute of Bio-Colloid Chemistry, National Academy of Sciences of Ukraine, Vernadskiy ave.42, 03142, Kyiv, Ukraine

[c]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA

[d]Department of Chemistry, University of Notre Dame, Notre Dame, IN 46556, USA

*corresponding author. E-mail: andriy.yaroshchuk@upc.edu and mbruenin@nd.edu

Supporting Information

Table of Contents

S1. Description of Symbols

A $\frac{2}{(\alpha^2+1)-2\frac{c_{\Delta,o}}{c_0}(\alpha^2-1)}$; constant defined for convenience

c salt concentration in solution in the ion-exchange patch system

$\tilde{c}$ c/c_0 salt concentration divided by the bulk salt concentration in the ion-exchange patch system

c_0 salt concentration in the bulk solution in the ion-exchange patch problem

c_i concentration of ion i in the virtual solution for the boundary layer or in the numerical simulations, the real ion concentration in the boundary layer

$\bar{c}_i$ concentration of ion i in the real solution in the membrane or in the boundary layer

c_{i0} concentration of ion i in the left or right stirred solution

c_X concentration of fixed charge in the membrane

$\bar{C}$ sum of the mobile ion concentrations in the membrane

$C(\xi)$ or C sum of the concentrations of all ions in the virtual solution

C_0 sum of the concentrations of all ions in the bulk stirred solution

C_Δ $c_1 - c_2$; difference in the concentration of two counterions

$\bar{C}_\Delta$ $\bar{c}_1 - \bar{c}_2$; difference in the real counterion concentrations in the membrane

$C_{\Delta,l}$ $c_1 - c_2$ at the left side of the left boundary layer

$C_{\Delta,r}$ $c_1 - c_2$ at the right side of the right boundary layer

$C_{\Delta,o}$ $c_1 - c_2$ in the bulk solution

D_i ion diffusion coefficient in solution

$\overline{D}_i$ diffusion coefficient of ion i in the membrane, normalized by the boundary layer thickness

E_0 constant bulk electric field defined in the ion-exchange patch system

f $\frac{c_{10}}{c_{10}+c_{20}}$

F Faraday's constant

$g(\xi,\eta)$ function defined in Eq(62) for solving the Laplace equation

i index representing a specific ion

j_i flux of ion i

$j^{(1)}$ small correction to the flux of ion "1" given in Eq(48)

I current density

$\tilde{I}$ current density divided by Faraday's constant

$\tilde{I}_{lim}$ limiting current density divided by Faraday's constant

$\check{I}$ $\frac{\tilde{I}}{C_0\sqrt{P_1P_2}}$; dimensionless current

K_c integration constant in Eq(63)

K_φ integration constant in Eq(64)

l half width of an ion-exchange patch

L Half thickness of the membrane divided by the boundary layer thickness

P_i boundary layer permeance to ion i, i.e. permeability divided by boundary layer thickness

P_i^* $\Gamma_i D_i$; permeability of ion i

P_s salt permeance of the membrane

R gas constant

S_j $\sum_i \frac{j_i}{P_i}$; sum of permeance-normalized fluxes

$\bar{S}_j$ $\frac{j_1}{\bar{D}_1} + \frac{j_2}{\bar{D}_2}$; sum of fluxes divided by the normalized diffusion coefficients in the membrane

S_Z $\sum_i Z_i \cdot \frac{j_i}{P_i}$; sum of the ion charge multiplied by the permeance-normalized fluxes

S_Δ $\frac{j_1}{P_1} - \frac{j_2}{P_2}$; difference of permeance-normalized counterion fluxes

$\bar{S}_\Delta$ $\frac{j_1}{\bar{D}_1} - \frac{j_2}{\bar{D}_2}$; differences in counterion fluxes divided by normalized diffusion coefficients in the membrane

t_1 $\frac{P_1 c_{10}}{P_1 c_{10} + P_2 c_{20}}$; transference number for counterion "1" in the boundary layer with an ideally permselective membrane

t_2 $\frac{P_2 c_{20}}{P_1 c_{10} + P_2 c_{20}}$; transference number for counterion "2" in the boundary layer with an ideally permselective membrane

T temperature

x coordinate for one-dimensional diffusion or a coordinate for the ion-exchange patch

y $\frac{S_j}{C_0}$ or a coordinate for the ion-exchange patch

y_0 the value of $\frac{S_j}{C_0}$ when $\beta = 0$

y_1 a constant for linear correction of y, i.e. $y = y_0 + \beta y_1$

Z_i charge of ion i

α $\sqrt{\frac{P_2}{P_1}}$; square root of the ratio of permeances to counterion "2" and counterion "1" in the boundary layer

$\bar{\alpha}$ $\sqrt{\frac{\bar{D}_2}{\bar{D}_1}}$; square root of the ratio of diffusion coefficients for counterion "2" and counterion "1" in the membrane

β $\frac{L}{c_X/C_0} \cdot \sqrt{\frac{P_1 P_2}{\bar{D}_1 \bar{D}_2}}$; parameter defined for the linear correction

δ boundary layer thickness

γ_i activity coefficient of ion i in a virtual solution

$\bar{\gamma}_i$ activity coefficient of ion i in a real solution

Γ_i $\frac{\bar{c}_i}{c_i}$; partition coefficient for ion i between a real and virtual solution

η y-coordinate divided by the patch width

λ $\frac{FE_0 l}{2RT}$ dimensionless voltage drop on the half width of the ion-exchange patch

$\bar{\mu}_i$ electrochemical potential of ion i for a real or virtual solution

μ_i^o standard state chemical potential of ion i in the virtual solution

$\bar{\mu}_i^o$ real solution standard state chemical potential of ion i

ν_i stoichiometric coefficient of ion i in a salt

ξ x/δ; x coordinate divided by either the boundary layer thickness or the thickness of an ion-exchange membrane patch

ξ_0 any specificed x-coordinate in the boundary layers divided by the boundary layer thickness

φ virtual electrostatic potential multiplied by F/RT

$\bar{\varphi}$ real electrostatic potential multiplied by F/RT

ϕ virtual electrostatic potential with dimensions

$\bar{\phi}$ real electrostatic potential with dimensions

ψ_D Donnan potential at the membrane-boundary interface

S2. Origin of Eq(1), ion fluxes

In one dimension with no convection, Eq(S1) describes the transport of ion i,

$$j_i = -\frac{\bar{c}_i D_i}{RT}\frac{d\bar{\mu}_i}{dx} \tag{S1}$$

where $\bar{\mu}_i$ is the electrochemical potential of ion i, D_i is the ion diffusion coefficient, $\bar{c}_i$ is the real concentration of this ion, R is the gas constant and T is temperature. Eq(S2) gives the electrochemical potential of the ion, where

$$\bar{\mu}_i = \bar{\mu}_i^o + RTln(\bar{\gamma}_i\bar{c}_i) + Z_iF\bar{\phi} \tag{S2}$$

$\bar{\mu}_i^o$ is the standard-state electrochemical potential of the ion, $\bar{\gamma}_i$ is the activity coefficient, Z_i is the ion charge and $\bar{\phi}$ is the real electrostatic potential.

Assuming that $\bar{\gamma}_i = 1$, differentiating Eq(S2) and substituting into Eq(S1) yields the typical Nernst-Planck equation.

$$j_i = -\bar{c}_i D_i\left(\frac{1}{\bar{c}_i}\frac{d\bar{c}_i}{dx} + \frac{Z_iF}{RT}\frac{d\bar{\phi}}{dx}\right) = -D_i\frac{d\bar{c}_i}{dx} - D_i\frac{\bar{c}_i Z_i F}{RT}\frac{d\bar{\phi}}{dx} \tag{S3}$$

Use of this equation requires both partition coefficients (to obtain boundary conditions for real concentrations) and diffusion coefficients. The use of virtual solutions, or solutions that could be in equilibrium with a given point in the membrane, simplifies the model in that it requires only a single permeability coefficient. For the virtual solution, we obtain

$$\bar{\mu}_i = \mu_i^o + RTln(\gamma_i c_i) + Z_iF\phi \tag{S4}$$

where c_i and ϕ are the virtual concentration and electrical potential, respectively. We define the partition coefficient

$$\Gamma_i = \frac{\bar{c}_i}{c_i} \tag{S5}$$

Differentiation of Eq(S4), substitution into Eq(S1), and the use of Eq(S5) leads to

$$j_i = -\Gamma_i D_i c_i\left(\frac{1}{c_i}\frac{dc_i}{dx} + \frac{Z_iF}{RT}\frac{d\phi}{dx}\right) = -P_i^*\left(\frac{dc_i}{dx} + c_i\frac{Z_iF}{RT}\frac{d\phi}{dx}\right) \tag{S6}$$

In this equation, we defined $P_i^* = \Gamma_i D_i$, where P_i^* is the permeability to the ion.

We also define a dimensionless coordinate, ξ, where $\xi = x/\delta$ and δ is the boundary layer thickness. Additionally, we define a dimensionless electrostatic potential $\varphi = \phi\frac{F}{RT}$. This leads to

$$j_i = -P_i\left(\frac{dc_i}{d\xi} + c_i Z_i\frac{d\varphi}{d\xi}\right) \tag{S7}$$

In this equation P_i=P_i^*/δ, which is the membrane permeance.

S3. Derivation of Eq(20), potential drop across the membrane (not including the boundary layers) under conditions of equal counterion electrochemical potentials

As noted in the text, equating ion electrochemical potentials in Eq(S4) for the ideal virtual solutions on the two faces of the membrane gives

$$ln\big(c_1(-0)\big) + \varphi(-0) = ln\big(c_1(+0)\big) + \varphi(+0) \quad \text{(S8)}$$

$$ln\big(c_2(-0)\big) + \varphi(-0) = ln\big(c_2(+0)\big) + \varphi(+0) \quad \text{(S9)}$$

where -0 and $+0$ denote the left and right surfaces of the infinitely thin membrane (see Fig. 1). Thus far, we solved the differential equations for the sum of ion concentrations and the potentials in the boundary layers (see Eq(6) and Eq(11)), but we need to know the individual ion concentrations to substitute into Eq(S8) or Eq(S9) to solve for the potential drop across the infinitesimally thin membrane.

By subtracting Eq(S9) from Eq(S8), one obtains

$$ln\left(\frac{c_1(-0)}{c_2(-0)}\right) = ln\left(\frac{c_1(+0)}{c_2(+0)}\right) \quad \text{(S10)}$$

We define the following variable

$$C_\Delta \equiv c_1 - c_2 \quad \text{(S11)}$$

Using the definitions of C_Δ and C, and noting that for a solution containing only monovalent ions $c_1 + c_2 - c_3 = 0$ (electroneutrality) in the boundary layers,

$$c_1 \equiv \frac{1}{4}\cdot(C + 2C_\Delta) \quad \text{(S12)}$$

$$c_2 \equiv \frac{1}{4}\cdot(C - 2C_\Delta) \quad \text{(S13)}$$

Substituting Eqs(S12,S13) into Eq(S10) leads to

$$\frac{C(-0)+2C_\Delta(-0)}{C(-0)-2C_\Delta(-0)} = \frac{C(+0)+2C_\Delta(+0)}{C(+0)-2C_\Delta(+0)} \quad \text{(S14)}$$

This equation transforms to

$$\frac{C_\Delta(-0)}{C(-0)} = \frac{C_\Delta(+0)}{C(+0)} \quad \text{(S15)}$$

Substituting Eq(S12,S13) into Eq (S8) leads to

$$\varphi(-0) - \varphi(+0) = ln\left(\frac{c_1(+0)}{c_1(-0)}\right) = ln\left(\frac{C(+0)+2C_\Delta(+0)}{C(-0)+2C_\Delta(-0)}\right) = ln\left(\frac{C(+0)\left(1+2\frac{C_\Delta(+0)}{C(+0)}\right)}{C(-0)\left(1+2\frac{C_\Delta(-0)}{C(-0)}\right)}\right) \quad \text{(S16)}$$

Finally, using Eq(15) gives

$$\varphi(-0) - \varphi(+0) = ln\left(\frac{C(+0)}{C(-0)}\right) = ln\left(\frac{C_0+S_j}{C_0-S_j}\right) \quad \text{(S17)}$$

S4. Derivation of Eq(27), potential drop allowing for the resistance of the membrane and introduction of a third differential equation in the solution and in the membrane

Introduction of a third differential equation

The boundary layers.

To introduce a third differential equation, we define the following variable

$$S_\Delta \equiv \frac{j_1}{P_1} - \frac{j_2}{P_2} \tag{S18}$$

where ions "1" and "2" have the same monovalent charge sign and are counterions of the ion-exchange membrane. Subtracting Eq(1) for ion "2" from Eq(1) for ion "1" yields

$$-S_\Delta = \frac{dC_\Delta}{d\xi} + C_\Delta \cdot \frac{d\varphi}{d\xi} \tag{S19}$$

This is a first-order ordinary differential equation that can be solved in quadratures. The solution is

$$C_\Delta(\xi) = exp\big(\varphi(\xi_0) - \varphi(\xi)\big) \cdot \left[C_\Delta(\xi_0) - S_\Delta \cdot \int_{\xi_0}^{\xi} exp\big(\varphi(\xi') - \varphi(\xi_0)\big) d\xi'\right] \tag{S20}$$

By substituting Eq(11), $\varphi(\xi) - \varphi(\xi_0) = \frac{S_Z}{S_j} \cdot ln\left(\frac{C(\xi)}{C(\xi_0)}\right)$, we obtain

$$C_\Delta(\xi) = \left(\frac{C(\xi)}{C(\xi_0)}\right)^{-\frac{S_Z}{S_j}} \left[C_\Delta(\xi_0) - S_\Delta \cdot \int_{\xi_0}^{\xi} \left(\frac{C(\xi')}{C(\xi_0)}\right)^{\frac{S_Z}{S_j}} d\xi'\right] \tag{S21}$$

Substituting Eq(6), $C(\xi) - C(\xi_0) = -S_j \cdot (\xi - \xi_0)$ into the numerator of the integral, after integration and transformation one obtains

$$C_\Delta(\xi) = \left(C_\Delta(\xi_0) - \frac{S_\Delta \cdot C(\xi_0)}{S_j + S_Z}\right) \cdot \left(\frac{C(\xi)}{C(\xi_0)}\right)^{-\frac{S_Z}{S_j}} + \frac{S_\Delta \cdot C(\xi_0)}{S_j + S_Z} \cdot \frac{C(\xi)}{C(\xi_0)} \tag{S22}$$

With complete blockage of coions from the membrane and monovalent positive counterions

$$j_3 = 0 \tag{S23}$$

$$S_Z = S_j \tag{S24}$$

Substituting Eq(S24) into Eq(S22) yields

$$C_\Delta(\xi) = \left(C_\Delta(\xi_0) - \frac{S_\Delta \cdot C(\xi_0)}{2S_j}\right) \cdot \left(\frac{C(\xi)}{C(\xi_0)}\right)^{-1} + \frac{S_\Delta \cdot C(\xi_0)}{2S_j} \cdot \frac{C(\xi)}{C(\xi_0)} \tag{S25}$$

Eq(6) and Eq(S25) are relationships between the ion fluxes (contained in the constants S_Δ and S_j) and solution composition (given by $C(x)$ and $C_\Delta(x)$ since due to the electro-neutrality of virtual solutions only two virtual ion concentrations are independent.

