Appendix to the section:

Channel Selectivity for Ions of One Sign

This appendix contains

- more detailed results
- a homework problem

C. Peskin

<u>Selectivity for ions of one sign</u>

$$i^+ = -aq\mu\left(kT\frac{\partial c^+}{\partial x} + q\frac{\partial \phi}{\partial x}c^+\right), \qquad \frac{\partial i^+}{\partial x} = 0$$

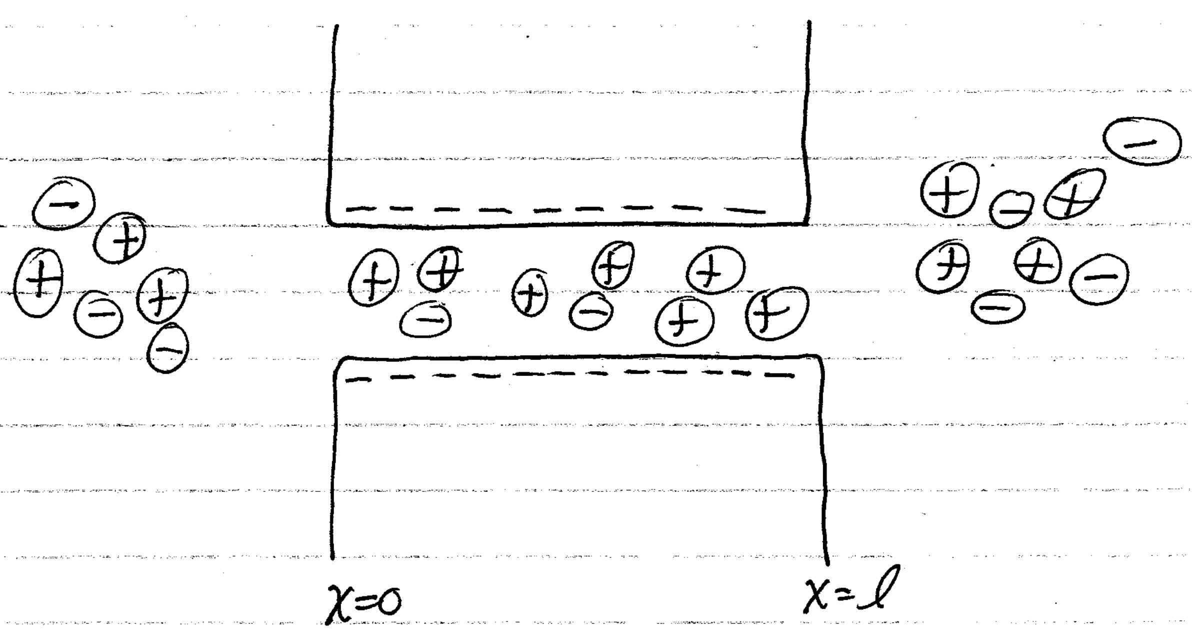
$$i^- = aq\mu\left(kT\frac{\partial c^-}{\partial x} - q\frac{\partial \phi}{\partial x}c^-\right), \qquad \frac{\partial i^-}{\partial x} = 0$$

$$-\frac{\partial^2 \phi}{\partial x^2} = \frac{q\left(c^+ - c^- - c^*\right)}{\varepsilon}$$

$c^+(0) = c_1^+$ $\qquad$ $c^+(\ell) = c_2^+$

$c^-(0) = c_1^-$ $\qquad$ $c^-(\ell) = c_2^-$

$\phi(0) = v$ $\qquad$ $\phi(\ell) = 0$



(For simplicity, assume μ is the same for both ions)

Dimensionless equations

$$I^{+} = -\left(\frac{\partial C^{+}}{\partial X} + \frac{\partial \Phi}{\partial X} C^{+}\right) \qquad \frac{\partial I^{+}}{\partial X} = 0$$

$$I^{-} = \left(\frac{\partial C^{-}}{\partial X} - \frac{\partial \Phi}{\partial X} C^{-}\right) \qquad \frac{\partial I^{-}}{\partial X} = 0$$

$$\beta^{2} \frac{\partial \Phi}{\partial X} = \left(C^{+} - C^{-} - 1\right)$$

$$C^{+}(0) = C_1^{+} \qquad C^{+}(1) = C_2^{+}$$

$$C^{-}(0) = C_1^{-} \qquad C^{-}(1) = C_2^{-}$$

$$\Phi(0) = V \qquad \Phi(1) = 0$$

As before $\beta = l_D / l$ $\qquad l_D = \sqrt{\frac{kT\varepsilon}{q^{2} C^{*}}}$

