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Supplementary Information

A Symmetry Onsager matrix

Regardless of the origins of $\mathbf{L}$, the definition of $\mathbf{L}$ with the excess salt flux $J_{\text{exc}} = J - 2\rho_s Q$ instead of the total salt flux J ensures that $\mathbf{L}$ is symmetric. The Onsager matrix is namely symmetric only if the flux and the associated driving force are congruent, such that the product of the flux and the driving force gives the dissipation rate due to that flux[1–3]. We can write the dissipation rate $T\dot{S}$ as[3]

$$T\dot{S} = -\sum_{i=0}^{2} j_i \Delta v_i, \tag{1}$$

where Δv_i is the total electrochemical potential difference of the ith species between the two reservoirs and $i = 0$ for the solvent, $i = 1$ for the cation and $i = 2$ for the anion. We can write down the electrochemical potential of the ions as

$$\Delta v_i = v_i \Delta p + \Delta\mu_i + z_i e \Delta V, \tag{2}$$

with v_i, ρ_i and z_i the volume of a particle, the density and the valency of species i, Δp the pressure drop, ΔV the voltage drop and $\Delta\mu_i = k_{\text{B}}T\Delta(\log\rho_i)$ the chemical potential drop across the channel. Note that $\Delta\mu_1 = \Delta\mu_2$ due to the charge neutrality of the reservoirs. We assume the solvent to be incompressible, and therefore we can write the partial solvent pressure Δp_0 as

$$\Delta v_0 = v_0 \Delta p_0. \tag{3}$$

Now we can use van 't Hoffs law to write the total pressure p as

$$p = p_0 + \Pi = p_0 + 2\rho_s k_{\text{B}} T, \tag{4}$$

with Π the partial solute pressure. Note that in equilibrium, p is constant even if Π is not. Now we can write the dissipation rate as

$$\begin{aligned} T\dot{S} &= -j_0 v_0 \Delta p_0 - (j_1 v_1 + j_2 v_2)\Delta p - J\Delta\mu - I\Delta V, \\ &= -Q\Delta p + j_0 v_0 \Delta\pi - J\Delta\mu - I\Delta V, \end{aligned} \tag{5}$$

where we have defined the volume flux $Q = j_0 v_0 + j_1 v_1 + j_2 v_2$, solute or salt flux $J = j_1 + j_2$, charge flux $I = e(j_1 - j_2)$ and chemical potential drop $\Delta\mu = k_{\text{B}}T\Delta(\log\rho_s)$ (equal for both ions due to charge neutrality in the bulk). For dilute solutions we have that $Q \approx j_0 v_0$, and we can rewrite

$$\begin{aligned} T\dot{S} &= -Q\Delta p + 2k_{\text{B}}TQ\Delta\rho_s - J\Delta\mu - I\Delta V \\ &= -Q\Delta p - J_{\text{exc}}\Delta\mu - I\Delta V, \end{aligned} \tag{6}$$

where we have identified the excess salt flux J_{exc}

$$J_{\text{exc}} = J - 2k_{\text{B}}TQ\frac{\Delta\rho_s}{\Delta\mu}. \tag{7}$$

In order for $\mathbf{L}$ to be symmetric, J_{exc} is congruent to $\Delta\mu$. Additionally, (7) shows how to obtain the total salt flux J from the excess salt flux J_{exc} even if $\Delta\mu \neq 0$. Note that

$$\lim_{\Delta\rho_s \to 0} k_{\text{B}}T\frac{\Delta\rho_s}{\Delta\mu} = \lim_{\Delta\rho_s \to 0} k_{\text{B}}T\frac{\Delta\rho_s}{\log\left(1 + \frac{\Delta\rho_s}{\rho_1}\right)} = \rho_s, \tag{8}$$

with $\Delta\rho_s = \rho_2 - \rho_1$ the salinity drop over the channel.

B Derivation $\mathbf{G}^{\text{vol}}$

The volume contribtions of the Onsager matrix are given by

$$\mathbf{L}^{\text{vol}} = \begin{pmatrix} L_{11} & 0 & 0 \\ 0 & me^2\rho_s & me\beta\rho_s \\ 2\rho_s L_{11} & 2(me\beta + L_{12})\rho_s & 2(m + L_{13})\rho_s \end{pmatrix}, \tag{9}$$

with $m = \frac{D_+ + D_-}{2k_{\text{B}}T}$ the salt mobility, with the inverse

$$\left(\mathbf{L}^{\text{vol}}\right)^{-1} = \begin{pmatrix} \dfrac{1}{L_{11}} & 0 & 0 \\ -\dfrac{\beta}{B} & -\dfrac{m + L_{13}}{2meB}\dfrac{1}{\rho_s(z)} & \dfrac{\beta}{2B}\dfrac{1}{\rho(z)} \\ \dfrac{e}{B} & \dfrac{\beta(me + L_{12})}{2meB}\dfrac{1}{\rho_s(z)} & -\dfrac{e}{2B}\dfrac{1}{\rho_s(z)} \end{pmatrix}. \tag{10}$$

with $B = \beta^2(me + L_{12}) - e(m + L_{13})$ a constant. Given a linear $\rho_s(z) = \rho_1 + \frac{z}{\ell}\Delta\rho$, with $\Delta\rho = \rho_2 - \rho_1$, we have that

$$\int_0^\ell \mathrm{d}z \frac{1}{\rho_s(z)} = \ell \frac{\log\frac{\rho_2}{\rho_1}}{\Delta\rho}, \tag{11}$$

and we find $\left(\Delta\mu = k_{\text{B}}T\log\frac{\rho_2}{\rho_1}\right)$

$$\mathbf{G}^{\text{vol}} = \begin{pmatrix} L_{11} & 0 & 0 \\ 0 & 2De^2\frac{\Delta\rho}{\Delta\mu} & 2De\frac{\Delta\rho}{\Delta\mu}\beta \\ \frac{k_{\text{B}}T\Delta\rho}{\Delta\mu}L_{11} & 2(De + k_{\text{B}}TL_{12})\frac{\Delta\rho}{\Delta\mu}\beta & 2(D + k_{\text{B}}TL_{13})\frac{\Delta\rho}{\Delta\mu} \end{pmatrix}. \tag{12}$$

C Entrance effects

As mentioned in the main text, the salinity at both ends of the channel are not equal to the salinities imposed on the bulk, ρ_{max} and ρ_{min}. The effect is not necessarily strong, but a small change in especially the low salinity can have a significant effect on the (local) conductivity. It is therefore important to take these entrance effects into account, and the predictions are indeed much more accurate if we do. We cannot solve for the concentration profile