Inside the membrane

Next, we consider the membrane phase. Defining

$$\bar{C}_\Delta \equiv \bar{c}_1 - \bar{c}_2 \text{ and } \bar{S}_\Delta \equiv \frac{j_1}{\bar{D}_1} - \frac{j_2}{\bar{D}_2} \tag{S26}$$

we obtain this first-order ordinary differential equation with constant coefficients for the difference of real counter-ion concentrations in the membrane.

$$\frac{d\bar{C}_\Delta}{d\xi} - \bar{C}_\Delta \cdot \frac{\bar{S}_j}{c_X} + \bar{S}_\Delta = 0 \tag{S27}$$

(This equation relies on the identity that $\bar{C}_\Delta \cdot \frac{\bar{S}_j}{c_X} = -\bar{c}_1 \frac{d\bar{\varphi}}{d\xi} + \bar{c}_2 \frac{d\bar{\varphi}}{d\xi}$ and stems from Eq(S3) with non-dimensionalized coordinate and potential and complete coion exclusion. We took the difference of the modified Eq(S3) for the two counterions.) Eq(S27) has this exponential solution that relates the function $\bar{C}_\Delta$ at two arbitrary points inside the membrane:

$$\bar{C}_\Delta(\xi') = \bar{C}_\Delta(\xi) \cdot exp\left(\frac{\bar{S}_j}{c_X} \cdot (\xi' - \xi)\right) + c_X \cdot \frac{\bar{S}_\Delta}{\bar{S}_j} \cdot \left(1 - exp\left(\frac{\bar{S}_j}{c_X} \cdot (\xi' - \xi)\right)\right) \tag{S28}$$

Next, we apply the boundary conditions of known solution compositions in the perfectly-stirred reservoirs and of Donnan equilibria at the membrane surfaces. Virtual concentrations just outside a membrane surface are related to the real concentrations just on the other side of this interface (inside the membrane) via exponentials of the Donnan potential.

Therefore, at the membrane surfaces

$$(c_1 + c_2) \cdot exp(-\psi_D) = \bar{c}_1 + \bar{c}_2 = c_X \tag{S29}$$

where ψ_D is the Donnan potential. Since, just outside the membrane, $c_1 + c_2 = \frac{C}{2}$

$$exp(-\psi_D) = \frac{2c_X}{C} \tag{S30}$$

Accordingly,

$$\bar{C}_\Delta(membrane\ boundary) = C_\Delta(solution\ boundary) \cdot exp(-\psi_D) = C_\Delta \frac{2c_X}{C} \tag{S31}$$

In particular, at the left and right membrane surfaces

$$\bar{C}_\Delta(-L + 0) = C_\Delta(-L - 0) \cdot \frac{2c_X}{C(-L-0)} \tag{S32}$$

$$\bar{C}_\Delta(L - 0) = C_\Delta(L + 0) \cdot \frac{2c_X}{C(L+0)} \tag{S33}$$

where *L* is the membrane half-thickness scaled on the boundary-layer thickness. At the same time, using $\xi' = L$ and $\xi = -L$ in Eq(S28) gives

$$\bar{C}_\Delta(L-0) = \bar{C}_\Delta(-L+0)\cdot exp\left(\frac{2L\bar{S}_j}{c_X}\right) + c_X\cdot\frac{\bar{S}_\Delta}{\bar{S}_j}\cdot\left(1 - exp\left(\frac{2L\bar{S}_j}{c_X}\right)\right) \tag{S34}$$

By substituting Eqs(S32,S33) into Eq(S34), we obtain

$$\frac{C_\Delta(L+0)}{C(L+0)} = \frac{C_\Delta(-L-0)}{C(-L-0)}\cdot exp\left(\frac{2L\bar{S}_j}{c_X}\right) + \frac{\bar{S}_\Delta}{2\bar{S}_j}\cdot\left(1 - exp\left(\frac{2L\bar{S}_j}{c_X}\right)\right) \tag{S35}$$

When $\frac{2L\bar{S}_j}{c_X} \to 0$, Eq(S35) becomes Eq(S15), consistent with the limiting case of zero differences of electrochemical potentials of counterions that should occur for very thin (small L), highly charged (large c_X) and permeable (small $\bar{S}_j$) membranes.

The derivation of Eqs(12-13) and Eq(S25) is not specific to the way we treat the membrane. Substituting coordinates into these three equations gives

$$C(-L-0) = C_0 - S_j \tag{S36}$$

$$C(L+0) = C_0 + S_j \tag{S37}$$

$$C_\Delta(-L-0) = \left(C_\Delta(-L-1) - \frac{S_\Delta\cdot C_0}{2S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right) + \frac{S_\Delta(C_0-S_j)}{2S_j} \tag{S38}$$

$$C_\Delta(L+0) = \left(C_\Delta(L+1) - \frac{S_\Delta\cdot C_0}{2S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right) + \frac{S_\Delta\cdot(C_0+S_j)}{2S_j} \tag{S39}$$

Note that $-L-0$ and $L+0$ correspond to positions in solution just to the left and right (see Fig. 2) of the membrane, respectively. Substituting Eqs(S36-S39) into Eq(S35) with rearrangements and noting the definition of the sinh function gives

$$\left(\frac{C_{\Delta,l}}{C_0} - \frac{S_\Delta}{2S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2\cdot exp\left(\frac{L\bar{S}_j}{c_X}\right) - \left(\frac{C_{\Delta,r}}{C_0} - \frac{S_\Delta}{2S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2\cdot exp\left(-\frac{L\bar{S}_j}{c_X}\right) = -\left(\frac{S_\Delta}{S_j} - \frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot sinh\left(\frac{L\bar{S}_j}{c_X}\right) \tag{S40}$$

where

$$C_{\Delta,l} \equiv C_\Delta(-L-1) \tag{S41}$$

$$C_{\Delta,r} \equiv C_\Delta(L+1) \tag{S42}$$

The voltage drop across the system when the membrane has a finite thickness

Now we consider the entire system (boundary layers plus membrane). Eqs(14,15) still apply (repeated below), but the values of the parameter S_j will be different from the limiting case of zero electrochemical-potential differences and the coordinates will be different.

$$\varphi(-1) - \varphi(-0) = \frac{S_Z}{S_j}\cdot ln\left(\frac{C_o}{C_o-S_j}\right) \qquad \text{(left boundary layer)} \tag{14}$$

$$\varphi(+0) - \varphi(+1) = \frac{S_Z}{S_j} \cdot ln\left(\frac{C_0+S_j}{C_0}\right) \qquad \text{(right boundary layer)} \qquad (15)$$

If the membrane has a finite thickness, the left hand side of Eq(14) will represent $\varphi(-1-L) - \varphi(-0-L)$. Similarly the left hand side of Eq(15) will represent $(\varphi(L+0) - \varphi(+1+L)$.

Substituting the coordinates into Eq(26) gives the difference of the real electrostatic potentials at the two interior sides of the membrane.

$$\bar{\varphi}(-L+0) - \bar{\varphi}(L-0) = \frac{2L\bar{S}_j}{c_X} \qquad (S43)$$

Additionally the total potential drop between the two boundary layers should also include the difference between the two Donnan potentials (defined as the membrane potential minus the solution potential in both cases). Using Eq(S30)

$$\psi_D(-L) - \psi_D(L) = ln\left(\frac{C(-0-L)}{C(L+0)}\right) \equiv ln\left(\frac{C_0-S_j}{C_0+S_j}\right) \qquad (S44)$$

Summing Eq(S43) and Eq(S44) gives the total potential drop between the boundary layers.

$$\varphi(-L+0) - \varphi(L-0) \equiv \bar{\varphi}(-L+0) - \bar{\varphi}(L-0) - \left(\psi_D(-L) - \psi_D(L)\right) = \frac{2L\bar{S}_j}{c_X} + ln\left(\frac{C_0+S_j}{C_0-S_j}\right) \quad (S45)$$

Finally, adding up the virtual-potential drops across the boundary layers (Eq(17) and the membrane (Eq(S45)), for the total electrostatic-potential difference we obtain

$$\varphi(-1-L) - \varphi(1+L) = 2\left[\frac{L\bar{S}_j}{c_X} + ln\left(\frac{C_0+S_j}{C_0-S_j}\right)\right] \qquad (S46)$$

Note that Eq(S46) assumes $\frac{S_Z}{S_j} = 1$.

S5. Derivation of Eqs(29-35), Concentration profiles under bi-ionic conditions with equal electrochemical potentials across the membrane

In the bi-ionic configuration with different 1:1 salts on each side of the membrane, but at the same concentration C_0, the following apply with complete coion exclusion. (Ion "1" is not present in the right perfectly stirred layer and ion "2" is not present in the left perfectly stirred layer.)

$$C_{\Delta,l} = C_0/2 \qquad (S47)$$

$$C_{\Delta,r} = -C_0/2 \qquad (S48)$$

$$j_2 = -j_1 \qquad (S49)$$

Based on the definitions of S_j and S_Δ,

$$\frac{S_\Delta}{S_j} = \frac{P_2+P_1}{P_2-P_1} \qquad (S50)$$

Starting from Eq(S25) (repeated here for convenience),

$$C_\Delta(\xi) = \left(C_\Delta(\xi_0) - \frac{S_\Delta \cdot C(\xi_0)}{2S_j}\right) \cdot \left(\frac{C(\xi)}{C(\xi_0)}\right)^{-1} + \frac{S_\Delta \cdot C(\xi_0)}{2S_j} \cdot \frac{C(\xi)}{C(\xi_0)} \tag{S25}$$

for the infinitesimally thin membrane with substitution of Eqs(12,13) we obtain

$$C_\Delta(-0) = \left(C_{\Delta,l} - \frac{S_\Delta \cdot C_0}{2S_j}\right) \cdot \left(\frac{C_0}{C_0 - S_j}\right) + \frac{S_\Delta \cdot (C_0 - S_j)}{2S_j} \tag{S51}$$

$$C_\Delta(+0) = \left(C_{\Delta,r} - \frac{S_\Delta \cdot C_0}{2S_j}\right) \cdot \left(\frac{C_0}{C_0 + S_j}\right) + \frac{S_\Delta \cdot (C_0 + S_j)}{2S_j} \tag{S52}$$

Inserting Eqs(S51,S52) and Eqs(12,13) into Eq(S15) gives

$$\left(C_{\Delta,l} - \frac{S_\Delta \cdot C_0}{2S_j}\right) \cdot \frac{1}{(C_0 - S_j)^2} = \left(C_{\Delta,r} - \frac{S_\Delta \cdot C_0}{2S_j}\right) \cdot \frac{1}{(C_0 + S_j)^2} \tag{S53}$$

Substituting Eq(S47,S48, and S50) into Eq(S53), with appropriate rearrangements, we obtain

$$\frac{S_j}{C_0} = \frac{\alpha - 1}{\alpha + 1} \tag{S54}$$

where

$$\alpha^2 \equiv P_2 / P_1 \tag{S55}$$

In the left boundary layer, Eq(6) $C(\xi) - C(\xi_0) = -S_j \cdot (\xi - \xi_0)$ leads to

$$\frac{C(\xi)}{C_0} = 1 - \frac{S_j}{C_0}(\xi + 1) \tag{S56}$$

Substituting Eq(S54) into Eq(S56) gives

$$\frac{C(\xi)}{C_0} = 1 - \left(\frac{\alpha - 1}{\alpha + 1}\right)(1 + \xi) \tag{S57}$$

Starting from Eq(S12), $c_1 = \frac{1}{4} \cdot (C + 2C_\Delta)$ and inserting the expression for $C_\Delta(\xi)$ in Eq(S25) leads to

$$c_1 \equiv \frac{1}{4} \cdot \left(C(\xi) + \left(C_0 - \frac{S_\Delta \cdot C_0}{S_j}\right)\left(\frac{C(\xi)}{C_0}\right)^{-1} + \frac{S_\Delta \cdot C(\xi)}{S_j}\right) \tag{S58}$$

Substituting Eq(S50) and appropriate transformations leads to

$$c_1(\xi) = \frac{C_0}{2} \cdot \frac{\alpha^2 \cdot \frac{C(\xi)}{C_0} - \frac{C_0}{C(\xi)}}{\alpha^2 - 1} \tag{S59}$$

Similarly,

$$c_2(\xi) = \frac{C_0}{2} \cdot \frac{\frac{C_0}{C(\xi)} - \frac{C(\xi)}{C_0}}{\alpha^2 - 1} \tag{S60}$$

Derivation of the concentration profiles in the boundary layer on the right side of the membrane follows similarly.