Letting $\beta \to 0$ without rescaling, we get

$$I_0^+ = -\left(\frac{\partial C_0^+}{\partial X} + \frac{\partial \Phi_0}{\partial X} C_0^+\right) \qquad \frac{\partial I^+}{\partial X} = 0$$

$$I_0^- = \left(\frac{\partial C_0^-}{\partial X} - \frac{\partial \Phi_0}{\partial X} C_0^-\right) \qquad \frac{\partial I^-}{\partial X} = 0$$

$$0 = C_0^{d+} - C_0^- - 1$$

The general thus is inconsistent with the boundary conditions, so there have to be boundary layers.

let $X = \beta X'$ etc., and then let $\beta \to 0$

We get

$$0 = -\left(\frac{\partial (C_0^{d+})'}{\partial X'} + \frac{\partial \Phi_0'}{\partial X'} (C_0^{d+})'\right)$$

$$0 = \left(\frac{\partial (C_0^{d-})'}{\partial X'} - \frac{\partial \Phi_0'}{\partial X'} (C_0^{d-})'\right)$$

$$\frac{\partial^2 \Phi_0'}{\partial (X')^2} = (C_0^{d+})' - (C_0^{d-})' - 1$$

for all X':

$$\log (C_0^+)' + \Phi_0' = \log C_1^+ + V$$
$$\log (C_0^-)' - \Phi_0' = \log C_1^- \quad V$$

$$(C_0^+)'(C_0^-)' = C_1^+ C_1^-$$

In particular

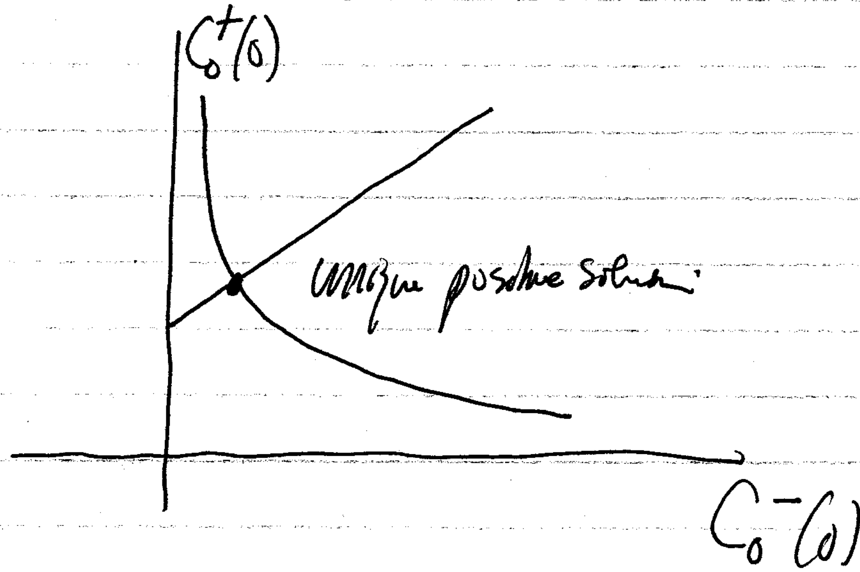
$$(C_0^+)'(\infty)(C_0^-)'(\infty) = C_1^+ C_1^-$$

$$\quad \| \qquad\qquad \|$$

$$C_0^+(0) \quad C_0^-(0) \quad = C_1^+ C_1^-$$

But also,

$$C_0^+(0) - C_0^-(0) = 1$$



Solve for $C_0^+(0)$ and $C_0^-(0)$:

$$C_0^+(0) - \frac{C_1^+C_1^-}{C_0^+(0)} = 1$$

$$\left(C_0^+(0)\right)^2 - C_0^+(0) - C_1^+C_1^- = 0$$

$$\boxed{\begin{aligned} C_0^+(0) &= \frac{1 + \sqrt{1 + 4C_1^+C_1^-}}{2} \\ C_0^-(0) &= \frac{-1 + \sqrt{1 + 4C_1^+C_1^-}}{2} \end{aligned}}$$