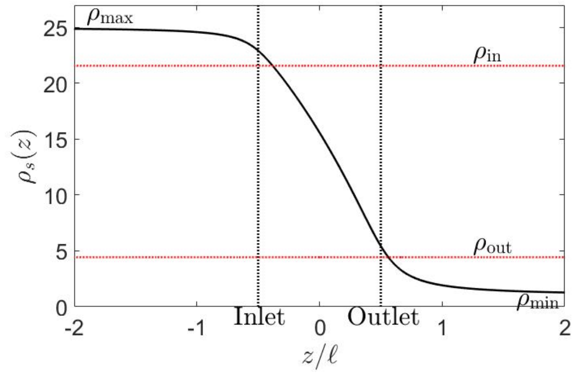

Fig. 1 Density profile at the axis of the channel calculated with FEM (black full line) for $R = 60$ nm and $\ell = 300$ nm. The dashed red lines indicate the inlet and outlet salinity ρ_{in} and ρ_{out}, and the black dashed lines indicate the location of the inlet ($z = -\frac{1}{2}\ell$) and outlet ($z = -\frac{1}{2}\ell$).

exactly (due to the complicated fluid flow en electrostatic potential profile), but we can get a good estimate by assuming that the concentration profile outside the channel drops off over a typical distance R. Since the diffusion equation has no intrinsic length scale, the geometric length R should characterise the concentration gradients outside the channel. Therefore we approximate

$$\rho_{\text{out}} \approx \rho_{\min} + R\partial_z \rho_s, \qquad \rho_{\text{in}} \approx \rho_{\max} - R\partial_z \rho_s, \tag{13}$$

where ρ_{out} is the salinity at the outlet (low salinity side) and ρ_{in} the salinity at the entrance (high salinity side). Note that the salinity gradient must be expressed in terms of ρ_{out} and ρ_{in}, $\partial_z \rho_s = \frac{\rho_{\text{out}} - \rho_{\text{in}}}{\ell}$ which we can plug into Eq. (13) and solve for ρ_{out} and ρ_{in} to find

$$\rho_{\text{out}} \approx \rho_{\min} + \frac{R}{\ell + 2R}\Delta\rho, \qquad \rho_{\text{in}} \approx \rho_{\max} - \frac{R}{\ell + 2R}\Delta\rho, \tag{14}$$

where $\Delta\rho = \rho_{\max} - \rho_{\min}$ is the imposed salinity drop across the channel. As has been shown in the main text, the entrance effect are relevant even for needle-shaped channels. As the aspect ratio increases, however, the entrance effects become even stronger. For example, Fig. 1 shows the entrance effects for a channel with $R = 60$ nm and $\ell = 300$ nm. Here we see that ρ_{in} is almost a factor 5 larger than $\rho_{\min}$, significantly affecting the total conductivity.

D Poisson-Boltzmann identities

For the calculation of $\mathbf{L}$ we assume that channel radius R, is significantly larger than the Debye length. This allows us to significantly simplify the equations in cylindrical coordinates for quantities evaluated close to the surface. In this case, we make a coordinate transformation $s = R - r$ such that

$$\nabla^2 f = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial f}{\partial r}\right) \approx \frac{\partial^2 f}{\partial s^2}, \qquad \int\limits_0^R \mathrm{d}r 2\pi r f(r) \approx 2\pi R \int\limits_0^R \mathrm{d}s f(s), \tag{15}$$

for any function $f(r)$ that only takes non-zero values inside the EDL. Therefore, if we are only considering quantities inside the EDL all calculations are basically the same if we consider a cylinder or parallel plate geometry, except for a prefactor. The parallel plate expressions can be found by simply substituting $\pi R \to H$, with H the plate separation. The error for the cylindrical geometry is of the order of λ_D/R, but for the parallel plate geometry the only error occurs as soon as the EDL significantly overlap. The expressions for $\mathbf{L}$ presented below assume non-overlapping EDLs. However, the theory remains accurate even for weakly-overlapping EDLs, since in that case the density profiles and electrostatic potential are very well approximated by the sum of the individual EDLs.

First we give the equilibrium Gouy-Chapmann expressions for a 1:1 salt[4,5] that we assume to hold for the electric double layer, where $\kappa = \lambda_D^{-1}$ is the inverse Debye length, σ the density of surface charges, z_s the sign of the surface charge, ϕ_0 the dimensionless surface potential and $\sigma^* = (2\pi\lambda_B\lambda_D)^{-1}$.

$$\begin{aligned}
&\phi(s) = 4\,\mathrm{arctanh}(\gamma e^{\kappa s}) = 2\log\frac{1+\gamma e^{-\kappa s}}{1-\gamma e^{-\kappa s}};\\
&\gamma = \tanh\frac{1}{4}\phi_0 = \frac{\sigma^*}{\sigma}\left(\sqrt{1+\left(\frac{\sigma}{\sigma^*}\right)^2} - 1\right),\\
&\rho_\pm = \rho_s e^{\mp\phi}; \qquad \frac{\sigma}{\sigma^*} = \frac{2\gamma}{1-\gamma^2}; \qquad 4\rho_s\lambda_D = \sigma^*;\\
&\sigma = \sigma^*\sinh\frac{1}{2}\phi_0;\\
&\sigma\gamma = \sqrt{\sigma^{*2}+\sigma^2} - \sigma^* = 4\rho_s\lambda_D(\cosh\frac{1}{2}\phi_0 - 1).
\end{aligned} \tag{16}$$

Next, we define a set of integrals as a function of the EDL potential which we encounter in the calculation of the Onsager coefficients. Each of these integrals are defined such they are positive, and each of these can be calculated analytically using the 1:1 Poisson-Boltzmann expressions, (16),

$$\begin{aligned}
P_1 =& \frac{z_s}{\lambda_D}\int\limits_0^\infty \mathrm{d}s\phi(s) = 2\left(\mathrm{Li}_2(|\gamma|) - \mathrm{Li}_2(-|\gamma|)\right),\\
P_2 =& \frac{1}{\lambda_D}\int\limits_0^\infty \mathrm{d}s(\cosh\phi(s) - 1) = 2(\cosh\frac{1}{2}\phi_0 - 1) = \frac{\sqrt{\sigma^{*2}+\sigma^2} - \sigma^*}{2\rho_s\lambda_D},\\
P_3 =& \frac{1}{\lambda_D^2}\int\limits_0^\infty \mathrm{d}ss(\cosh\phi(s) - 1) = 4\log\cosh\frac{1}{4}\phi_0,\\
P_4 =& \frac{1}{\lambda_D^3}\int\limits_0^\infty \mathrm{d}ss^2(\cosh\phi(s) - 1) = 2\mathrm{Li}_2(\gamma^2),\\
P_5 =& -\frac{z_s}{\lambda_D}\int\limits_0^\infty \mathrm{d}s(\phi - \phi_0)(\cosh\phi - 1) =\\
=& 2z_s\left(2\sinh\frac{1}{2}\phi_0 - \phi_0\right) = 4\frac{|\sigma|}{\sigma^*} - 2|\phi_0|,\\
P_6 =& -\frac{1}{\lambda_D}\int\limits_0^R \mathrm{d}s(\cosh\phi - 1)\log\left(1 - \gamma^2 e^{-\kappa s}\right) = 2P_3\cosh^2\frac{1}{4}\phi_0 - P_2,\\
P_3&P_2 - 2P_6 = 2P_2 - 4P_3.
\end{aligned} \tag{17}$$