S6. Derivation of ion fluxes (Eq(36)) under bi-ionic conditions and equal electrochemical potentials across the membrane

For complete coion exclusion $j_1 = -j_2$ and

$$S_j \equiv \sum_i \frac{j_i}{P_i} = \frac{j_1}{P_1} - \frac{j_1}{P_2} \quad \text{(S61)}$$

Dividing this expression by C_0 and substituting Eq(S54) along with appropriate transformations leads to

$$j_1 = \frac{C_0}{\left(\frac{1}{\sqrt{P_1}}+\frac{1}{\sqrt{P_2}}\right)^2} \quad \text{(S62)}$$

S7. Derivation of an expression for the bi-ionic potential drop, (Eq(37)), under conditions of equal electrochemical potentials across the membrane

Starting from Eq(21) and substituting the expression for $\frac{S_j}{C_0}$ in Eq(S54) leads to

$$\varphi(-1) - \varphi(1) = 2ln\left(\frac{C_0+S_j}{C_0-S_j}\right) = 2ln\left(\frac{1+\frac{S_j}{C_0}}{1-\frac{S_j}{C_0}}\right) = 2ln\left(\frac{1+\frac{\alpha-1}{\alpha+1}}{1-\frac{\alpha-1}{\alpha+1}}\right) \quad \text{(S63)}$$

Rearrangement gives

$$\varphi(-1) - \varphi(1) = 2ln\left(\frac{\frac{2\alpha}{\alpha+1}}{\frac{2}{\alpha+1}}\right) = 2ln(\alpha) = \ln(\alpha^2) = ln\left(\frac{P_2}{P_1}\right) \quad \text{(S64)}$$

S8. Derivation of a first-order flux correction (Eq(38)) to the limiting case of constant electrochemical potentials: Bi-ionic potentials

This derivation starts with Eq(S40), which we repeat hear for convenience.

$$\left(\frac{C_{\Delta,l}}{C_0} - \frac{S_\Delta}{2S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2 \cdot exp\left(\frac{L\bar{S}_j}{c_X}\right) - \left(\frac{C_{\Delta,r}}{C_0} - \frac{S_\Delta}{2S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2 \cdot exp\left(-\frac{L\bar{S}_j}{c_X}\right) = -\left(\frac{S_\Delta}{S_j} - \frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot sinh\left(\frac{L\bar{S}_j}{c_X}\right) \quad \text{(S40)}$$

We assume that the terms $\frac{L\bar{S}_j}{c_X}$ is small. This leads to the following linear approximations

$$sinh\left(\frac{L\bar{S}_j}{c_X}\right) = \frac{L\bar{S}_j}{c_X};\ exp\left(\frac{L\bar{S}_j}{c_X}\right) = 1 + \frac{L\bar{S}_j}{c_X};\ exp\left(-\frac{L\bar{S}_j}{c_X}\right) = 1 - \frac{L\bar{S}_j}{c_X} \quad \text{(S65)}$$

Inserting these approximations along with $\frac{C_{\Delta,l}}{C_0} = -\frac{C_{\Delta,r}}{C_0} = \frac{1}{2}$ (monovalent salts with only one salt in each stirred solution) leads to

$$\left(1-\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2+\frac{L\bar{S}_j}{c_X}\left(1-\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2-\left(-1-\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2+\frac{L\bar{S}_j}{c_X}\left(-1-\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2+$$
$$2\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot\frac{L\bar{S}_j}{c_X}=0 \quad \text{(S66)}$$

Rearranging yields

$$\left(1-\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2+\left(1+\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2+\frac{L\bar{S}_j}{c_X}\left\{\left(1-\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2-\left(1+\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2+\right.$$
$$\left.2\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\right\}=0 \quad \text{(S67)}$$

This equation relates sums and differences of fluxes to permeances, diffusion coefficients, and the bulk sum of concentration. Our task is to make the relationship between a specific ion flux and the permeances and normalized diffusion coefficients explicit. Based on their definitions, we also have the following expressions

$$\frac{S_\Delta}{S_j}=\frac{P_2+P_1}{P_2-P_1}=\frac{\alpha^2+1}{\alpha^2-1};\ \alpha,\bar{\alpha}\equiv\sqrt{\frac{P_2}{P_1}},\sqrt{\frac{\bar{D}_2}{\bar{D}_1}};\ \beta\equiv\frac{L}{c_X/C_0}\cdot\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}};\ y\equiv\frac{S_j}{C_0} \quad \text{(S68)}$$

Additionally, from the definitions of $\bar{S}_j$ and S_j, and the assumption of steady state and coion exclusion with $j_2=-j_1$

$$\frac{\bar{S}_j}{C_0}=\frac{S_j}{C_0}\cdot\frac{\frac{1}{\bar{D}_1}-\frac{1}{\bar{D}_2}}{\frac{1}{P_1}-\frac{1}{P_2}}=y\cdot\frac{P_2}{\bar{D}_2}\cdot\left(\frac{\bar{\alpha}^2-1}{\alpha^2-1}\right)=y\cdot\left(\frac{\bar{\alpha}^2-1}{\alpha^2-1}\right)\sqrt{\frac{P_2}{\bar{D}_2}}\cdot\sqrt{\frac{\bar{D}_1}{P_1}}\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}}=y\cdot\left(\frac{\bar{\alpha}^2-1}{\alpha^2-1}\right)\frac{\alpha}{\bar{\alpha}}\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}}\equiv y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}} \quad \text{(S69)}$$

Moreover, the definitions of $\bar{S}_\Delta$ and $\bar{S}_j$ and $j_2=-j_1$ give

$$\frac{\bar{S}_\Delta}{\bar{S}_j}=\frac{\frac{1}{\bar{D}_1}-\frac{1}{\bar{D}_2}}{\frac{1}{P_1}-\frac{1}{P_2}}=\frac{\bar{\alpha}^2+1}{\bar{\alpha}^2-1} \quad \text{(S70)}$$

Eq(S67) contains the term $\frac{L\bar{S}_j}{c_X}$. We can rewrite this term as

$$\frac{L\bar{S}_j}{c_X}\equiv\frac{L}{c_X/C_0}\frac{\bar{S}_j}{C_0}\equiv\frac{L}{c_X/C_0}y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}}\equiv\beta y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right) \quad \text{(S71)}$$

Substituting Eqs(S68,S70,S71) into Eq(67) gives

$$\left(1-\frac{\alpha^2+1}{\alpha^2-1}\right)\cdot\left(\frac{1}{1-y}\right)^2+\left(1+\frac{\alpha^2+1}{\alpha^2-1}\right)\cdot\left(\frac{1}{1+y}\right)^2+\left\{\left(1-\frac{\alpha^2+1}{\alpha^2-1}\right)\cdot\left(\frac{1}{1-y}\right)^2-\left(1+\frac{\alpha^2+1}{\alpha^2-1}\right)\cdot\left(\frac{1}{1+y}\right)^2+\right.$$
$$\left.2\left(\frac{\alpha^2+1}{\alpha^2-1}-\frac{\bar{\alpha}^2+1}{\bar{\alpha}^2-1}\right)\right\}\cdot\beta y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)=0 \quad \text{(S72)}$$

The use of common denominators leads to

$$\left(\frac{-2}{\alpha^2-1}\right)\cdot\left(\frac{1}{1-y}\right)^2+\left(\frac{2\alpha^2}{\alpha^2-1}\right)\cdot\left(\frac{1}{1+y}\right)^2+\left\{\left(\frac{-2}{\alpha^2-1}\right)\cdot\left(\frac{1}{1-y}\right)^2-\left(\frac{2\alpha^2}{\alpha^2-1}\right)\cdot\left(\frac{1}{1+y}\right)^2+2\left(\frac{\alpha^2+1}{\alpha^2-1}-\frac{\bar{\alpha}^2+1}{\bar{\alpha}^2-1}\right)\right\}\cdot\beta y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)=0 \quad \text{(S73)}$$

Noting that $\frac{\alpha^2+1}{\alpha^2-1}-\frac{\bar{\alpha}^2+1}{\bar{\alpha}^2-1}=\frac{(\alpha^2+1)(\bar{\alpha}^2-1)-(\alpha^2-1)(\bar{\alpha}^2+1)}{(\alpha^2-1)(\bar{\alpha}^2-1)}=\frac{2(\bar{\alpha}^2-\alpha^2)}{(\alpha^2-1)(\bar{\alpha}^2-1)}$, substituting this expression into Eq(S73) and multiplying both sides of Eq(S73) by $-\frac{(\alpha^2-1)}{2}$ leads to

$$\left(\frac{1}{1-y}\right)^2-\alpha^2\cdot\left(\frac{1}{1+y}\right)^2+\left\{\left(\frac{1}{1-y}\right)^2+\alpha^2\cdot\left(\frac{1}{1+y}\right)^2-\frac{2(\bar{\alpha}^2-\alpha^2)}{(\bar{\alpha}^2-1)}\right\}\cdot\beta y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)=0 \quad \text{(S74)}$$

Multiplying both sides of the equation by $(1+y)^2$ yields

$$\left(\frac{1+y}{1-y}\right)^2-\alpha^2+\left\{\left(\frac{1+y}{1-y}\right)^2+\alpha^2-(1+y)^2\cdot\frac{2(\bar{\alpha}^2-\alpha^2)}{(\bar{\alpha}^2-1)}\right\}\cdot\beta y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)=0 \quad \text{(S75)}$$

Next, we make assume a linear correction in the sum of the fluxes, S_j, due to the finite membrane thickness. We do this in the form

$$y=\frac{S_j}{C_0}=y_0+\beta y_1 \quad \text{(S76)}$$

In Eq(S76), y_0 is the value of $\frac{S_j}{C_0}$ when $\beta=0$, and y_1 is a constant. Note that when $\beta=0$, we return to the limiting case. Substituting Eq(S76) into Eq(S75) and retaining only expressions with linear terms in β leads to

$$\left(\frac{1+y_0+\beta y_1}{1-y_0-\beta y_1}\right)^2-\alpha^2+\left\{\left(\frac{1+y_0}{1-y_0}\right)^2+\alpha^2-(1+y_0)^2\cdot\frac{2(\bar{\alpha}^2-\alpha^2)}{(\bar{\alpha}^2-1)}\right\}\cdot\beta y_0\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)=0 \quad \text{(S77)}$$

Note that because the term in braces is multiplied by β, we discarded the corrections within the braces. Substituting $y_0=\frac{\alpha-1}{\alpha+1}$ (Eq(S54) and $\frac{1+y_0}{1-y_0}=\frac{\frac{\alpha+1+\alpha-1}{\alpha+1}}{\frac{\alpha+1-\alpha+1}{\alpha+1}}=\frac{2\alpha}{2}=\alpha$,

$$\left(\frac{1+y_0+\beta y_1}{1-y_0-\beta y_1}\right)^2-\alpha^2+\left\{\alpha^2+\alpha^2-\left(1+\frac{\alpha-1}{\alpha+1}\right)^2\cdot\frac{2(\bar{\alpha}^2-\alpha^2)}{(\bar{\alpha}^2-1)}\right\}\cdot\beta\cdot\left(\frac{\alpha-1}{\alpha+1}\right)\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)=0 \quad \text{(S78)}$$

Multiplying $\left(\frac{1+y_0+\beta y_1}{1-y_0-\beta y_1}\right)$ by $\left(\frac{1+y_0}{1-y_0}\right)\left(\frac{1-y_0}{1+y_0}\right)$ yields

$$\left(\frac{1+y_0+\beta y_1}{1-y_0-\beta y_1}\right)=\frac{1+y_0}{1-y_0}\left(\frac{1+\frac{\beta y_1}{1+y_0}}{1-\frac{\beta y_1}{1-y_0}}\right) \quad \text{(S79)}$$

Reemembering that $\frac{1+y_0}{1-y_0}=\alpha$ (rearrangement of Eq(S54) leads to

$$\left(\frac{1+y_0+\beta y_1}{1-y_0-\beta y_1}\right) = \alpha\left(\frac{1+\frac{\beta y_1}{1+y_0}}{1-\frac{\beta y_1}{1-y_0}}\right) \text{ so } \left(\frac{1+y_0+\beta y_1}{1-y_0-\beta y_1}\right)^2 = \alpha^2\left(\frac{1+\frac{\beta y_1}{1+y_0}}{1-\frac{\beta y_1}{1-y_0}}\right)^2 \tag{S80}$$

If $\frac{\beta y_1}{1+y_0}$ is small $\left(\frac{1+\frac{\beta y_1}{1+y_0}}{1-\frac{\beta y_1}{1-y_0}}\right)^2 \approx \left(1+\frac{2\beta y_1}{1+y_0}\right)\left(1+\frac{2\beta y_1}{1-y_0}\right)$. Thus, taking only linear terms

$$\left(\frac{1+y_0+\beta y_1}{1-y_0-\beta y_1}\right)^2 = \alpha^2\left(\frac{1+\frac{\beta y_1}{1+y_0}}{1-\frac{\beta y_1}{1-y_0}}\right)^2 \approx \alpha^2 + 2\alpha^2\beta y_1\left(\frac{1}{1+y_0}+\frac{1}{1-y_0}\right) = \alpha^2 + \frac{4\alpha^2\beta y_1}{1-y_0^2} \tag{S81}$$

Substituting for $y_0 = \frac{\alpha-1}{\alpha+1}$ and rearranging gives

$$\left(\frac{1+y_0+\beta y_1}{1-y_0-\beta y_1}\right)^2 = \alpha^2\left[1+\left(\frac{4\beta y_1\cdot(1+\alpha)^2}{(1+\alpha)^2-(1-\alpha)^2}\right)\right] \equiv \alpha^2\left[1+(1+\alpha)^2\left(\frac{\beta y_1}{\alpha}\right)\right] \tag{S82}$$

Subsituting Eq(S82) into Eq(S78) yields

$$\alpha^2\left[1+(1+\alpha)^2\left(\frac{\beta y_1}{\alpha}\right)\right] - \alpha^2 + \left\{2\alpha^2 - \left(\frac{2\alpha}{\alpha+1}\right)^2\cdot\frac{2\left(\bar{\alpha}^2-\alpha^2\right)}{\left(\bar{\alpha}^2-1\right)}\right\}\cdot\beta\cdot\left(\frac{\alpha-1}{\alpha+1}\right)\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right) = 0 \tag{S83}$$

This is identical to

$$\beta\left\{(1+\alpha)^2\cdot y_1 + 2\alpha\cdot\left[1-\left(\frac{2}{1+\alpha}\right)^2\cdot\frac{\left(\bar{\alpha}^2-\alpha^2\right)}{\left(\bar{\alpha}^2-1\right)}\right]\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)\cdot y_0\right\} = 0 \tag{S84}$$