Check:

$$C_0^+(0) - C_0^-(0) = 1 \quad \checkmark$$

$$C_0^+(0)\, C_0^-(0) = \frac{1 + 4C_1^+C_1^- - 1}{4} = C_1^+C_1^- \quad \checkmark$$

Similarly

$$\boxed{\begin{aligned} C_0^+(1) &= \frac{1 + \sqrt{1 + 4C_2^+C_2^-}}{2} \\ C_0^-(1) &= \frac{-1 + \sqrt{1 + 4C_2^+C_2^-}}{2} \end{aligned}}$$

Now find the potentials $\Phi_0(0)$ and $\Phi_0(1)$:

Setting $X' = \infty$ and using the matching conditions, we have the following 2 equations for $\Phi_0(0)$:

$$\log C_0^+(0) + \Phi_0(0) = \log C_1^+ + V$$

$$\log C_0^-(0) - \Phi_0(0) = \log C_1^- - V$$

These yield

$$\boxed{\begin{aligned} \Phi_0(0) &= V + \log \frac{C_1^+}{C_0^+(0)} = V + \log\left(\frac{2C_1^+}{1+\sqrt{1+4C_1^+C_1^-}}\right) \\ \Phi_0(0) &= V + \log \frac{C_0^-(0)}{C_1^-} = V + \log\left(\frac{-1+\sqrt{1+4C_1^+C_1^-}}{2C_1^-}\right) \end{aligned}}$$

These are consistent, since

$$\frac{2C_1^+}{1+\sqrt{1+4C_1^+C_1^-}} \equiv \frac{-1+\sqrt{1+4C_1^+C_1^-}}{2C_1^-}$$

Similarly we get 2 equivalent formulae for $\Phi_0(1)$:

$$\Phi_0(1) = \log\left(\frac{2C_2^+}{1+\sqrt{1+4C_2^+C_2^-}}\right)$$

$$= \log\left(\frac{-1+\sqrt{1+4C_2^+C_2^-}}{2C_2^-}\right)$$

Solution of the interior equations (subject to the above boundary conditions)

$$I_0^+ = -\left(\frac{\partial C_0^+}{\partial X} + \frac{\partial \Phi_0}{\partial X} C_0^+\right) \qquad \frac{\partial I_0^+}{\partial X} = 0$$

$$I_0^- = \left(\frac{\partial C_0^-}{\partial X} - \frac{\partial \Phi_0}{\partial X} C_0^-\right) \qquad \frac{\partial I_0^-}{\partial X} = 0$$

$$0 = C_0^+ - C_0^- - 1$$

let $C_0 = C_0^+ + C_0^-$, $I_0 = I_0^+ + I_0^-$, $J_0 = I_0^+ - I_0^-$

Then, since $C_0^+ - C_0^- = 1 =$ constant

$$I_0 = -\frac{\partial \Phi_0}{\partial X} C_0$$

$$J_0 = -\frac{\partial C_0}{\partial X} - \frac{\partial \Phi_0}{\partial X}$$

First, consider the special case $I_0 = 0$. Since $C_0 \neq 0$, this implies

$$\frac{\partial \Phi_0}{\partial X} = 0$$

$$\Phi_0(1) - \Phi_0(0) = 0$$

$$V = \log\left(\frac{C_2^+}{C_1^+}\left(\frac{1 + \sqrt{1 + 4C_1^+C_1^-}}{1 + \sqrt{1 + 4C_2^+C_2^-}}\right)\right)$$

(reversal potential)

For $C_1^+ C_1^- \ll 1$ and $C_2^+ C_2^- \ll 1$, this becomes

$$V \approx \log\left(\frac{C_2^+}{C_1^+}\left(\frac{1 + C_1^+ C_1^-}{1 + C_2^+ C_2^-}\right)\right) = \log\left(\frac{C_2^+ + (C_1^+ C_2^+)\, C_1^-}{C_1^+ + (C_1^+ C_2^+)\, C_2^-}\right)$$