The first integral P_1 can be solved by rewriting $\phi(s)$ in terms of the polylogarithmic function Li_1, and for the integrals P_2-P_6 we can use the Poisson-Boltzmann identities

$$\begin{aligned}
\phi(s) &= 2\log\frac{1+\gamma e^{-\kappa s}}{1-\gamma e^{-\kappa s}} = -\mathrm{Li}_1\left(\gamma e^{-\kappa s}\right) + \mathrm{Li}_1\left(-\gamma e^{-\kappa s}\right),\\
2(\cosh\phi - 1) &= \frac{4\gamma e^{-\kappa s}}{(1-\gamma e^{-\kappa s})^2} - \frac{4\gamma e^{-\kappa s}}{(1+\gamma e^{-\kappa s})^2}.
\end{aligned} \tag{18}$$

E Validation theory: parameter variation

Below we will show the validation of the presented theories under several parameter variations, for the diffusio-osmotic current $I_{\rm DO}$, average fluid velocity $\bar{u} = \frac{Q_{\rm DO}}{\pi R^2}$ and salt flux $J_{\rm DO}$. The red line represents the FEM results, the blue line the analytic approach (Eq. **??**), the black line exact approach (Eq. **??**). The numerical uncertainty of $I_{\rm DO}$ increases with $\rho_{\rm max}/\rho_{\rm min}$, and is typically of the order of a few pico Ampères for $\rho_{\rm max}/\rho_{\rm min} = 25$, i.e. typically much smaller than the size of the symbols. The figures below use the parameter set $\sigma = -0.05$ e/nm^2, $R = 60$ nm, $\ell = 1.5\,\mu$m, b=0 nm, and $\rho_{\rm min} = 1$ mM with a constant charge boundary condition, but with every figure one exception stated in the caption.

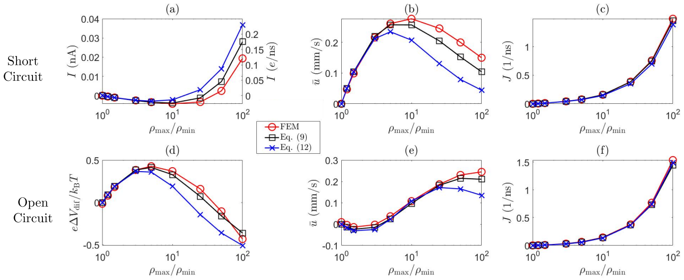

Fig. 2 NaCl (a)-(c) KCl (d)-(f), with a constant charge boundary condition (**??**) and the parameter set stated in the text.

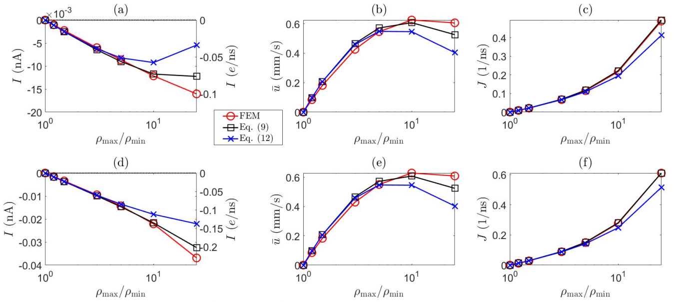

Fig. 3 NaCl (a)-(c) KCl (d)-(f), with $\sigma = -0.1$ e/nm^2 and the parameter set stated in the text.

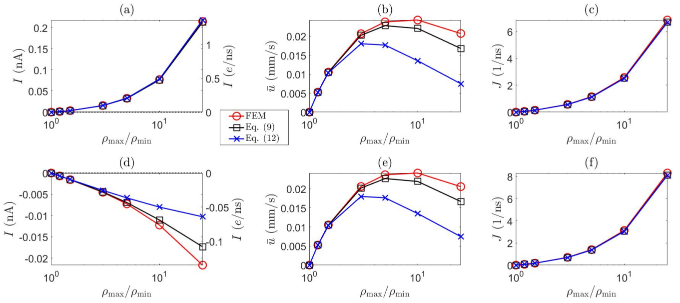

Fig. 4 NaCl (a)-(c) KCl (d)-(f), with $\rho_{\rm min} = 20$ mM and the parameter set stated in the text.

F Simulation domain

For each simulation domain use the boundary conditions.

1 (Red) Axis of rotational symmetry. All normal derivatives and velocities are zero, $\mathbf{n}\cdot\nabla\rho_i = 0 = \mathbf{n}\cdot\nabla\psi = \mathbf{n}\cdot\mathbf{u}$

2 (Dark blue) Inlet reservoir, where we fix the pressure $p = \Delta p$, salinities $\rho_\pm = \rho_{\rm max}$ and potential $\psi = \Delta V$

3,9 (Green) To simulate an infinite bulk, we impose no-slip boundary conditions $u_z = 0$ on the side of the bulk if $\Delta p \neq 0$, and otherwise an open boundary (force free boundary), and impose a fixed salinity ($\rho_\pm = \rho_{\rm max}$ for 3 and $\rho_\pm = \rho_{\rm min}$ for 9).

4,8 (Cyan) Hard walls with slip boundary condition $\mathbf{n_s}\cdot\nabla\mathbf{u}_t = b\mathbf{u}_t$ (with $\mathbf{u}_t$ the tangential component of the velocity), zero-charge $\mathbf{n}\cdot\nabla\psi = 0$ and no-flux boundary conditions, $\mathbf{n}\cdot\mathbf{J}_i = 0$

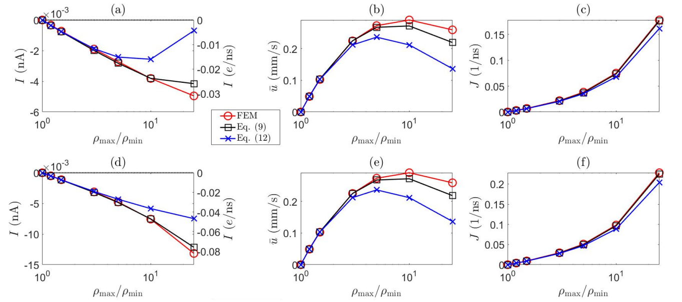

Fig. 5 NaCl (a)-(c) KCl (d)-(f), with $R = 30$ nm and the parameter set stated in the text.