Dividing by β and applying significant transformations leads to

$$(1+\alpha)^2\cdot y_1 + \frac{2\alpha^2}{\alpha^2-1}\cdot\left[\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)-\left(\frac{2}{\frac{1}{\sqrt{\alpha}}+\sqrt{\alpha}}\right)^2\cdot\left(\frac{\bar{\alpha}}{\alpha}-\frac{\alpha}{\bar{\alpha}}\right)\right]\cdot y_0 = 0 \tag{S85}$$

Finally,

$$y_1 = -\frac{2\alpha^2}{(1+\alpha)^2(\alpha^2-1)}\left[\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)-\left(\frac{2}{\frac{1}{\sqrt{\alpha}}+\sqrt{\alpha}}\right)^2\cdot\left(\frac{\bar{\alpha}}{\alpha}-\frac{\alpha}{\bar{\alpha}}\right)\right]\cdot y_0 = -\frac{2\alpha^2}{(1+\alpha)^2(\alpha^2-1)}\left[\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)-\left(\frac{2}{1+\alpha}\right)^2\cdot\left(\bar{\alpha}-\frac{\alpha^2}{\bar{\alpha}}\right)\right]\cdot y_0 \tag{S86}$$

From the definition of $S_j = \frac{j_1}{P_1}+\frac{j_2}{P_2}$, with complete coion exclusion ($j_2 = -j_1$),

$$j_1 = S_j\frac{P_1P_2}{P_2-P_1} = S_j\frac{\sqrt{P_1P_2}}{\alpha-\frac{1}{\alpha}} \tag{S87}$$

Additionally,

$$j_1 = \frac{S_j}{C_o} * \frac{C_o\sqrt{P_1P_2}}{\alpha-\frac{1}{\alpha}} = C_0\frac{\sqrt{P_1P_2}}{\alpha-\frac{1}{\alpha}}\cdot(y_0+\beta y_1) \tag{S88}$$

Substituting for y_1 using Eq(S86) and the definition of β (Eq(68) gives

$$j_1 = C_0 \frac{\sqrt{P_1 P_2}}{\alpha - \frac{1}{\alpha}} \cdot \left(y_0 - \frac{L}{c_X / C_0} \cdot \sqrt{\frac{P_1 P_2}{\bar{D}_1 \bar{D}_2}} \left(\frac{2\alpha^2}{(\alpha^2 - 1)(1+\alpha)^2} \left[\left(\bar{\alpha} - \frac{1}{\bar{\alpha}} \right) - \left(\frac{2}{1+\alpha} \right)^2 \cdot \left(\bar{\alpha} - \frac{\alpha^2}{\bar{\alpha}} \right) \cdot \right] y_0 \right) \right) \quad \text{(S89)}$$

Substituting $y_0 = \left(\frac{\alpha-1}{\alpha+1}\right)$ (see Eq(S54)) and using the definitions of $\alpha, \bar{\alpha} \equiv \sqrt{\frac{P_2}{P_1}}, \sqrt{\frac{\bar{D}_2}{\bar{D}_1}}$, one obtains after extensive rearrangement

$$j_1 = \frac{C_0}{\left(\frac{1}{\sqrt{P_1}} + \frac{1}{\sqrt{P_2}} \right)^2} \left\{ 1 - \frac{\frac{2L}{(c_X/C_0)}}{\left(\sqrt{\frac{P_2}{P_1}} - \sqrt{\frac{P_1}{P_2}} \right) \left(\frac{1}{\sqrt{P_1}} + \frac{1}{\sqrt{P_2}} \right)^2} \cdot \left[\left(\frac{1}{\bar{D}_1} - \frac{1}{\bar{D}_2} \right) - \left(\frac{2}{\sqrt{P_1} + \sqrt{P_2}} \right)^2 \cdot \left(\frac{P_1}{\bar{D}_1} - \frac{P_2}{\bar{D}_2} \right) \right] \right\} \quad \text{(S90)}$$

S9. Derivation of a first-order potential difference correction (Eq(39)) to the limiting case of constant electrochemical potentials: Bi-ionic potentials

This derivation begins with Eq(27), which we repeat below for convenience.

$$\varphi(-1-L) - \varphi(1+L) = 2\left[\frac{L\bar{S}_j}{c_X} + ln\left(\frac{C_0 + S_j}{C_0 - S_j} \right) \right] \quad \text{(27)}$$

We need to make small corrections to the values of $\bar{S}_j$ and S_j obtained with the assumption of equal electrochemical potentials of counterions across the membrane. Based on Eq(S71) and taking only linear terms in β

$$\frac{L\bar{S}_j}{c_X} = \beta y \cdot \left(\frac{\bar{\alpha} - \frac{1}{\bar{\alpha}}}{\alpha - \frac{1}{\alpha}} \right) \approx \beta y_0 \cdot \left(\frac{\bar{\alpha} - \frac{1}{\bar{\alpha}}}{\alpha - \frac{1}{\alpha}} \right) \quad \text{(S91)}$$

For the last term in the brackets in Eq(27),

$$ln\left(\frac{C_0+S_j}{C_0-S_j}\right) = ln\left(\frac{1+y}{1-y}\right) \approx ln\left(\frac{1+y_0}{1-y_0}\right) + ln\left(\frac{1+\frac{\beta y_1}{1+y_0}}{1-\frac{\beta y_1}{1-y_0}}\right) \approx ln(\alpha) + \beta y_1 \cdot \left(\frac{1}{1+y_0} + \frac{1}{1-y_0}\right) = ln(\alpha) + 2\beta y_1 \cdot \left(\frac{1}{1-y_0^2}\right) = ln(\alpha) + \frac{\beta y_1 \cdot (\alpha+1)^2}{2\alpha} \quad \text{(S92)}$$

Eq(S92) uses the approximation that $ln(1+x) = x$ and $ln\left(\frac{1}{1-x}\right) = x$ for small x. It also includes $y_0 = \frac{\alpha-1}{\alpha+1}$ so $\alpha = \frac{1+y_0}{1-y_0}$.

Substituting Eq(S92) and Eq(S91) into Eq(27) gives

$$\varphi(-1-L) - \varphi(1+L) \approx 2\left[\beta y_0 \cdot \left(\frac{\bar{\alpha} - \frac{1}{\bar{\alpha}}}{\alpha - \frac{1}{\alpha}} \right) + ln(\alpha) + \frac{\beta y_1 \cdot (\alpha+1)^2}{2\alpha} \right] \quad \text{(S93)}$$

Eq(S86) gives an expression for y_1. Use of this expression in Eq(S93) leads to

$$\varphi(-1-L)-\varphi(1+L)\approx 2\left[ln(\alpha)+\ \beta y_0\cdot\left\{\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)-\frac{\alpha}{(\alpha^2-1)}\left[\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)-\left(\frac{2}{\frac{1}{\sqrt{\alpha}}+\sqrt{\alpha}}\right)^2\cdot\left(\frac{\bar{\alpha}}{\alpha}-\frac{\alpha}{\bar{\alpha}}\right)\right]\right\}\right] \quad \text{(S94)}$$

Substituting $y_0=\frac{\alpha-1}{\alpha+1}$ and rearranging gives

$$\varphi(-1-L)-\varphi(1+L)\approx 2\left[ln(\alpha)+\ \beta\cdot\frac{1}{4}\left(\frac{2}{\frac{1}{\sqrt{\alpha}}+\sqrt{\alpha}}\right)^4\cdot\left(\frac{\bar{\alpha}}{\alpha}-\frac{\alpha}{\bar{\alpha}}\right)\right] \quad \text{(S95)}$$

Substituting $\beta\equiv\frac{L}{c_X/C_0}\cdot\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}}$ and $\alpha,\bar{\alpha}\equiv\sqrt{\frac{P_2}{P_1}},\sqrt{\frac{\bar{D}_2}{\bar{D}_1}}$ and rearranging finally yields

$$\varphi(-1-L)-\varphi(1+L)=ln\left(\frac{P_2}{P_1}\right)+\frac{8LC_0}{c_X}\cdot\frac{\frac{P_1}{\bar{D}_1}-\frac{P_2}{\bar{D}_2}}{\left(\sqrt[4]{\frac{P_2}{P_1}}+\sqrt[4]{\frac{P_1}{P_2}}\right)^4} \quad \text{(S96)}$$

S10. Derivation of Eqs(42, 43) for the flux and potential drop during current passage in the limiting case of constant electrochemical potentials across an ion-exchange membrane

For a membrane flanked by boundary layers and two perfectly stirred reservoirs with the same solution composition,

$$C_{\Delta,l}=C_{\Delta,r}=C_{\Delta,o} \quad \text{(S97)}$$

In this case, Eq(S53) becomes

$$\left(C_{\Delta,o}-\frac{S_\Delta\cdot C_0}{2S_j}\right)\cdot\frac{1}{\left(C_0-S_j\right)^2}=\left(C_{\Delta,o}-\frac{S_\Delta\cdot C_0}{2S_j}\right)\cdot\frac{1}{\left(C_0+S_j\right)^2} \quad \text{(S98)}$$

Because $\frac{1}{\left(C_0-S_j\right)^2}$ will in general not equal $\frac{1}{\left(C_0+S_j\right)^2}$, then

$$C_{\Delta,o}-\frac{S_\Delta\cdot C_0}{2S_j}=0\ so\ \frac{S_\Delta}{S_j}=\frac{2C_{\Delta,o}}{C_0} \quad \text{(S99)}$$

Using Eq(40), , $j_2=\tilde{I}-j_1$, and the definitions of S_Δ, S_j, and $C_{\Delta,o}$, and $C_0=2c_{10}+2c_{20}$, one can show that

$$\frac{S_\Delta}{S_j}\equiv\frac{j_1\cdot\left(\frac{P_2}{P_1}+1\right)-\tilde{I}}{j_1\cdot\left(\frac{P_2}{P_1}-1\right)+\tilde{I}}=\frac{2C_{\Delta,o}}{C_0}=\frac{c_{10}-c_{20}}{c_{10}+c_{20}} \quad \text{(S100)}$$

Accordingly, solving for j_1 gives

$$j_1=\frac{\tilde{I}}{\frac{P_2\cdot c_{20}}{P_1\cdot c_{10}}+1}=\frac{\tilde{I}P_1\cdot c_{10}}{P_2\cdot c_{20}+P_1\cdot c_{10}} \quad \text{(S101)}$$

Using the definition of S_j, Eq(40), and Eq(S101), we obtain

$$S_j \equiv j_1\left(\frac{1}{P_1}-\frac{1}{P_2}\right)+\frac{\tilde{I}}{P_2}=\tilde{I}\left[\frac{P_1c_{10}}{P_1c_{10}+P_2c_{20}}\left(\frac{1}{P_1}-\frac{1}{P_2}\right)+\frac{1}{P_2}\right]=\frac{\tilde{I}}{P_2}\left[\frac{c_{10}(P_2-P_1)}{P_1c_{10}+P_2c_{20}}+1\right]=\frac{\tilde{I}}{P_2}\frac{c_{10}(P_2-P_1)+P_1c_{10}+P_2c_{20}}{P_1c_{10}+P_2c_{20}}=$$
$$\tilde{I}\frac{c_{10}+c_{20}}{P_1c_{10}+P_2c_{20}}=\frac{C_0\tilde{I}/2}{P_1c_{10}+P_2c_{20}} \quad \text{(S102)}$$

Substituting Eq(S102) into Eq(21), $\varphi(-1)-\varphi(+1)=2ln\left(\frac{C_0+S_j}{C_0-S_j}\right)$, yields

$$\varphi(-1)-\varphi(1)=2ln\left(\frac{C_0+S_j}{C_0-S_j}\right)=2ln\left(\frac{C_0+\frac{C_0\tilde{I}/2}{P_1c_{10}+P_2c_{20}}}{C_0-\frac{C_0\tilde{I}/2}{P_1c_{10}+P_2c_{20}}}\right)=2ln\left(\frac{1+\frac{\tilde{I}/2}{P_1c_{10}+P_2c_{20}}}{1-\frac{\tilde{I}/2}{P_1c_{10}+P_2c_{20}}}\right)=2ln\left(\frac{P_1c_{10}+P_2c_{20}+\tilde{I}/2}{P_1c_{10}+P_2c_{20}-\tilde{I}/2}\right) \quad \text{(S103)}$$

S11. Derivation of Eq(45) for the flux of ion "1" during current passage: First-order correction to the limiting case of constant electrochemical potentials across an ion-exchange membrane

As with the bi-ionic potential, this derivation starts with Eq(S40), which we repeat hear for convenience.

$$\left(\frac{C_{\Delta,l}}{C_0}-\frac{S_\Delta}{2S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2\cdot exp\left(\frac{L\bar{S}_j}{c_X}\right)-\left(\frac{C_{\Delta,r}}{C_0}-\frac{S_\Delta}{2S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2\cdot exp\left(-\frac{L\bar{S}_j}{c_X}\right)=-\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot sinh\left(\frac{L\bar{S}_j}{c_X}\right) \quad \text{(S40)}$$

We again assume that the term $\frac{L\bar{S}_j}{c_X}$ is small, which leads to the linear approximations described previously.

$$sinh\left(\frac{L\bar{S}_j}{c_X}\right)=\frac{L\bar{S}_j}{c_X};\ exp\left(\frac{L\bar{S}_j}{c_X}\right)=1+\frac{L\bar{S}_j}{c_X};\ exp\left(-\frac{L\bar{S}_j}{c_X}\right)=1-\frac{L\bar{S}_j}{c_X} \quad \text{(S65)}$$

Substituting these approximations gives

$$\left(\frac{C_{\Delta,l}}{C_0}-\frac{S_\Delta}{2S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2+\frac{L\bar{S}_j}{c_X}\left(\frac{C_{\Delta,l}}{C_0}-\frac{S_\Delta}{2S_j}\right)\cdot\left(\frac{C_0}{C_0-S_j}\right)^2-\left(\frac{C_{\Delta,r}}{C_0}-\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2+\frac{L\bar{S}_j}{c_X}\left(\frac{C_{\Delta,r}}{C_0}-\frac{S_\Delta}{S_j}\right)\cdot\left(\frac{C_0}{C_0+S_j}\right)^2+$$
$$\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot\frac{L\bar{S}_j}{c_X}=0 \quad \text{(S104)}$$