This is of the form

$$V \approx \log\left(\frac{P^+ C_2^+ \;\; + P^- C_1^-}{P^+ C_1^+ \;\; + P^- C_2^-}\right)$$

where $\dfrac{P^-}{P^+} = C_1^+ C_2^+$

Thus, the ~~rest~~ reversed potential of the channel is given by the constant field expression for the reversed potential with a permeability ratio given by $\dfrac{P^-}{P^+} = C_1^+ C_2^+$

Note paradoxical result that a decrease in the bath cation concentration causes stronger discrimination against anions!

Reason: increased height of the potential barriers established by the boundary layers.

How to solve for I_0, J_0 (and hence I_0^+ and I_0^-):

Integrating over $(0, 1)$:

$$J_0 = C_0(0) - C_0(1) + \Phi_0(0) - \Phi_0(1)$$

$$= \left(\sqrt{1+4C_1^+C_1^-}\right) - \left(\sqrt{1+4C_2^+C_2^-}\right)$$

$$+ V + \log\left(\frac{C_1^+}{C_2^+}\left(\frac{1+\sqrt{1+4C_2^+C_2^-}}{1+\sqrt{1+4C_1^+C_1^-}}\right)\right)$$

To find I_0, eliminate $\partial\Phi_0/\partial X$ to obtain

$$J_0 = -\frac{dC_0}{dX} + \frac{I_0}{C_0}$$

$$C_0\frac{dC_0}{dX} = I_0 - C_0 J_0$$

$$\frac{C_0\, dC_0}{I_0 - C_0 J_0} = dX$$

$$\frac{1}{J_0}\left(\frac{I_0}{I_0 - C_0 J_0} - 1\right) dC_0 = dX$$

$$\left[-\frac{I_0}{J_0^2}\log\left(I_0 - C_0 J_0\right) - \frac{C_0}{J_0}\right]\Bigg|_{X=0}^{X=1} = 1$$

$$\frac{I_0}{J_0}\log\frac{I_0-C_0(0)J_0}{I_0-C_0(1)J_0}+C_0(0)-C_0(1)=J_0$$

$$\frac{I_0}{J_0}\log\frac{(I_0/J_0)-C_0(0)}{(I_0/J_0)-C_0(1)}=J_0-(C_0(0)-C_0(1))$$

$$=\Phi_0(0)-\Phi_0(1)$$

$$\left(\frac{I_0}{J_0}\right)\log\left(\frac{(I_0/J_0)-\sqrt{1+4C_1^+C_1^-}}{(I_0/J_0)-\sqrt{1+4C_2^+C_2^-}}\right)=V+\log\left(\frac{C_1^+}{C_2^+}\left(\frac{1+\sqrt{1+4C_2^+C_2^-}}{1+\sqrt{1+4C_1^+C_1^-}}\right)\right)$$

In summary

$$J_0=\left(\sqrt{1+4C_1^+C_1^-}-\sqrt{1+4C_2^+C_2^-}\right)+(V-V_r)$$

$$\left(\frac{I_0}{J_0}\right)\log\left(\frac{(I_0/J_0)-\sqrt{1+4C_1^+C_1^-}}{(I_0/J_0)-\sqrt{1+4C_2^+C_2^-}}\right)=V-V_r$$

where

$$V_r=\log\left(\frac{C_2^+}{C_1^+}\left(\frac{1+\sqrt{1+4C_1^+C_1^-}}{1+\sqrt{1+4C_2^+C_2^-}}\right)\right)$$

let $C_1^+ C_1^- \to 0$ and $C_2^+ C_2^- \to 0$ with C_2^+/C_1^+ fixed

and assume that $V \neq \log (C_2^+/C_1^+)$

Then $$V_r \to \log \frac{C_2^+}{C_1^+}$$

$$V - V_r \to \Delta V \neq 0$$

$$J_0 \to \Delta V$$

$$I_0 / J_0 \to \gamma = ?$$

Suppose $\gamma \neq 1$, then

$$\gamma \log\left(\frac{\gamma - 1}{\gamma - 1}\right) = \Delta V$$

$$0 = \Delta V \quad \underline{\text{contradiction}}$$

Therefore $\gamma = 1$. $\quad I_0/J_0 \to 1 \quad I_0 \to \Delta V$

Thus, in the limit

$$I_0 = J_0 = V - \log \frac{C_2^+}{C_1^+}$$

$$I_0^+ = V - \log \frac{C_2^+}{C_1^+} \qquad I_0^- = 0$$

Without taking this limit, we can get a plot of I_0 and J_0 vs. V with $\gamma = I_0/J_0$ as a parameter. The computation is:

$$(V-V_r) = \gamma \log \frac{\gamma - \sqrt{1+4C_1^+C_1^-}}{\gamma - \sqrt{1+4C_2^+C_2^-}}$$

$$J_0 = (V-V_r) + \left(\sqrt{1+4C_1^+C_1^-} - \sqrt{1+4C_2^+C_2^-}\right)$$

$$I_0 = \gamma J_0$$

$$-\infty < \gamma < \min\left(\sqrt{1+4C_1^+C_1^-}, \sqrt{1+4C_2^+C_2^-}\right)$$

$$\max\left(\sqrt{1+4C_1^+C_1^-}, \sqrt{1+4C_2^+C_2^-}\right) < \gamma < \infty$$

Note: As $\gamma \to \pm\infty$, $V-V_r = \gamma \log \dfrac{1-\sqrt{1+4C_1^+C_1^-}/\gamma}{1-\sqrt{1+4C_2^+C_2^-}/\gamma}$

$$= \gamma\left[\frac{\sqrt{1+4C_2^+C_2^-} - \sqrt{1+4C_1^+C_1^-}}{\gamma} + \frac{2(C_2^+C_2^- - C_1^+C_1^-)}{\gamma^2} + \cdots\right]$$

$$= \sqrt{1+4C_2^+C_2^-} - \sqrt{1+4C_1^+C_1^-} + \frac{2}{\gamma}(C_2^+C_2^- - C_1^+C_1^-) + \cdots$$

Therefore

$$J_0 = \frac{2}{\gamma}(C_2^+C_2^- - C_1^+C_1^-) + \cdots$$

$$I_0 = 2(C_2^+C_2^- - C_1^+C_1^-) + \cdots$$

$$(V-V_r) \to \sqrt{1+4C_2^+C_2^-} - \sqrt{1+4C_1^+C_1^-}$$

$$J_0 \to 0$$

$$I_0 \to 2(C_2^+C_2^- - C_1^+C_1^-)$$

<u>Special case</u>: $C_1^+ C_1^- = C_2^+ C_2^-$ (Not covered by the foregoing)

We can construct a solution in which C_0^+, C_0^-, and $d\Phi_0/dX$ are all constant:

$$C_0^+(X) = \frac{1+\sqrt{1+4C_1^+C_1^-}}{2} = \frac{1+\sqrt{1+4C_2^+C_2^-}}{2}$$

$$C_0^-(X) = \frac{-1+\sqrt{1+4C_1^+C_1^-}}{2} = \frac{-1+\sqrt{1+4C_2^+C_2^-}}{2}$$

$$-\frac{d\Phi_0}{dX} = \Phi_0(0)-\Phi_0(1) = V + \log\left(\frac{C_1^+}{C_2^+}\right) = V - \log\frac{C_2^+}{C_1^+}$$

Then, from the original equations

$$I_0^+ = -\frac{\partial\Phi_0}{\partial X}C_0^+ = \left(V-\log\frac{C_2^+}{C_1^+}\right)\left(\frac{1+\sqrt{1+4C^+C^-}}{2}\right)$$

$$I_0^- = -\frac{\partial\Phi_0}{\partial X}C_0^- = \left(V-\log\frac{C_2^+}{C_1^+}\right)\left(\frac{-1+\sqrt{1+4C^+C^-}}{2}\right)$$

Where $C^+C^- = C_1^+C_1^- = C_2^+C_2^-$

Homework:

Plot I_0^+, I_0^-, and I_0 against V for the case

$$C_1^+ = C_1^- = 0.01$$

$$C_2^+ = C_2^- = 0.1$$

Hint: Use γ as a parameter

(see page 12)