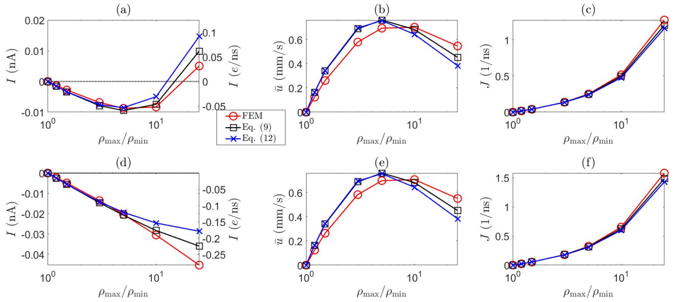

Fig. 6 NaCl (a)-(c) KCl (d)-(f), with $\ell = 0.375\,\mu$m and the parameter set stated in the text.

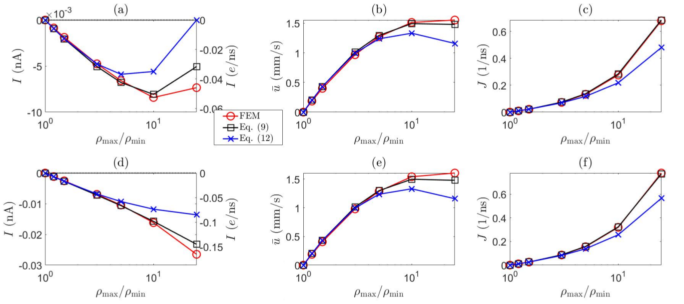

Fig. 7 NaCl (a)-(c) KCl (d)-(f), with b=10 nm, and $\rho_{\rm min} = 1$ mM and the parameter set stated in the text.

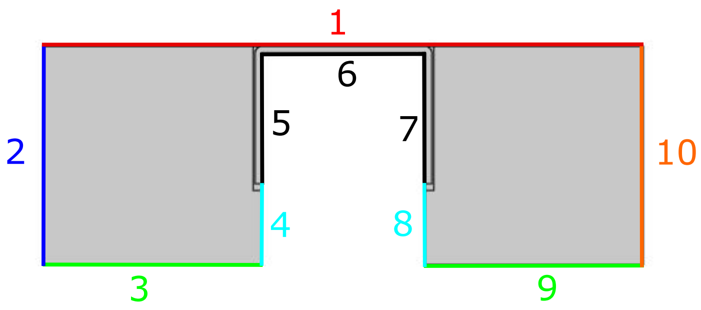

Fig. 8 Domain on which the governing equations are solved numerically with the boundaries marked (boundary conditions explained in the text.

5,6,7 (**Black**) The charged wall. The same boundary conditions as 4/8 except for a charged boundary condition $\mathbf{n}\cdot\nabla\psi = -\frac{\sigma}{\varepsilon}$, with ε the permittivity and the surface charge σ determined by the wished boundary condition (constant charge, charge regulation etc.).

10 (Orange) Outlet reservoir, $\rho_\pm = \rho_{\min}$, $\psi = 0$ and an open-boundary condition for the fluid.

G The Onsager matrix

G.1 Calculation L_{11}

Poiseuille flow through a cylindrical channel is given by

$$u_z(r) = -\frac{\partial_z p}{4\eta}\left(R^2 - r^2 + 2Rb\right) \tag{19}$$

This allows us to find the volumetric flow rate and thus the first Onsager coefficient

$$L_{11} = \frac{1}{\pi R^2}\frac{Q_S}{-\partial_z p} = \frac{\ell}{\pi R^2 \Delta p}\int_0^R \mathrm{d}r 2\pi r u(r) = -\frac{R^2}{8\eta}\left(1+\frac{4b}{R}\right), \tag{20}$$

where $\partial_z p = -\Delta p/\ell$.

G.2 Calculation L_{12}

The generated charge current due to fluid flow is given by

$$I_S = 2\pi e\int_0^r \mathrm{d}r r\rho_e(r)u(r). \tag{21}$$

We use the Poisson equation to eliminate ρ_e, and then use partial integration twice to obtain

$$\begin{aligned} I_S &= -2\pi R\varepsilon\left(-\partial_s\psi(0)u(0) + \psi(0)\partial_s u(0) + \int_0^R \mathrm{d}s\psi\partial_s^2 u\right), \\ &= -2\pi R\varepsilon\frac{\partial_z p}{4\eta}\left(-\frac{e\sigma}{\varepsilon}2bR - 2R\psi_0 + z_s\frac{k_\mathrm{B}T\lambda_D}{e}P_1\right). \end{aligned} \tag{22}$$

Here we used Gauss' law $\varepsilon\partial_s\psi(0) = -\sigma$, with σ the areal density of surface charges, and that $\partial_s^2 u = \partial_z p/(4\eta)$ from (19). Additionally, we defined $\psi_0 = \psi(0)$ as the surface potential and P_1 is one of the Poisson-Boltzmann integrals defined above (Eq. 17). Note that P_1 is a positive, dimensionless number which is still a function of the surface charge. We can now write the next Onsager coefficient as

$$L_{12} = \frac{1}{\pi R^2}\frac{I_S}{-\partial_z p} = -\frac{\varepsilon\psi_0 + be\sigma}{\eta} + z_s\frac{e\lambda_D}{2\pi\lambda_B\eta R}P_1, \tag{23}$$

G.3 Calculation L_{31}

Lastly, we must calculate the ion flux $J_{\mathrm{S,exc}} = J_s - 2\rho_s Q_S$, given by

$$\begin{aligned} J_{\mathrm{exc,S}} = J_\mathrm{S} - 2\rho_s Q_\mathrm{S} &= 2\pi\int_0^R \mathrm{d}r r(\rho_+ + \rho_- 2\rho_s)u \\ &= 2\pi\int_0^R \mathrm{d}r r(\rho_+ + \rho_- - 2\rho_s)u. \end{aligned} \tag{24}$$

This integral can now straightforwardly be rewritten as

$$J_{\mathrm{exc,S}} = \frac{\pi\rho_s\partial_z p}{\eta}R\int_0^R \mathrm{d}s(\cosh\phi(s) - 1)\left(2R(s+b) - s^2\right). \tag{25}$$