Using $C_{\Delta,l}=C_{\Delta r}=C_{\Delta,o}$, Eq(S97), and rearranging gives

$$\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{2S_j}\right)\left[\left(\frac{C_0}{C_0-S_j}\right)^2-\left(\frac{C_0}{C_0+S_j}\right)^2\right]+\frac{L\bar{S}_j}{c_X}\left\{\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{2S_j}\right)\cdot\left[\left(\frac{C_0}{C_0-S_j}\right)^2+\left(\frac{C_0}{C_0+S_j}\right)^2\right]+\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\right\}=0 \quad \text{(S105)}$$

We will look at the different terms in this expression to eventually solve for the fluxes of individual ions. First, we remember that for applications of a constant current

$$j_2=\tilde{I}-j_1 \quad \text{(40)}$$

Accordingly based on the definitions of S_j and $\bar{S}_j$ (sums of fluxes divided by permeances)

$$S_j \equiv j_1\cdot\left(\frac{1}{P_1}-\frac{1}{P_2}\right)+\frac{\tilde{I}}{P_2} \quad \text{(S106)}$$

$$\bar{S}_j \equiv j_1\cdot\left(\frac{1}{\bar{D}_1}-\frac{1}{\bar{D}_2}\right)+\frac{\tilde{I}}{\bar{D}_2} \quad \text{(S107)}$$

$$j_1 \equiv \frac{S_j - \frac{\tilde{I}}{P_2}}{\left(\frac{1}{P_1} - \frac{1}{P_2}\right)} \tag{S108}$$

The use of Eq(S108) in Eq(S107) gives

$$\bar{S}_j \equiv \frac{S_j - \frac{\tilde{I}}{P_2}}{\left(\frac{1}{P_1} - \frac{1}{P_2}\right)} \cdot \left(\frac{1}{\bar{D}_1} - \frac{1}{\bar{D}_2}\right) + \frac{\tilde{I}}{\bar{D}_2} \tag{S109}$$

With sufficient identical transformations and substitution of $\alpha, \bar{\alpha} \equiv \sqrt{\frac{P_2}{P_1}}, \sqrt{\frac{\bar{D}_2}{\bar{D}_1}}$ into this equation, we obtain

$$\bar{S}_j \equiv \sqrt{\frac{P_1 P_2}{\bar{D}_1 \bar{D}_2}} \cdot \left[S_j \cdot \left(\frac{\bar{\alpha} - \frac{1}{\bar{\alpha}}}{\alpha - \frac{1}{\alpha}}\right) + \frac{\tilde{I}}{\sqrt{P_1 P_2}} \cdot \frac{\frac{\alpha}{\bar{\alpha}} - \frac{\bar{\alpha}}{\alpha}}{\alpha - \frac{1}{\alpha}}\right] \tag{S110}$$

As in prior derivations of corrections to bionic potentials, defining $y \equiv S_j / C_0$ leads to

$$\frac{\bar{S}_j}{C_0} \equiv \sqrt{\frac{P_1 P_2}{\bar{D}_1 \bar{D}_2}} \cdot \left[y \cdot \left(\frac{\bar{\alpha} - \frac{1}{\bar{\alpha}}}{\alpha - \frac{1}{\alpha}}\right) + \check{I} \cdot \left(\frac{\frac{\alpha}{\bar{\alpha}} - \frac{\bar{\alpha}}{\alpha}}{\alpha - \frac{1}{\alpha}}\right)\right] \tag{S111}$$

where we define a dimensionless current, $\check{I}$

$$\check{I} = \frac{\tilde{I}}{C_0 \sqrt{P_1 P_2}} \tag{S112}$$

Using Eq(S111) and the definition $\beta \equiv \frac{L}{c_X / C_0} \cdot \sqrt{\frac{P_1 P_2}{\bar{D}_1 \bar{D}_2}}$

$$\frac{L \bar{S}_j}{c_X} = L \frac{\bar{S}_j / C_0}{c_X / C_0} \equiv \frac{L}{c_X / C_0} \sqrt{\frac{P_1 P_2}{\bar{D}_1 \bar{D}_2}} \cdot \left[y \cdot \left(\frac{\bar{\alpha} - \frac{1}{\bar{\alpha}}}{\alpha - \frac{1}{\alpha}}\right) + \check{I} \cdot \left(\frac{\frac{\alpha}{\bar{\alpha}} - \frac{\bar{\alpha}}{\alpha}}{\alpha - \frac{1}{\alpha}}\right)\right] = \beta \cdot \left[y \cdot \left(\frac{\bar{\alpha} - \frac{1}{\bar{\alpha}}}{\alpha - \frac{1}{\alpha}}\right) + \check{I} \cdot \left(\frac{\frac{\alpha}{\bar{\alpha}} - \frac{\bar{\alpha}}{\alpha}}{\alpha - \frac{1}{\alpha}}\right)\right] \tag{S113}$$

Substituting Eq(S108) and Eq(40) into the definition of S_Δ

$$S_\Delta = \frac{S_j - \frac{\tilde{I}}{P_2}}{\left(\frac{1}{P_1} - \frac{1}{P_2}\right)} \cdot \left(\frac{1}{P_1} + \frac{1}{P_2}\right) - \frac{\tilde{I}}{P_2} \tag{S114}$$

With appropriate transformations and substitution of $\alpha = \sqrt{\frac{P_2}{P_1}}$,

$$S_\Delta = S_j \cdot \frac{\frac{1}{P_1} + \frac{1}{P_2}}{\frac{1}{P_1} - \frac{1}{P_2}} - \frac{\tilde{I}}{P_2} \cdot \left(1 + \frac{\frac{1}{P_1} + \frac{1}{P_2}}{\frac{1}{P_1} - \frac{1}{P_2}}\right) = S_j \cdot \frac{P_2 + P_1}{P_2 - P_1} - 2\tilde{I} \cdot \left(\frac{1}{P_2 - P_1}\right) = S_j \cdot \frac{\alpha + \frac{1}{\alpha}}{\alpha - \frac{1}{\alpha}} - \frac{2\tilde{I}}{\sqrt{P_1 P_2}} \cdot \left(\frac{1}{\alpha - \frac{1}{\alpha}}\right) \tag{S115}$$

Finally, dividing by both sides by S_j and substituting the definition of $y \equiv S_j / C_0$ and $\check{I} = \frac{\tilde{I}}{C_0 \sqrt{P_1 P_2}}$ yields

$$\frac{S_\Delta}{S_j} \equiv \left(\frac{\alpha + \frac{1}{\alpha}}{\alpha - \frac{1}{\alpha}}\right) - \frac{1}{y} \cdot \left(\frac{2\check{I}}{\alpha - \frac{1}{\alpha}}\right) \tag{S116}$$

Using a similar procedure

$$\bar{S}_\Delta \equiv \bar{S}_j \cdot \left(\frac{\bar{\alpha}+\frac{1}{\bar{\alpha}}}{\bar{\alpha}-\frac{1}{\bar{\alpha}}}\right) - \frac{2\tilde{I}}{\sqrt{\bar{D}_1\bar{D}_2}} \cdot \left(\frac{1}{\alpha-\frac{1}{\bar{\alpha}}}\right) \tag{S117}$$

Dividing both sized of Eq(117) by $\bar{S}_j$ and in the second term on the right substituting for $\bar{S}_j$from Eq(S113) leads to

$$\frac{\bar{S}_\Delta}{\bar{S}_j} = \left(\frac{\bar{\alpha}+\frac{1}{\bar{\alpha}}}{\bar{\alpha}-\frac{1}{\bar{\alpha}}}\right) - \frac{\frac{2\tilde{I}}{C_0\sqrt{\bar{D}_1\bar{D}_2}}\cdot\left(\frac{\bar{\alpha}}{\bar{\alpha}^2-1}\right)}{\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}}\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]} = \left(\frac{\bar{\alpha}+\frac{1}{\bar{\alpha}}}{\bar{\alpha}-\frac{1}{\bar{\alpha}}}\right) - \frac{\left(\frac{2\check{I}}{\bar{\alpha}-\frac{1}{\bar{\alpha}}}\right)}{y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)} \tag{S118}$$

Looking at Eq(S105), which we repeat here for convenience,

$$\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{2S_j}\right)\left[\left(\frac{C_0}{C_0-S_j}\right)^2-\left(\frac{C_0}{C_0+S_j}\right)^2\right]+\frac{L\bar{S}_j}{c_X}\left\{\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{2S_j}\right)\cdot\left[\left(\frac{C_0}{C_0-S_j}\right)^2+\left(\frac{C_0}{C_0+S_j}\right)^2\right]+\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\right\}=0 \tag{S105}$$

Considering the limiting case where $\frac{L}{c_X}$ approaches zero, $\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{S_j}\right)$ must be zero so the first term goes to zero. Thus, for small linear corrections, $\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{S_j}\right)$ should be small. In this approximation

$$\frac{L\bar{S}_j}{c_X}\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{2S_j}\right)\cdot\left[\left(\frac{C_0}{C_0-S_j}\right)^2+\left(\frac{C_0}{C_0+S_j}\right)^2\right]\approx 0 \tag{S119}$$

because it contains the product of two small terms, namely $\frac{L\bar{S}_j}{c_X}$ and $\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{2S_j}\right)$. Taking into account Eq(S119), Eq(S105) becomes

$$\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{2S_j}\right)\left[\left(\frac{C_0}{C_0-S_j}\right)^2-\left(\frac{C_0}{C_0+S_j}\right)^2\right]+\frac{L\bar{S}_j}{c_X}\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\approx 0 \tag{S120}$$

With the substitution that $y = S_j/C_0$,

$$\left(\frac{C_0}{C_0-S_j}\right)^2-\left(\frac{C_0}{C_0+S_j}\right)^2=\left(\frac{1}{1-y}\right)^2-\left(\frac{1}{1+y}\right)^2=\frac{4y}{(1-y^2)^2} \tag{S121}$$

Substituting Eq(121) and Eq(S113) into Eq(S120) gives

$$\left(2\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{S_j}\right)\cdot\frac{4y}{(1-y^2)^2}+2\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot\beta\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]\approx 0 \tag{S122}$$

Identical transformations lead to

$$2\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]=2\left\{\left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)-\left(\frac{\bar{\alpha}+\frac{1}{\bar{\bar{\alpha}}}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}\right)+\frac{\left(\frac{2\tilde{I}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}\right)}{y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\tilde{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)}-\frac{1}{y}\cdot\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\right\}\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]=2\left[\left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)-\left(\frac{\bar{\alpha}+\frac{1}{\bar{\bar{\alpha}}}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}\right)-\frac{1}{y}\cdot\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\right]\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]+\frac{4\check{I}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}} \quad \text{(S123)}$$

Noting that $\left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)-\left(\frac{\bar{\alpha}+\frac{1}{\bar{\bar{\alpha}}}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}\right)\equiv\frac{\alpha\bar{\alpha}-\frac{\alpha}{\bar{\bar{\alpha}}}+\frac{\bar{\alpha}}{\alpha}-\frac{1}{\alpha\bar{\bar{\alpha}}}-\left(\alpha\bar{\alpha}+\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}-\frac{1}{\alpha\bar{\bar{\alpha}}}\right)}{\left(\alpha-\frac{1}{\alpha}\right)\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)}\equiv-\frac{2\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)}{\left(\alpha-\frac{1}{\alpha}\right)\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)}$,

$$2\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]=2\left[\left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)-\left(\frac{\bar{\alpha}+\frac{1}{\bar{\bar{\alpha}}}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}\right)-\frac{1}{y}\cdot\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\right]\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]+\frac{4\check{I}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}=2\left[-\frac{2\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)}{\left(\alpha-\frac{1}{\alpha}\right)\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)}-\frac{1}{y}\cdot\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\right]\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\tilde{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]+\frac{4\check{I}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}=-\frac{4}{\left(\alpha-\frac{1}{\alpha}\right)^2}\left[\frac{\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)}{\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)}+\left(\frac{\check{I}}{y}\right)\right]\cdot\left[y\cdot\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)+\check{I}\cdot\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)\right]+\frac{4\check{I}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}=-\frac{4}{\left(\alpha-\frac{1}{\alpha}\right)^2}\left[y\cdot\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)+\check{I}\cdot\frac{\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)^2}{\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)}+\check{I}\cdot\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)+\frac{\check{I}^2}{y}\cdot\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)\right]+\frac{4\check{I}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}} \quad \text{(S124)}$$

In the absence of small corrections, i.e. in the limiting case where L approaches zero, the first term of Eq(105), $\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{2S_j}\right)$ must be zero. Using Eq(116)

$$\frac{2C_{\Delta,o}}{C_0}=\frac{S_\Delta}{S_j}=\left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)-\frac{1}{y_o}\cdot\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right) \quad \text{(S125)}$$

Solving Eq(S125) for y_0 yields

$$y_0=\frac{2\alpha\check{I}}{(\alpha^2+1)-2\frac{C_{\Delta,o}}{C_0}(\alpha^2-1)}=\alpha A\check{I} \quad \text{(S126)}$$

$$A=\frac{2}{(\alpha^2+1)-2\frac{C_{\Delta,o}}{C_0}(\alpha^2-1)}=\frac{1}{f+\alpha^2\cdot(1-f)};\ f=\frac{c_{10}}{c_{10}+c_{20}} \quad \text{(S127)}$$

In Eq(S122), we multiply $2\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]$ by$\cdot\,\beta$, so we can approximate y_0 for y in Eq(S124). This leads to

$$2\left(\frac{S_\Delta}{S_j}-\frac{\bar{S}_\Delta}{\bar{S}_j}\right)\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]=-\frac{4\check{I}}{\left(\alpha-\frac{1}{\alpha}\right)^2}\left[\alpha A\cdot\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)+\frac{\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)^2}{\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)}+\left(\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}\right)+\frac{1}{\alpha A}\cdot\left(\frac{\alpha}{\bar{\bar{\alpha}}}-\frac{\bar{\alpha}}{\alpha}\right)\right]+\frac{4\check{I}}{\bar{\alpha}-\frac{1}{\bar{\bar{\alpha}}}} \quad \text{(S128)}$$

In Eq(S122), with the correction, the term $\left(\frac{C_{\Delta,o}}{C_0}-\frac{S_\Delta}{S_j}\right)$ will be small. Thus, we can also susbstitute y_0 for y in the term $\frac{4y}{(1-y^2)^2}$. Finally, we return to $\frac{S_\Delta}{S_j}\equiv\left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)-\frac{1}{y}\cdot\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)$ in Eq(S116). With the substitution of $y=y_0+\beta y_1$, the expression becomes

$$\frac{S_\Delta}{S_j} \equiv \left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right) - \frac{1}{y_0+\beta y_1}\cdot\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right) \tag{S129}$$

Using the approximation that for small x, $\frac{1}{1+x} = 1 - x$,

$$\frac{S_\Delta}{S_j} \equiv \left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right) - \frac{1}{y_0\left(1+\frac{\beta y_1}{y_0}\right)}\cdot\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right) \approx \left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right) - \left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\cdot\frac{1}{y_0}\left(1-\frac{\beta y_1}{y_0}\right) = \left[\left(\frac{\alpha+\frac{1}{\alpha}}{\alpha-\frac{1}{\alpha}}\right) - \left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\cdot\frac{1}{y_0}\right] + \left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\cdot\frac{\beta y_1}{y_0^2} \tag{S130}$$

Substituting from Eq(S125)

$$\frac{S_\Delta}{S_j} = \frac{2C_{\Delta,o}}{C_0} + \left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\cdot\frac{\beta y_1}{y_0^2} \tag{S131}$$

Thus,

$$\left(\frac{2C_{\Delta,o}}{C_0} - \frac{S_\Delta}{S_j}\right)\cdot\frac{4y_0}{\left(1-y_0^2\right)^2} \approx -\frac{4y_0}{\left(1-y_0^2\right)^2}\left(\frac{2\check{I}}{\alpha-\frac{1}{\alpha}}\right)\cdot\frac{\beta y_1}{y_0^2} = -\left(\frac{8\check{I}}{\alpha-\frac{1}{\alpha}}\right)\cdot\frac{\beta y_1}{y_0\cdot\left(1-y_0^2\right)^2} \tag{S132}$$

Substituting Eq(S132) and Eq(S128) int Eq(S122) and dividing both sided by β leads to

$$-\left(\frac{8\check{I}}{\alpha-\frac{1}{\alpha}}\right)\cdot\frac{y_1}{y_0\left(1-y_0^2\right)^2} - \frac{4\check{I}}{\left(\alpha-\frac{1}{\alpha}\right)^2}\left[\alpha A\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right) + \frac{\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{}\right)^2}{\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)} + \left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right) + \frac{1}{\alpha A}\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\right] + \frac{4\check{I}}{\bar{\alpha}-\frac{1}{\bar{\alpha}}} = 0 \tag{S133}$$

Substituting $y_0 = \frac{2\alpha\check{I}}{(\alpha^2+1)-2\frac{C_{\Delta,o}}{C_0}(\alpha^2-1)} = \alpha A\check{I}$ and multiplying by by $\left(\alpha-\frac{1}{\alpha}\right)/4$ gives

$$-\frac{2y_1}{\alpha A\cdot(1-(\alpha A\check{I})^2)^2} - \frac{\check{I}}{\left(\alpha-\frac{1}{\alpha}\right)}\left[\alpha A\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right) + \frac{\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)^2}{\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)} + \left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right) + \frac{1}{\alpha A}\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\right] + \check{I}\cdot\frac{\left(\alpha-\frac{1}{\alpha}\right)}{\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)} = 0 \tag{S134}$$

Rearranging yields

$$-\frac{2y_1}{\alpha A(1-(\alpha A\check{I})^2)^2} - \frac{\check{I}}{\left(\alpha-\frac{1}{\alpha}\right)}\left[\left(\alpha A+\frac{1}{\alpha A}\right)\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right) + \frac{\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)^2}{\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)} + \left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)\right] + \check{I}\cdot\frac{\left(\alpha-\frac{1}{\alpha}\right)}{\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)} = 0 \tag{S135}$$

Through the series of transformations shown in the non-numbered equations below

$$\left(\alpha A+\frac{1}{\alpha A}\right)\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right) + \frac{\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)^2}{\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)} \equiv \left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\left[\left(\alpha A+\frac{1}{\alpha A}\right) + \frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\bar{\alpha}-\frac{1}{\bar{\alpha}}}\right] \equiv \left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\bar{\alpha}-\frac{1}{\bar{\alpha}}}\right)\left[\left(\alpha A+\frac{1}{\alpha A}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right) + \left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\right]$$

$$-\frac{2y_1}{\alpha A(1-(\alpha A\check{I})^2)^2} - \frac{\check{I}}{\left(\alpha-\frac{1}{\alpha}\right)}\left\{\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\bar{\alpha}-\frac{1}{\bar{\alpha}}}\right)\left[\left(\alpha A+\frac{1}{\alpha A}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right) + \left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\right] + \left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)\right\} + \check{I}\cdot\frac{\left(\alpha-\frac{1}{\alpha}\right)}{\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)} = 0$$

$$-\frac{2y_1}{\alpha A(1-(\alpha A\check{I})^2)^2}-\frac{\check{I}}{\left(\alpha-\frac{1}{\alpha}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)}\left\{\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\left[\left(\alpha A+\frac{1}{\alpha A}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)+\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\right]+\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)^2\right\}+\check{I}\cdot\frac{\left(\alpha-\frac{1}{\alpha}\right)}{\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)}=0$$

$$y_1=-\frac{\alpha A\left(1-(\alpha A\check{I})^2\right)^2}{2}\cdot\frac{\check{I}}{\left(\alpha-\frac{1}{\alpha}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)}\cdot\left\{\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\left[\left(\alpha A+\frac{1}{\alpha A}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)+\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\right]+\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)^2-\left(\alpha-\frac{1}{\alpha}\right)^2\right\}$$

$$\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)^2-\left(\alpha-\frac{1}{\alpha}\right)^2\equiv\left[\bar{\alpha}-\frac{1}{\bar{\alpha}}-\left(\alpha-\frac{1}{\alpha}\right)\right]\left[\bar{\alpha}-\frac{1}{\bar{\alpha}}+\left(\alpha-\frac{1}{\alpha}\right)\right]\equiv\left[\bar{\alpha}-\alpha-\left(\frac{1}{\bar{\alpha}}-\frac{1}{\alpha}\right)\right]\left[\bar{\alpha}+\alpha-\left(\frac{1}{\bar{\alpha}}+\frac{1}{\alpha}\right)\right]\equiv(\bar{\alpha}-\alpha)\left(1+\frac{1}{\bar{\alpha}\alpha}\right)(\bar{\alpha}+\alpha)\left(1-\frac{1}{\bar{\alpha}\alpha}\right)\equiv(\bar{\alpha}^2-\alpha^2)\left(1-\frac{1}{(\bar{\alpha}\alpha)^2}\right)\equiv\left(\frac{\bar{\alpha}^2-\alpha^2}{\bar{\alpha}\alpha}\right)\left(\bar{\alpha}\alpha-\frac{1}{\bar{\alpha}\alpha}\right)\equiv-\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\left(\bar{\alpha}\alpha-\frac{1}{\bar{\alpha}\alpha}\right)$$

$$y_1=-\frac{\alpha A\cdot\left(1-(\alpha A\check{I})^2\right)^2}{2}\cdot\frac{\check{I}\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)}{\left(\alpha-\frac{1}{\alpha}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)}\cdot\left\{\left[\left(\alpha A+\frac{1}{\alpha A}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)+\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\right]-\left(\bar{\alpha}\alpha-\frac{1}{\bar{\alpha}\alpha}\right)\right\}$$

$$\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)-\left(\bar{\alpha}\alpha-\frac{1}{\bar{\alpha}\alpha}\right)\equiv-\bar{\alpha}\alpha+\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}+\frac{1}{\bar{\alpha}\alpha}\equiv-\alpha\cdot\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)-\frac{1}{\alpha}\cdot\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)\equiv-\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)\left(\alpha+\frac{1}{\alpha}\right)$$

$$y_1=-\frac{\alpha A\cdot\left(1-(\alpha A\check{I})^2\right)^2}{2}\cdot\frac{\check{I}\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)}{\left(\alpha-\frac{1}{\alpha}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)}\cdot\left\{\left[\left(\alpha A+\frac{1}{\alpha A}\right)\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)-\left(\bar{\alpha}-\frac{1}{\bar{\alpha}}\right)\left(\alpha+\frac{1}{\alpha}\right)\right]\right\}\equiv-\frac{\alpha A\cdot\left(1-(\alpha A\check{I})^2\right)^2}{2}\cdot\frac{\check{I}\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)}{\left(\alpha-\frac{1}{\alpha}\right)}\cdot\left\{\left[\left(\alpha A+\frac{1}{\alpha A}\right)-\left(\alpha+\frac{1}{\alpha}\right)\right]\right\}$$

$$\frac{1}{\alpha A}-\frac{1}{\alpha}\equiv\frac{1}{\alpha}\left(\frac{1}{A}-1\right)\equiv\frac{1}{\alpha}(f+\alpha^2\cdot(1-f)-1)\equiv\frac{1}{\alpha}\cdot(1-f)(\alpha^2-1)\equiv(1-f)\left(\alpha-\frac{1}{\alpha}\right)$$

$$\alpha(A-1)\equiv\alpha\cdot\left(\frac{1}{f+\alpha^2\cdot(1-f)}-1\right)\equiv\alpha\cdot\frac{1-f-\alpha^2\cdot(1-f)}{f+\alpha^2\cdot(1-f)}\equiv\alpha\cdot(1-f)\frac{1-\alpha^2}{f+\alpha^2\cdot(1-f)}$$

$$\left(\alpha A+\frac{1}{\alpha A}\right)-\left(\alpha+\frac{1}{\alpha}\right)\equiv\alpha\cdot(1-f)\frac{1-\alpha^2}{f+\alpha^2\cdot(1-f)}+(1-f)\left(\alpha-\frac{1}{\alpha}\right)\equiv(1-f)\left(\alpha-\frac{1}{\alpha}\right)\left[1-\frac{\alpha^2}{f+\alpha^2\cdot(1-f)}\right]\equiv(1-f)\left(\alpha-\frac{1}{\alpha}\right)\frac{f+\alpha^2\cdot(1-f)-\alpha^2}{f+\alpha^2\cdot(1-f)}\equiv(1-f)\left(\alpha-\frac{1}{\alpha}\right)\frac{f\cdot(1-\alpha^2)}{f+\alpha^2\cdot(1-f)}$$

we finally obtain

$$y_1=-\frac{\alpha A\cdot\left(1-(\alpha A\check{I})^2\right)^2}{2}\cdot\frac{\check{I}\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)}{f+\alpha^2\cdot(1-f)}\cdot(1-f)\cdot f\cdot(1-\alpha^2)=-\frac{f\cdot(1-f)}{2}\cdot\alpha\cdot(1-\alpha^2)\cdot A^2\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\cdot\left[1-\left(\alpha A\check{I}\right)^2\right]^2\cdot\check{I} \quad \text{(S136)}$$

Thus,

$$y=\frac{S_j}{C_o}=y_0+\beta y_1=\alpha A\check{I}\cdot\left\{1+\frac{f\cdot(1-f)}{2}\cdot\beta\cdot(\alpha^2-1)\cdot A\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\cdot\left[1-\left(\alpha A\check{I}\right)^2\right]^2\right\} \quad \text{(S137)}$$

Remembering that y is the sum of ion fluxes divided by the total ion concentration in the bulk solution, we now need to develop this into an expression for individual ion fluxes. Based on the definition of S_j and Eq(40),

$$j_1 \cdot \left(\frac{1}{P_1} - \frac{1}{P_2}\right) \equiv S_j - \frac{\tilde{I}}{P_2} \quad \text{(S138)}$$

$$\frac{j_1}{C_0} = \frac{y - \frac{\tilde{I}}{C_0 P_2}}{\frac{1}{P_1} - \frac{1}{P_2}} = \sqrt{P_1 P_2}\frac{y - \sqrt{\frac{P_1}{P_2}} \cdot \frac{\tilde{I}}{C_0\sqrt{P_1P_2}}}{\alpha - \frac{1}{\alpha}} = \sqrt{P_1P_2} \cdot \frac{y - \frac{\check{I}}{\alpha}}{\alpha - \frac{1}{\alpha}} = \sqrt{P_1P_2} \cdot \frac{y_0 - \frac{\check{I}}{\alpha} + \beta y_1}{\alpha - \frac{1}{\alpha}} \quad \text{(S139)}$$

In principle, we can simply substitute Eq(137) into Eq(139) to obtain an expression for j_1. However, a simpler form in terms of only permeances and ion concentrations is preferable. To obtain such an expression we note that from Eq(S127) that $A = \frac{2}{(\alpha^2+1) - 2\frac{C_{\Delta,0}}{C_0}(\alpha^2-1)} = \frac{1}{f + \alpha^2 \cdot (1-f)}$; $f = \frac{c_{10}}{c_{10}+c_{20}}$.

Using Eq(S126), one can show that

$$\alpha A \check{I} = \frac{\alpha \check{I}}{f + \alpha^2 \cdot (1-f)} = \frac{\sqrt{\frac{P_2}{P_1}} \frac{\tilde{I}}{C_0\sqrt{P_1P_2}}}{\frac{c_1}{c_1+c_2} + \frac{P_2}{P_1} \cdot \left(\frac{c_2}{c_1+c_2}\right)} = \frac{\frac{\tilde{I}}{2P_1}}{c_1 + \frac{P_2}{P_1}c_2} = \frac{\frac{\tilde{I}}{2}}{P_1c_1 + P_2c_2} = \frac{\tilde{I}}{\tilde{I}_{lim}} = \frac{I}{I_{lim}} \quad \text{(S140)}$$

In Eq(S140), $\tilde{I}_{lim} = 2(P_1c_{10} + P_2c_{20})$.