In order to calculate $J_{\mathrm{S,exc}}$, we need three Poisson-Boltzmann integrals P_2, P_3 and P_4 defined above ((17)), such that we can write the next Onsager coefficient can thus be expressed as

$$L_{13} = \frac{1}{\pi R^2}\frac{J_{\mathrm{exc,S}}}{-\partial_z p} = \frac{1}{4\pi\lambda_B\eta}\left(\frac{b}{\lambda_D}P_2 + P_3 - \frac{\lambda_D}{2R}P_4\right). \tag{26}$$

G.4 Calculation L_{12}

In the electrically driven case we have no externally applied pressure gradient and Stokes' equation reduces to

$$\eta\nabla^2 u + \rho_e E = 0, \tag{27}$$

where $E = \Delta V/\ell$ is the applied electric field, ΔV the applied potential drop over the channel and ℓ the length of the channel. Substituting Poisson's equation we find

$$\partial_z^2 u = \frac{\varepsilon E}{\eta}\partial_z^2\psi. \tag{28}$$

This equation can be integrated twice to give

$$u(s) = u_0 + \frac{\varepsilon E}{\eta}(\psi(s) - \psi_0) = \frac{E}{\eta}(\varepsilon(\psi(s) - \psi_0) - be\sigma). \tag{29}$$

Now we can calculate electro-osmotic volumetric flow rate Q_{EO},

$$Q_{\mathrm{EO}} = 2\pi\int_0^R \mathrm{d}r r u(r) = \pi R^2 u_{\mathrm{EO}} + 2\pi R\int_0^R \mathrm{d}s(u(r) - u_{\mathrm{EO}}), \tag{30}$$

here, u_{EO} is the electro-osmotic fluid flow, the (constant) fluid velocity outside of the EDL, and we have used that $u - u_{\mathrm{EO}}$ is only non-zero in the EDL. Now we find

$$Q_{\mathrm{EO}} = 2\pi\int_0^R \mathrm{d}r r u(r) = -\pi R^2 E\frac{\varepsilon\psi_0 + be\sigma}{\eta} + 2\pi R\frac{\varepsilon E}{\eta}\frac{z_s k_\mathrm{B}T}{e}\lambda_D P_1, \tag{31}$$

and subsequently the next Onsager coefficient L_{21},

$$L_{21} = \frac{1}{\pi R^2}\frac{Q_{\mathrm{EO}}}{E} = -\frac{be\sigma + \varepsilon\psi_0}{\eta} + \frac{z_s e\lambda_D}{2\pi\lambda_B\eta R}P_1. \tag{32}$$

Here we see that indeed $L_{12} = L_{21}$ as it should.

G.5 Calculation L_{22}

In the electrically driven case, we have both electric field and a fluid flow, so the current is composed of an advective ($I_{\mathrm{EO,adv}}$) and a conductive current ($I_{\mathrm{EO,con}}$). The conductive contribution to the current can expressed as

$$\begin{aligned} I_{\mathrm{EO,con}} &= 2\pi\frac{e^2}{k_{\mathrm{B}}T}E\int_0^R \mathrm{d}rr(D_+\rho_+(r) + D_-\rho_-(r)), \\ &= \pi\frac{e^2}{k_{\mathrm{B}}T}D\rho_s E\int_0^R \mathrm{d}rr(\cosh\phi - \beta\sinh\phi), \end{aligned} \tag{33}$$

where $D = \frac{1}{2}(D_+ + D_-)$, with $D_\pm$ the diffusion constant of the cation/anion and $\beta = \frac{D_+ - D_-}{D_+ + D_-}$. We must be careful here, since the integrand is not only non-zero inside the EDL, so we should not simply change coordinates to s. Therefore we split the integral in a bulk and a surface contribution,

$$I_{\mathrm{EO,con}} = 4\pi\frac{e^2}{k_{\mathrm{B}}T}D\rho_s E\left(\int_0^R \mathrm{d}rr + R\int_0^R \mathrm{d}s(\cosh\phi - 1 - \beta\sinh\phi)\right), \tag{34}$$

where we have changed the coordinates from r to s in the second integral since the integrand is only non-zero inside the EDL. We can recognise P_2 in the second term on the right hand side, and the last term is easily determined using charge conservation condition

$$\int_0^R \mathrm{d}s(\rho_+ - \rho_-) = -2\rho_s\int_0^R \mathrm{d}s\sinh\phi = -\sigma, \tag{35}$$

This allows us to write down the conductive contribution to the current,

$$I_{\mathrm{EO,cond}} = 4\pi R\frac{e^2}{k_{\mathrm{B}}T}D\rho_s E\left(\frac{1}{2}R + \lambda_D P_2 - \frac{1}{2}R\beta\frac{\sigma}{\rho_s}\right). \tag{36}$$

This leaves us to determine the advective contribution to the current $I_{\mathrm{EO,adv}}$ using (29)

$$I_{\mathrm{EO,adv}} = 2\pi Re\frac{E}{\eta}\int_0^R \mathrm{d}s(\rho_+ - \rho_-)(\varepsilon(\psi(s) - \psi_0) - be\sigma). \tag{37}$$

Interestingly, we find in $I_{\mathrm{EO,adv}}$ the self energy of the EDL, which can be expressed as

$$\frac{1}{2}e\int_0^R \mathrm{d}s(\rho_+ - \rho_-)\psi = -\frac{1}{2}e\sigma\psi_0 - \frac{k_{\mathrm{B}}T}{4\pi\lambda_B\lambda_D}P_2. \tag{38}$$

Combining this with the charge neutrality condition used above, Eq. (35), we find

$$I_{\mathrm{EO,adv}} = 2\pi Re^2\frac{E}{\eta}\left(b\sigma^2 + \frac{2}{(4\pi\lambda_B)^2\lambda_D}P_2\right). \tag{39}$$

Collecting all terms we find for the total electro-osmotically driven electric current and thus L_{22}

$$\begin{aligned} L_{22} =& \frac{1}{\pi R^2}\frac{I_{\mathrm{EO}}}{E} \\ =& \frac{2De^2}{k_{\mathrm{B}}T}\left(\rho_s + \frac{2\rho_s\lambda_D}{R}P_2\left(1 + \frac{k_{\mathrm{B}}T}{2\pi\lambda_B\eta D}\right) - \beta\frac{\sigma}{R}\right) \\ &+ 2\frac{b}{R}\frac{e^2\sigma^2}{\eta} \end{aligned} \tag{40}$$