Substituting from Eq(S126),

$$y_0 - \frac{\check{I}}{\alpha} = \alpha A \check{I} - \frac{\check{I}}{\alpha} = \check{I} \cdot \left(\alpha A - \frac{1}{\alpha}\right) \quad \text{(S141)}$$

Moreover, based on Eq(127),

$$\alpha A - \frac{1}{\alpha} = \frac{1}{\frac{f}{\alpha} + \alpha \cdot (1-f)} - \frac{1}{\alpha} = \frac{\alpha - \frac{f}{\alpha} - \alpha \cdot (1-f)}{f + \alpha^2 \cdot (1-f)} = \frac{f \cdot \left(\alpha - \frac{1}{\alpha}\right)}{f + \alpha^2 \cdot (1-f)}. \quad \text{(S142)}$$

Substituting Eqs(S136, S141,S142) into Eq(S139) and rearranging gives

$$\frac{j_1}{C_0\sqrt{P_1P_2}} = \frac{y_0 - \frac{\check{I}}{\alpha} + \beta y_1}{\alpha - \frac{1}{\alpha}} = \check{I} \cdot \frac{f}{f + \alpha^2 \cdot (1-f)} + \frac{\beta y_1}{\alpha - \frac{1}{\alpha}} = \frac{f \cdot \check{I}}{f + \alpha^2 \cdot (1-f)} + \alpha A \check{I} \cdot \left\{\frac{f \cdot (1-f)}{2} \cdot \beta \cdot \alpha A \cdot \left(\frac{\alpha}{\bar{\alpha}} - \frac{\bar{\alpha}}{\alpha}\right) \cdot \left[1 - \left(\alpha A \check{I}\right)^2\right]^2\right\} \quad \text{(S143)}$$

Further substituting Eq(S140) and the definitions of $\frac{\alpha}{\bar{\alpha}}, \frac{\bar{\alpha}}{\alpha}$, and $\beta \equiv \frac{L}{c_X/C_0} \cdot \sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}}$ while noting that $\beta\left(\frac{\alpha}{\bar{\alpha}} - \frac{\bar{\alpha}}{\alpha}\right) = \frac{L}{c_X/C_0}\left(\frac{P_2}{\bar{D}_2} - \frac{P_1}{\bar{D}_1}\right)$ leads to

$$\frac{j_1}{C_0\sqrt{P_1P_2}} = \frac{f \cdot \check{I}}{f + \alpha^2 \cdot (1-f)} + \frac{L}{c_X/C_0} \cdot \left(\frac{\tilde{I}}{\tilde{I}_{lim}}\right) \frac{f \cdot (1-f)}{2} \cdot \alpha A \left(\frac{P_2}{\bar{D}_2} - \frac{P_1}{\bar{D}_1}\right)\left(1 - \left(\frac{\tilde{I}}{\tilde{I}_{lim}}\right)^2\right)^2 \quad \text{(S144)}$$

Finally, solving for j_1, noting that $\tilde{I} = \check{I}C_0\sqrt{P_1P_2}$; $f = \frac{c_{10}}{c_{10}+c_{20}}$; $C_0 = 2c_{10} + 2c_{20}$, using Eq(S140) and rearranging yields

$$j_1 = \frac{f\cdot\tilde{I}}{f+\alpha^2\cdot(1-f)} + C_0\sqrt{P_1P_2}\frac{L}{c_X/C_0}\cdot\left(\frac{I}{I_{lim}}\right)\frac{f\cdot(1-f)}{2}\cdot\alpha A\left(\frac{P_2}{\bar{D}_2}-\frac{P_1}{\bar{D}_1}\right)\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)^2 = \frac{P_1c_{10}}{P_1c_{10}+P_2c_{20}}\cdot\tilde{I} + \sqrt{P_1P_2}\frac{L}{c_X}\cdot\left(\frac{I}{I_{lim}}\right)2c_{10}c_{20}\cdot\alpha A\left(\frac{P_2}{\bar{D}_2}-\frac{P_1}{\bar{D}_1}\right)\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)^2 = \frac{P_1c_{10}}{P_1c_{10}+P_2c_{20}}\cdot\tilde{I} + \sqrt{P_1P_2}\left(\frac{L}{c_X}\right)\cdot\left(\frac{I}{I_{lim}}\right)\cdot\frac{2c_{10}c_{20}}{\frac{f}{\alpha}+\alpha\cdot(1-f)}\left(\frac{P_2}{\bar{D}_2}-\frac{P_1}{\bar{D}_1}\right)\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)^2 = \frac{P_1c_{10}}{P_1c_{10}+P_2c_{20}}\cdot\tilde{I} + \left(\frac{L}{c_X/C_0}\right)\cdot\left(\frac{I}{I_{lim}}\right)\cdot\frac{c_{10}c_{20}P_1P_2}{P_1c_{10}+P_2c_{20}}\left(\frac{P_2}{\bar{D}_2}-\frac{P_1}{\bar{D}_1}\right)\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)^2 = 2P_1c_{10}\left(\frac{I}{I_{lim}}\right)\cdot\left\{1-\left(\frac{L}{2c_X/C_0}\right)\cdot\frac{c_{20}P_2}{P_1c_{10}+P_2c_{20}}\left(\frac{P_1}{\bar{D}_1}-\frac{P_2}{\bar{D}_2}\right)\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)^2\right\} \quad \text{(S145)}$$

S12. Derivation of Eq(46) for the potential drop during current passage through an ion-exchange membrane: First-order correction to the limiting case of constant electrochemical potentials across an ion-exchange membrane

This derivation begins with Eq(27), which we repeat below for convenience.

$$\varphi(-1-L) - \varphi(1+L) = 2\left[\frac{L\bar{S}_j}{c_X} + ln\left(\frac{C_0+S_j}{C_0-S_j}\right)\right] \quad (27)$$

We derived Eq(27) in Section S3. Remembering that $y = S_j/C_0$

$$\varphi(-1-L) - \varphi(1+L) = 2\left[\frac{L\bar{S}_j}{c_X} + ln\left(\frac{1+y}{1-y}\right)\right] \quad \text{(S146)}$$

As shown previously in Eq(S113),

$$\frac{L\bar{S}_j}{c_X} = \beta\cdot\left[y\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right) + \check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right] \quad \text{(S113)}$$

Note that in Eq(S113) y is multiplied by β, which is small, so we can neglect the correction and replace y with $y_0 = \alpha A\check{I}$ (Eq(S126)).

With appropriate substitutions of Eqs(S113,S126), and using the first-order correction $y = y_0 + \beta y_1$, we obtain

$$\varphi(-1-L) - \varphi(1+L) \approx 2\beta\cdot\left[\alpha A\check{I}\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right) + \check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right] + 2\left[ln\left(\frac{1+y_0}{1-y_0}\right) + ln\left(\frac{1+\frac{\beta y_1}{1+y_0}}{1-\frac{\beta y_1}{1-y_0}}\right)\right] \quad \text{(S147)}$$

Noting that for small $x, \ln(1+x) = x\ and\ \ln(1-x) = -x$

$$\varphi(-1-L) - \varphi(1+L) \approx 2\beta\cdot\left[\alpha A\check{I}\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right) + \check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right] + 2\left[ln\left(\frac{1+y_0}{1-y_0}\right) + \beta y_1\left(\frac{1}{1+y_0}+\frac{1}{1-y_0}\right)\right] \quad \text{(S148)}$$

Identical transformations give

$$\varphi(-1-L)-\varphi(1+L)\approx 2\beta\cdot\left[\alpha A\check{I}\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)\right]+2\left[ln\left(\frac{1+y_0}{1-y_0}\right)+\frac{2\beta y_1}{1-y_0^2}\right]=2ln\left(\frac{1+y_0}{1-y_0}\right)+2\beta\cdot\left[\alpha A\check{I}\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)+\check{I}\cdot\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)+\frac{2y_1}{1-y_0^2}\right] \quad \text{(S149)}$$

Based on Eqs(S126,S140), $y_0=\frac{\tilde{I}}{\tilde{I}_{lim}}=\frac{I}{I_{lim}}$, Additionally, with appropriate identical transformations, $\alpha A\cdot\left(\frac{\bar{\alpha}-\frac{1}{\bar{\alpha}}}{\alpha-\frac{1}{\alpha}}\right)+\left(\frac{\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}}{\alpha-\frac{1}{\alpha}}\right)=\frac{\alpha\left[\frac{\bar{\alpha}}{\alpha}f+\frac{\alpha}{\bar{\alpha}}(1-f)\right]}{f+\alpha^2(1-f)}=\frac{\frac{\bar{\alpha}}{\alpha}\cdot f+\frac{\alpha}{\bar{\alpha}}\cdot(1-f)}{\frac{f}{\alpha}+\alpha\cdot(1-f)}$. Substituting these expressions into Eq(S149), along with Eq(S136) and Eq(S140) gives

$$\varphi(-1-L)-\varphi(1+L)\approx 2ln\left(\frac{1+I/I_{lim}}{1-I/I_{lim}}\right)+2\beta\check{I}\cdot\left[\frac{\frac{\bar{\alpha}}{\alpha}\cdot f+\frac{\alpha}{\bar{\alpha}}\cdot(1-f)}{\frac{f}{\alpha}+\alpha\cdot(1-f)}+f\cdot(1-f)\cdot\alpha\cdot(\alpha^2-1)\cdot A^2\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\cdot\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)\right] \quad \text{(S150)}$$

Noting that $\alpha A=\frac{1}{\frac{f}{\alpha}+\alpha\cdot(1-f)}$, Eq(S150) becomes

$$\varphi(-1-L)-\varphi(1+L)=2ln\left(\frac{1+I/I_{lim}}{1-I/I_{lim}}\right)+2\beta\alpha A\check{I}\cdot\left[\left(\frac{\bar{\alpha}}{\alpha}\cdot f+\frac{\alpha}{\bar{\alpha}}\cdot(1-f)\right)+f\cdot(1-f)\cdot(\alpha^2-1)\cdot A\cdot\left(\frac{\alpha}{\bar{\alpha}}-\frac{\bar{\alpha}}{\alpha}\right)\cdot\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)\right] \quad \text{(S151)}$$

Using the following identities

$$\beta\equiv\frac{L}{c_X/C_0}\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}};\frac{\bar{\alpha}}{\alpha}\equiv\sqrt{\frac{\bar{D}_2P_1}{\bar{D}_1P_2}};\beta\frac{\bar{\alpha}}{\alpha}=\frac{L}{c_X/C_0}\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}}\sqrt{\frac{\bar{D}_2P_1}{\bar{D}_1P_2}}=\frac{L}{c_X/C_0}\frac{P_1}{\bar{D}_1};\beta\frac{\alpha}{\bar{\alpha}}\equiv\frac{L}{c_X/C_0}\sqrt{\frac{P_1P_2}{\bar{D}_1\bar{D}_2}}\sqrt{\frac{\bar{D}_1P_2}{\bar{D}_2P_1}}\equiv\frac{L}{c_X/C_0}\frac{P_2}{\bar{D}_2}$$

$$\varphi(-1-L)-\varphi(1+L)=2ln\left(\frac{1+I/I_{lim}}{1-I/I_{lim}}\right)+\frac{2LC_0}{c_X}\cdot\left(\frac{I}{I_{lim}}\right)\cdot\left[\left(\frac{P_1}{\bar{D}_1}\cdot f+\frac{P_2}{\bar{D}_2}\cdot(1-f)\right)+f\cdot(1-f)\cdot\left(\alpha-\frac{1}{\alpha}\right)\cdot\alpha A\cdot\left(\frac{P_2}{\bar{D}_2}-\frac{P_1}{\bar{D}_1}\right)\cdot\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)\right] \quad \text{(S152)}$$

Noting that $C_0f\cdot(1-f)\cdot\left(\alpha-\frac{1}{\alpha}\right)\cdot\alpha A=\frac{2c_{10}c_{20}}{c_{10}+c_{20}}\frac{P_2-P_1}{fP_1+(1-f)P_2}=\frac{2c_{10}c_{20}\cdot(P_2-P_1)}{P_1c_{10}+P_2c_{20}}$ and using identical transformations leads to

$$\varphi(-1-L)-\varphi(1+L)=2\left\{ln\left(\frac{1+I/I_{lim}}{1-I/I_{lim}}\right)+\frac{2L}{c_X}\cdot\left(\frac{I}{I_{lim}}\right)\left[\frac{P_1c_{10}}{\bar{D}_1}+\frac{P_2c_{20}}{\bar{D}_2}+\frac{c_{10}c_{20}\cdot(P_1-P_2)}{P_1c_{10}+P_2c_{20}}\cdot\left(\frac{P_1}{\bar{D}_1}-\frac{P_2}{\bar{D}_2}\right)\cdot\left(1-\left(\frac{I}{I_{lim}}\right)^2\right)\right]\right\} \quad \text{(S153)}$$

S13. Numerical simulations of bi-ionic potentials and fluxes

Nernst-Planck Equation. The model for ion transport includes diffusion and electromigration in the two boundary layers, ion partitioning at the boundary layer/membrane interfaces, and diffusion and electromigration in the membrane. We employ the Nernst-Planck equation (S154) to describe the fluxes, j_i, of specific ions in the boundary layer.

$$-\frac{j_i}{D_i} = \frac{dc_i}{dx} + z_i c_i \frac{d\varphi}{dx} \qquad \text{(S154)}$$

As previously described, D_i is the diffusion coefficient in solution, c_i is the real ion concentration, which depends on the coordinate x, z_i is the ion charge, and φ is dimensionless (in F/RT units) real electrical potential. In the ion-exchange membrane, equation (S155) describes the fluxes.

$$-\frac{j_i}{\bar{D}_i} = \frac{d\bar{c}_i}{d\bar{x}} + z_i \bar{c}_i \frac{d\bar{\varphi}}{d\bar{x}} \qquad \text{(S155)}$$

The overbars denote that the specific variables apply to the ion-exchange membrane. The concentrations and electrical potential are real, rather than virtual, quantities because we use a diffusion coefficient rather than a permeability coefficient. Thus, we also need to determine partitioning at the interface of the boundary later and the membrane. In this case, we employ the Donnan model to describe ion partitioning.