G.6 Calculation L_{32}

Just like I_{EO}, J_{EO} contains contributions from both conduction and advection. The conduction contribution can be calculated similar to $I_{\mathrm{EO,cond}}$,

$$\begin{aligned} J_{\mathrm{EO,cond}} &= 2\pi\frac{e}{k_{\mathrm{B}}T}\int_0^R \mathrm{d}rr(D_+\rho_+ - D_-\rho_-)E \\ &= 4\pi\beta D\rho_s eE\int_0^R \mathrm{d}rr(-\sinh\phi + \beta(\cosh\phi - 1) + \beta) \end{aligned} \tag{41}$$

We have already solved these equation above, (34), so here it suffices to state the result

$$J_{\mathrm{EO,cond}} = 2\pi R\frac{e}{k_{\mathrm{B}}T}DE\left(-\sigma + \beta(\rho_s R + 2\rho_s\lambda_D P_2)\right). \tag{42}$$

We can find the advective contribution $J_{\mathrm{EO,adv}}$ as

$$\begin{aligned} J_{\mathrm{exc,EO,adv}} &= 2\pi R\int_0^R \mathrm{d}s(\rho_+ + \rho_- - 2\rho_s)u \\ &= 4\pi R\frac{E}{\eta}\int_0^R \mathrm{d}s(\cosh\phi - 1)(\varepsilon(\psi - \psi_0) - be\sigma). \end{aligned} \tag{43}$$

This integral introduces yet another Poisson-Boltzmann identity P_5, see (17), and we find

$$J_{\mathrm{exc,EO,adv}} = -2\rho_s\pi R^2\frac{eE\lambda_D}{\eta R}\left(\frac{z_s}{2\pi\lambda_B}P_5 + 2b\sigma P_2\right). \tag{44}$$

This gives the next Onsager coefficient

$$\begin{aligned} L_{23} = \frac{1}{\pi R^2}\frac{J_{\mathrm{EO}}}{E} =& -\frac{2De}{k_{\mathrm{B}}T}\left(\frac{\sigma}{R} - \beta\rho_s\left(1 + \frac{2\lambda_D}{R}P_2\right)\right) \\ &- \frac{e}{2\pi\lambda_B\lambda_D\eta R}\left(\frac{z_s}{4\pi\lambda_B}P_5 + b\sigma P_2\right) \end{aligned} \tag{45}$$

G.7 Calculation L_{13}

Contrary to an applied pressure or voltage difference, a concentration gradient does not directly induce a fluid flow because there is no body force directly related to the concentration gradient. In order for a concentration gradient to induce a fluid flow, an external potential is required that works in a direction perpendicular to the concentration gradient. In the case of a concentration gradient along a charged surface, this external potential is the electrostatic potential of the EDL. We will again assume that the EDL is in (local) equilibrium at every point along the surface. Since the salinity ρ_s is a function of z, ψ is a function of both z as well as r. Interestingly, as we will see, the lateral electric field originating from $\psi(r,z)$ will not affect the resulting fluid flow profile. First, we write the ion densities as

$$\rho_{\pm}(r,z) = \rho_s(z)e^{\mp\phi(r,z)}, \tag{46}$$

where $\phi = \frac{e}{k_{\mathrm{B}}T}\psi$ is the dimensionless EDL potential. Assuming that the r component of the fluid velocity vanishes, so we can write down the r component of Stoke's equation

$$\partial_r p = -k_{\mathrm{B}}T\rho_0(z)\left(e^{-\phi} - e^{\phi}\right)\partial_r\phi = 2k_{\mathrm{B}}T\rho_s(z)\partial_r(\cosh\phi). \tag{47}$$

Now we can easily solve for pressure, and since the pressure must be constant (p_0) outside of the EDL (a concentration gradient cannot induce a fluid flow without the external potential) we find

$$p(r,z) = p_0 + 2k_{\mathrm{B}}T\rho_s(z)(\cosh\phi(r,z) - 1). \tag{48}$$

It is this pressure, which results from a concentration gradient through the EDL, which induces the fluid flow. Plugging (48) in Stokes equation we find

$$\begin{aligned}\eta\partial_r^2 u &= 2k_{\mathrm{B}}T\partial_z(\rho_s(z)(\cosh\phi(r,z) - 1)) - e\rho_e E_z\\ &= 2k_{\mathrm{B}}T\partial_z\rho_s(\cosh\phi - 1) + 2k_{\mathrm{B}}T\rho_s\sinh\phi\,\partial_z\phi - e\rho_e(r)E_z\\ &= 2k_{\mathrm{B}}T\partial_z\rho_s(\cosh\phi - 1) - e\rho_e\partial_z\psi - e\rho_e E_z,\\ &= 2k_{\mathrm{B}}T\partial_z\rho_s(\cosh\phi - 1),\end{aligned} \tag{49}$$

where we defined $E_z = -\partial_z\psi$. Interestingly, this is the same result as the result we woudl obtain if we neglected the z dependence of the EDL potential $\phi(r,z) = \phi(r)$, although we should keep in mind that u is now a function of z even in linear response theory.

It is possible to find an exact solution to this equation with the Poisson-Boltzmann formalism. To solve for the diffusio-osmotic flow profile, we change our coordinates again to $s = R - r$ (because the driving force is only non-zero inside the EDL) and use (18), which makes it easier to integrate (49) twice and obtain

$$u_{\mathrm{DO}}(s) = -\frac{4k_{\mathrm{B}}T\lambda_D}{\eta}\partial_z\rho_s\left(\lambda_D\log\left(1 - \gamma^2 e^{-2\kappa s}\right) + (2+c)s + d\right), \tag{50}$$

where c and d are integration constants. Since all derivatives vanish on the channel axis ($s = R$), we have that the fluid flow must be constant outside of the EDL. This allows us to fix $c = -2$ such that the linear term cancels. The final constant d can then be found by imposing the slip boundary condition for u_z. The solution to the diffusio-osmotic fluid flow is then found as

$$u(s) = -\frac{k_{\mathrm{B}}T}{2\pi\eta\lambda_B}\frac{\partial_z\rho_s}{\rho_s}\left(\log\left(\frac{1-\gamma^2 e^{-2\kappa s}}{1-\gamma^2}\right) + \frac{b}{2\lambda_D}P_2\right). \tag{51}$$

We can write the diffusio-osmotic flow outside of the EDL, u_{DO}, as

$$u_{\mathrm{DO}} = -\frac{\partial_z\mu}{4\pi\eta\lambda_B}\left(P_3 + \frac{b}{\lambda_D}P_2\right) \tag{52}$$

This allows us to calculate the volumetric flow rate due to diffusio-osmosis,

$$\begin{aligned}Q_{\mathrm{DO}} =& \pi R^2 u_{\mathrm{DO}} - \frac{\partial_z\mu}{2\pi\eta\lambda_B}2\pi R\int_0^R \mathrm{d}s\log\left(1 - \gamma^2 e^{-2\kappa s}\right)\\ =& -\pi R^2\frac{\partial_z\mu}{4\pi\lambda_B\eta}\left(\frac{b}{\lambda_D}P_2 + P_3 - \frac{\lambda_D}{2R}P_4\right)\end{aligned} \tag{53}$$

and thus we find the next Onsager coefficient

$$L_{31} = \frac{1}{\pi R^2}\frac{Q_{\mathrm{DO}}}{-\partial_z\mu} = \frac{1}{4\pi\lambda_B\eta}\left(\frac{b}{\lambda_D}P_2 + P_3 - \frac{\lambda_D}{2R}P_4\right). \tag{54}$$

By comparing L_{31} with (26) we have that $L_{31} = L_{13}$ as it should.

G.8 Calculation L_{23}

The diffusio-osmotic I_{DO} consists of two contributions, from diffusion ($I_{\mathrm{DO,dif}}$) and from advection ($I_{\mathrm{DO,adv}}$). The novel contribution to L_{23} mentioned in the main text originates from $I_{\mathrm{DO,dif}}$,

$$\begin{aligned}I_{\mathrm{DO,dif}} &= -2\pi e\int_0^R \mathrm{d}r\,r\left(D_+\partial_z\rho_+ - D_-\partial_z\rho_-\right)\\ &= -4\pi De\partial_z\rho_s\int_0^R \mathrm{d}r\,r\left(-\sinh\phi + \beta(\cosh\phi - 1) + \beta\right)\end{aligned} \tag{55}$$

The first expression can be calculated using charge neutrality of the EDL and the second term is the integral P_2 defined above ((17)). We thus find

$$I_{\mathrm{DO,dif}} = -2\pi R^2\frac{De}{k_{\mathrm{B}}T}\partial_z\mu\left(-\frac{\sigma}{R} + \rho_s\beta(1 + 2\frac{\lambda_D}{R}P_2)\right). \tag{56}$$

The advective contribution to the electric current is given by

$$I_{\mathrm{DO,adv}} = 2\pi Re\int_0^R \mathrm{d}s\,\rho_e u = -2\pi R\varepsilon\int_0^R \mathrm{d}s\,u\partial_s^2\psi, \tag{57}$$

We have already calculated the $u(s)$ above. To solve for $I_{\mathrm{DO,adv}}$ it is best to rewrite this expression by partial integrating it twice,

$$I_{\mathrm{DO,adv}} = -2\pi R\varepsilon\left(-\frac{\sigma_e}{\varepsilon}u_0 + \int_0^R \mathrm{d}s(\psi - \psi_0)\partial_s^2 u(s)\right), \tag{58}$$

where we used that $\partial_s u(s = R) = 0$. Now we can plug in (49) to eliminate the $\partial_s^2 u$. This leaves the integral defined above as P_5, and we can write $I_{\mathrm{DO,adv}}$ as

$$\frac{I_{\mathrm{DO,adv}}}{\pi R^2} = \frac{e\partial_z\mu}{2\pi\lambda_B\lambda_D\eta R}\left(b\sigma P_2 + \frac{z_s}{4\pi\lambda_B}P_5\right). \tag{59}$$

Now we can write down the next Onsager coefficient,

$$\begin{aligned} L_{32} =& \frac{1}{\pi R^2}\frac{I_{\mathrm{DO}}}{-\partial_z\mu} = -\frac{2De}{k_{\mathrm{B}}T}\left(\frac{\sigma}{R} - \rho_s\beta\left(1 + 2\frac{\lambda_D}{R}P_2\right)\right) \\ & - \frac{e}{2\pi\lambda_B\lambda_D\eta R}\left(b\sigma P_2 + \frac{1}{4\pi\lambda_B}P_5\right). \end{aligned} \tag{60}$$

Comparing L_{32} with L_{23} we see that the two coefficients are indeed equal, as required.

There is, however, a subtlety involved with the above computation. This problem becomes apparent if we write the first term of $I_{\mathrm{DO,dif}}$ differently and applying charge neutrality (35) again,

$$I_{\mathrm{DO,dif}} = -4\pi De\partial_z\left(\rho_s\int_0^R \mathrm{d}rr\left(-\sinh\phi + \beta(\cosh\phi - 1) + \beta\right)\right), \tag{61}$$

Now, the problem only concerns the first term on the right hand side of (61), so we omit the terms proportional to β for clarity. We can namely use charge neutrality (35) before calculating the derivative to obtain

$$\begin{aligned} I_{\mathrm{DO,dif}} &= -4\pi De\partial_z\left(\rho_s\int_0^R \mathrm{d}rr\left(-\sinh\phi\right)\right) \\ &= -\pi DeR^2\partial_z\left(-\frac{\sigma}{R}\right) = 0, \end{aligned} \tag{62}$$

in the case of a constant σ. We thus find that, contrary to (56), this term vanishes. Both cannot be correct, and there must be a faulty assumption underlying either (56) or (56). (62) seems to be more exact, as it only relies on charge neutrality, which is probably the reason this has been adopted by previous studies[6,7]. However, we have concluded in (62) that the derivative of this term vanishes even though the only z dependence of comes from ρ_s, which is mathematically inconsistent. This does not imply that the charge neutrality condition is incorrect. On the contrary, in order for charge neutrality ((35)) to be consistent we have that ϕ also depends on z in such a way that (35) will hold. (62) therefore only holds for a consistent analysis of diffusio-osmosis that incorporates the z dependency of ϕ. Interestingly, we find that we regain (56) from such an analysis, as we will show below.

We have already shown that the fluid flow is unaffected by a laterally varying ϕ, because the resulting lateral electric field E_z cancels the electric body force in the Stokes equation. However, E_z does contribute to the electric current.. To continue, we assume that we can still use the same Poisson-Boltzmann equations for ϕ, but that this solution is now also a function of z via ρ_s and thus λ_D. This allows us to determine E_z from (16), which can be written in terms of the normal derivative $\partial_s\phi$,

$$\partial_z\phi = \frac{1}{2}\partial_s\phi\left(s + \frac{\lambda_D}{\cosh\frac{1}{2}\phi_0}\right)\partial_z(\log\rho_s). \tag{63}$$

Although this electric field will not influence the fluid flow, and thus Q_{DO} and $I_{\mathrm{DO,adv}}$, we do obtain a novel, conductive contribution to the generated electric current,

$$\begin{aligned} I_{\mathrm{DO,con}} &= -2\pi Re\int_0^R \mathrm{d}s(D_+\rho_+ + D_-\rho_-)\partial_z\phi \\ &= -4\pi RD\rho_s e\int_0^R \mathrm{d}s(\cosh\phi - \beta\sinh\phi)\partial_z\phi. \end{aligned} \tag{64}$$