The Donnan model. In equilibrium partitioning of an ion between two phases, the ion's electrochemical potentials should be equal in the two phases. Considering membrane, M, and solution, S, phases, this gives equation (S156),

$$\bar{\mu}_i^M = \bar{\mu}_i^S \qquad \text{(S156)}$$

where $\bar{\mu}_i^M$ and $\bar{\mu}_i^S$ are the electrochemical potentials in the membrane and solution, respectively. Substituting for the electrochemical potentials leads to

$$\mu_i^{oM} + RTlna_i^M + z_i F\phi^M = \mu_i^{oS} + RTlna_i^S + z_i F\phi^S \qquad \text{(S157)}$$

In these equations, μ_i^o is the standard state chemical potential, a_i is the ion activity, and ϕ is the electrical potential for the denoted phase. Further, z_i is the ion charge, R is the gas constant and T is temperature. The Donnan model assumes that μ_i^{oM}=μ_i^{oS} and that activity coefficients are unity so activities equal concentrations. These assumptions lead to

$$\phi^M - \phi^S = \frac{RT}{z_i F} ln \frac{C_i^S}{C_i^M} \qquad \text{(S158)}$$

For a system with three ions, we can equate the potential differences for all three ions.

$$\frac{RT}{z_1 F} ln \frac{C_1^S}{C_1^M} = \frac{RT}{z_2 F} ln \frac{C_2^S}{C_2^M} = \frac{RT}{z_3 F} ln \frac{C_3^S}{C_3^M} \text{ or } \left(\frac{C_1^M}{C_1^S}\right)^{1/z_1} = \left(\frac{C_2^M}{C_2^S}\right)^{1/z_2} = \left(\frac{C_3^M}{C_3^S}\right)^{1/z_3} \qquad \text{(S159)}$$

We define a partition coefficient Γ_i

$$\Gamma_i = \frac{C_i^M}{C_i^S} \tag{S160}$$

Substituting this definition into equation (S159) yields

$$\Gamma_2 = \frac{C_2^M}{C_2^S} = \Gamma_1^{\frac{z_2}{z_1}} \text{ and } \Gamma_3 = \frac{C_3^M}{C_3^S} = \Gamma_1^{\frac{z_3}{z_1}} \tag{S161}$$

For a three-ion system, the electrical neutrality condition inside the membrane is

$$z_1 C_1^M + z_2 C_2^M + z_3 C_3^M + z_x C_x^M = 0. \tag{S162}$$

Using equations (S161) to define the concentrations in the membrane, equation (S162) becomes

$$z_1 C_1^S \Gamma_1 + z_2 C_2^S \Gamma_1^{\frac{z_2}{z_1}} + z_3 C_3^S \Gamma_1^{\frac{z_3}{z_1}} + z_x C_x^M = 0 \tag{S163}$$

Knowing the ion concentrations in solution, for a mixture of KCl and LiCl this is a quadratic equation that one can solve for Γ_1. Subsequently equation (S161) allows calculation of other ion partition coefficients and the concentrations of each ion in the membrane.

Numerical Procedures. Equations (S154 and S155) are systems of three equations (one equation for each ion). We assume that the ion-exchange membrane is homogeneous ($\frac{dc_x}{d\bar{x}} = 0$). With the assumption of electroneutrality ($\sum_i z_i c_i = 0 \; and \; \sum_i z_i \overline{c_i} = c_x$), one can transform equations (S154 and S155) into:

$$\frac{dc_i}{dx} = -\frac{j_i}{D_i} + z_i c_i \frac{\sum_i z_i \frac{j_i}{D_i}}{\sum_i z_i^2 c_i} \tag{S164}$$

$$\frac{d\overline{c_i}}{d\bar{x}} = -\frac{j_i}{\overline{D}_i} + z_i \overline{c_i} \frac{\sum_i z_i \frac{j_i}{\overline{D}_i}}{\sum_i z_i^2 \bar{c}_i} \tag{S165}$$

We assumed a thermodynamic equilibrium established at the boundary layer/membrane interface and employed the Donnan model to relate c_i and $\overline{c_i}$ at the interfaces. We treated equations (S164 and S165) as initial value problems by specifying one set of the bulk concentrations $c_i\ (-1 - L)$ as initial conditions. By inputting two ion fluxes (the third flux is specified by the zero-current condition, $\sum_i z_i j_i = 0$), we solved equations (S164 and S165) using a differential equation solver that is based on an explicit Runge-Kutta formula to get the ion concentration profiles in the boundary layers and in the membrane. In the MATLAB program, we performed iterations on the two ion fluxes until the other set of bulk concentrations $c_i\ (1 + L)$, obtained from the solver, converged with the ones we specified.

S14. Numerical simulations of current-induced concentrations polarization

The procedures for simulating current-induced concentrations polarization are largely like the ones we employed in section S13. However, the zero-current condition ($\sum_i z_i j_i = 0$) is replaced with equation (S166):

$$F \sum_i z_i j_i = I \tag{S166}$$

F is the Faraday's constant and I is the current density. We employed the same Nernst-Planck equations to describe ion transport and the Donnan model to describe ion partitioning. The numerical procedures are the same as well. We treated equations (S164 and S165) as initial value problems by specifying one set of the bulk concentrations $c_i\ (-1-L)$ as initial conditions. By specifying current density and inputting two ion fluxes (the third flux is specified by equation (S166)), we solved equations (S164 and S165) using a differential equation solver that is based on an explicit Runge-Kutta formula to get the ion concentration profiles in the boundary layers and in the membrane. In the MATLAB program, we performed iterations on the two ion fluxes until the other set of bulk concentrations $c_i\ (1+L)$, obtained from the solver, converged with the ones we specified. We provide the MATLAB program here.

MATLAB code

This is a sample program that solves the concentration profiles of K^+, Li^+, and Cl^-. The current density is 5.5 A/dm^2. The fixed charge density of the cation-exchange membrane is 1M (negative in the program to account for the negative fixed charges). Boundary layers are each 100 µm thick while the membrane is 50 µm thick. We employed literature infinite dilution values for diffusion coefficients of ions in the boundary layer and assumed different extents of reduction of diffusion coefficients in the cation exchange membrane. The bulk concentrations are 0.1 M KCl and 0.1 M LiCl in the mixture. All parameters can be easily changed in the program. However, one should input reasonable initial guesses to facilitate the iteration process.

```
clear
clf
clc

z1=1; %charge of K
z2=1; %charge of Li
z3=-1; %charge of Cl
c1L=0.1; %K concentration at the left bulk solution in M
c2L=0.1; %Li concentration at the left bulk solution in M
c3L=(z1*c1L+z2*c2L)/-(z3);
c1R=0.1; %K concentration at the right bulk solution in M
c2R=0.1; %Li concentration at the right bulk solution in M
c3R=(z1*c1R+z2*c2R)/-(z3);
cx=-1; %fixed charge density of cation exchange membrane in M
l1=100*10^-5; %boundary layer thickness in dm
l2=50*10^-5; %membrane thickness in dm
D1=1.96*10^-7; %K diffusion coefficient in boundary layer in dm^2/s
D2=1.03*10^-7; %Li diffusion coefficient in boundary layer in dm^2/s
D3=2.03*10^-7; %Cl diffusion coefficient in boundary layer in dm^2/s
D1_m=1.96*10^-8; %K diffusion coefficient in membrane in dm^2/s
D2_m=D1_m/4; %Li diffusion coefficient in membrane in dm^2/s
D3_m=D1_m*D3/D1; %Cl diffusion coefficient in membrane in dm^2/s
I=5.5; %Current Density in A/dm^2
F=96485.33; %Faraday’s constant in C/mol

j1=3.8e-5; %initial K flux guess in mol/dm^2/s
j2=1.5e-5; %initial Li flux guess in mol/dm^2/s
```

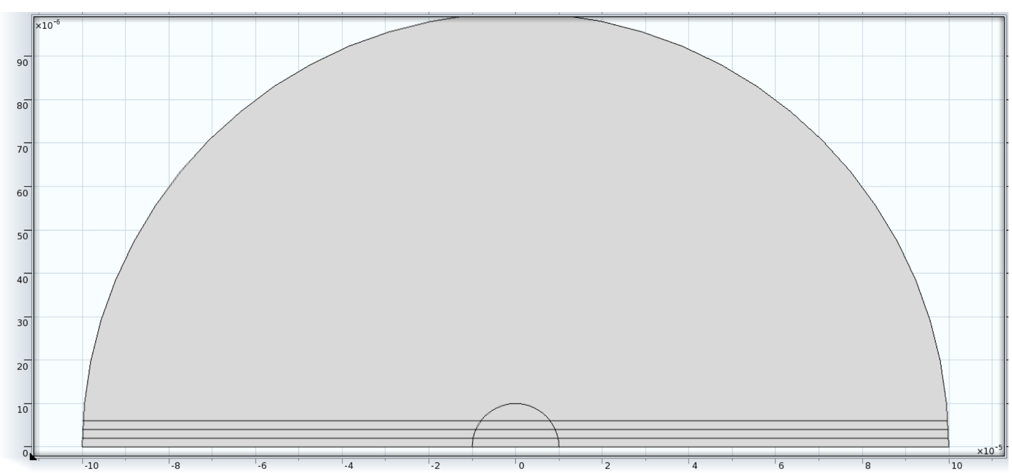
```
options = optimset('TolX',1e-18,'TolFun',1e-18,'MaxFunEvals',1e13,'MaxIter',1e13);
sol = fminsearch(@(j) funcSolve(j, z1,z2,z3,
c1L,c2L,c3L,c1R,c2R,c3R,cx,l1,l2,D1,D2,D3,D1_m,D2_m,D3_m,I,F), [j1,j2],options);
j1=sol(1);
j2=sol(2);




function [res] = funcSolve (j, z1,z2,z3,c1L,c2L,c3L,c1R,c2R,c3R,cx,l1,l2,D1,D2,D3,D1_m,D2_m,D3_m,I,F)
j1 = j(1);
j2 = j(2);
j3=(I-z1*F*j1-z2*F*j2)/z3/F;

[t1,c1]=ode45(@(t1,c1) func1(c1, D1,D2,D3,z1,z2,z3,j1,j2,j3,l1), [0 1], [c1L,c2L,c3L]);

c1_int1=c1(end,1);
c2_int1=c1(end,2);
c3_int1=c1(end,3);

p1 = [z1*c1_int1+z2*c2_int1 cx z3*c3_int1];
r1= roots(p1);
gamma1=r1(imag(r1)==0 & r1>=0);

co1=gamma1*c1_int1;
co2=(gamma1^(z2/z1))*c2_int1;
co3=(gamma1^(z3/z1))*c3_int1;

[t2,c2]=ode45(@(t2,c2) func1(c2, D1_m,D2_m,D3_m,z1,z2,z3,j1,j2,j3,l2), [0 1], [co1,co2,co3]);

ce1=c2(end,1);
ce2=c2(end,2);
ce3=c2(end,3);

p2 = [z3*ce3 0 z1*ce1+z2*ce2];
r2 = roots(p2);
gamma2=r2(imag(r2)==0 & r2>=0);

c1_int2 = ce1/gamma2;
c2_int2 = ce2/gamma2^(z2/z1);
c3_int2 = ce3/gamma2^(z3/z1);

[t3,c3]=ode45(@(t3,c3) func1(c3, D1,D2,D3,z1,z2,z3,j1,j2,j3,l1), [0 1], [c1_int2,c2_int2,c3_int2]);

c1R_out=c3(end,1);
c2R_out=c3(end,2);
```

```
c3R_out=c3(end,3);

res = (c1R_out/c1R-1)^2+(c2R_out/c2R-1)^2+(c3R_out/c3R-1)^2;

function dc = func1(c, D1,D2,D3,z1,z2,z3,j1,j2,j3,l)
dc =[-j1*l/D1+(z1*c(1)*l*((z1*j1/D1)+(z2*j2/D2)+(z3*j3/D3)))/(z1*z1*c(1)+z2*z2*c(2)+z3*z3*c(3));
      -j2*l/D2+(z2*c(2)*l*((z1*j1/D1)+(z2*j2/D2)+(z3*j3/D3)))/(z1*z1*c(1)+z2*z2*c(2)+z3*z3*c(3));
      -j3*l/D3+(z3*c(3)*l*((z1*j1/D1)+(z2*j2/D2)+(z3*j3/D3)))/(z1*z1*c(1)+z2*z2*c(2)+z3*z3*c(3))];
end
end
```

S15. Numerical simulations for modelling concentration profiles above a bipolar ion-exchange patch

To calculate the salt-concentration profiles in the two-dimensional system with a patch of a perfectly selective ion exchanger, we used Comsol Multiphysics 4.2 software. Ion fluxes in the electrolyte solution above the wall with the IEX patch were modeled using the extended Nernst-Planck Equation module, which generally accounts for diffusion, electro-migration and convective components of ion flows. However, we set the fluid flow rate to zero, as we assumed negligible convective flow. The diffusion coefficients of the ions of a 1:1 electrolyte were assumed to be $D_1 = D_2 = 2 \cdot 10^{-9}\, m^2/s$, and their electrical mobility was defined as $u_{1,2} = \frac{D_{1,2}}{RT}$. We assumed the patch width to be equal to 20 µm positioning it on the x-axis from *x* = -10 µm to *x* = + 10 µm.

The electrolyte domain was chosen in the form of a hemi-cylinder located above the wall with the center in the middle of the patch and with a radius of 100 µm. For graphing purposes, additional sections were made at the heights of 2 µm, 4 µm, and 6 µm. The mesh was generated automatically with the largest element size being 0.5 µm and the smallest being 0.001 µm. A mesh layer with increased resolution was added at the wall for improving the accuracy.



Computational domain

Since the problem involves finding two quantities, salt concentration and electrostatic potential, on each of the sections of the boundary it is necessary to set two boundary conditions. On the semi-circular boundary of the domain we set a constant electrolyte concentration equal to the bulk concentration (assumed to be 1 mM) and an electric potential that corresponds to an uniform electric field of a given strength: $\varphi = -U_0 x$.

At the wall outside the patch, the boundary conditions reflect the absence of flux of both ions normal to the surface. Obviously, these conditions automatically mean zero electrical current through the wall. For the coions the zero normal flux condition applies to the patch region, too. The second boundary condition at the patch reflects its very high permeability to the counterions so their electrochemical potential along the patch does not change:
$\mu_1 = \mu_1^0 + RT\ln C + FZ_1\varphi$ is a constant, so $RT\ln C + FZ_1\varphi$ is also a constant.

We iterated on the value of $RT\ln C + FZ_1\varphi$ so that the net normal flux of counter-ions (and electric current) through the patch was zero. At the same time, the counterions were allowed to “enter” the patch from the solution in one part of it, but had to “exit” it from another. Thus, the condition for choosing μ_1 reflects the fact that the patch is insulated from external sources of ions.