In order to determine $I_{\mathrm{DO,con}}$, we first solve the integral

$$\begin{aligned} n_1 &= \int_0^R \mathrm{d}s(\cosh\phi - \beta\sinh\phi)\partial_s\phi = \int_{\phi_0}^0 \mathrm{d}\phi(\cosh\phi - \beta\sinh\phi) \\ &= -\sinh\phi_0 + \beta(\cosh\phi_0 - 1). \end{aligned} \tag{65}$$

The solution to this integral aids in solving the second integral

$$\begin{aligned} n_2 &= \int_0^R \mathrm{d}s(\cosh\phi - \beta\sinh\phi)s\partial_s\phi \\ &= [s\sinh\phi - s\beta\cosh\phi]_{s=0}^{s=R} - \int_0^R \mathrm{d}s(\sinh\phi - \beta\cosh\phi) \\ &= -\int_0^R \mathrm{d}s(\sinh\phi - \beta(\cosh\phi - 1)) = \frac{\sigma}{2\rho_s} + \beta\lambda_D P_2, \end{aligned} \tag{66}$$

where, in the last line, we have inserted the solutions to the integral P_2. The conductive contribution to the diffusio-osmotic current can, after some algebra, be written as

$$\begin{aligned} I_{\mathrm{DO,con}} &= -2\pi R\partial_z\mu\frac{De}{k_{\mathrm{B}}T}\rho_s\lambda_D\left(\frac{n_1}{\cosh\frac{1}{2}\phi_0} + \frac{n_2}{\lambda_D}\right) \\ &= 2\pi R^2\frac{De}{k_{\mathrm{B}}T}\partial_z\mu\left(\frac{\sigma}{R} - \frac{\sigma^*}{2R}\beta\left(P_2 + \frac{\cosh\frac{1}{2}\phi_0 - 1}{\cosh\frac{1}{2}\phi_0}\right)\right). \end{aligned} \tag{67}$$

As discussed, the diffusive contribution to $I_{\mathrm{DO,dif}}$ must be calculated differently if the surface potential depends on z too. Starting with (61) we find

$$\begin{aligned} I_{\mathrm{DO,dif}} &= -4\pi De\partial_z\left(-R\sigma + \beta\left(R\rho_s\lambda_D P_2 + \frac{1}{2}R^2\rho_s\right)\right) \\ &= -2\pi R^2 De\beta\left(\partial_z\rho_s + \frac{\sigma^*}{2R}\frac{\cosh\frac{1}{2}\phi_0 - 1}{\cosh\frac{1}{2}\phi_0}\partial_z\log\rho_s\right), \end{aligned} \tag{68}$$

where we used that $\partial_z(\rho_s\lambda_D P_2) = \frac{\sigma^*}{4}\left(\frac{\cosh\frac{1}{2}\phi_0 - 1}{\cosh\frac{1}{2}\phi_0}\right)$ and $\partial_z\sigma = 0$. Adding $I_{\mathrm{DO,con}}$ and $I_{\mathrm{DO,dif}}$ we find

$$I_{\mathrm{DO,dif}} + I_{\mathrm{DO,con}} = 2\pi R^2\frac{De}{k_{\mathrm{B}}T}\partial_z\mu\left(\frac{\sigma}{R} - \beta\left(1 + \frac{2\lambda_D}{R}P_2\right)\right), \tag{69}$$

which is, interestingly, exactly the same as the expression we found using before, (55). Therefore we find that even though the surface will develop a lateral electric field due to the laterally varying EDL potential, this will not alter the final equations for Q_{DO} and I_{DO} we would get if we assume a constant surface potential. This means that we can safely ignore the z dependence of ϕ, and treat it as if it is a function of r only. This gives the same result as if we would take this into account, but is much less laborious.

G.9 Calculating L_{33}

Lastly, we determine the diffusio-osmosic salt flux J_{DO}. The salt flux has two contributions, one from diffusion and one from advection,

$$J_{\mathrm{DO,dif}} = -4\pi \frac{D}{k_{\mathrm{B}}T} \partial_z \mu \int_0^R \mathrm{d}r r \left(\cosh\phi - \beta \sinh\phi\right). \tag{70}$$

These integrals are already discussed above, (34), so this allows us to write the diffusive contributions as

$$J_{\mathrm{DO,dif}} = -2\pi R^2 \partial_z \mu \frac{D}{k_{\mathrm{B}}T} \rho_s \left(1 + 2\frac{\lambda_D}{R} P_2 - \beta \frac{\sigma}{\rho_s R}\right). \tag{71}$$

This leaves us to determine the advective contribution to the salt flux,

$$\begin{aligned} J_{\mathrm{exc,DO,adv}} &= 2\pi\rho_s \int_0^R \mathrm{d}r r(\rho_+ + \rho_-)u - 2\rho_s Q_{\mathrm{DO}} \\ &= 2\pi \int_0^R \mathrm{d}r r(\rho_+ + \rho_- - 2\rho_s)u. \end{aligned} \tag{72}$$

To continue, it is convenient to split up the fluid velocity in u_{DO} and a contribution that is only non-zero inside the EDL. Then we obtain

$$\begin{aligned} J_{\mathrm{exc,DO,adv}} = -\frac{\rho_s \partial_z \mu}{\lambda_B \eta} \Bigg(&\left(P_3 + \frac{b}{\lambda_D} P_2\right) \int_0^R \mathrm{d}s(\cosh\phi - 1) \\ &+ 2\int_0^R \mathrm{d}s(\cosh\phi - 1)\log\left(1 - \gamma^2 e^{-\kappa s}\right) \Bigg), \end{aligned} \tag{73}$$

where we used the expression for u_{DO}, (52). Here we encounter a final Poisson-Boltzmann integral P_6, (17), such that we find

$$J_{\mathrm{exc,DO,adv}} = -R\frac{\partial_z \mu}{\lambda_B \eta} \rho_s \lambda_D \left(P_2\left(P_3 + \frac{b}{\lambda_D}P_2\right) - 2P_6\right). \tag{74}$$

This gives the final Onsager coefficient

$$\begin{aligned} L_{33} = \frac{1}{\pi R^2} \frac{J_{\mathrm{exc,DO}}}{-\partial_z \mu} = &\frac{2D}{k_{\mathrm{B}}T}\left(\rho_s + \frac{2\rho_s\lambda_D}{R}P_2 - \beta\frac{\sigma}{R}\right) \\ &+ \frac{\rho_s \lambda_D}{\pi \lambda_B \eta R}\left(2P_2 - 4P_3 + \frac{b}{\lambda_D}P_2^2\right). \end{aligned} \tag{75}$$

Notes and references

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