Electrodialysis with bipolar membranes

a) Conc. NaOH — Dilute Na$_2$SO$_4$ — Conc. H$_2$SO$_4$

Cathode — BPM — CEM — AEM — BPM — Anode

Na$^+$ OH$^-$ H$^+$ SO$_4^{2-}$ OH$^-$ H$^+$

Dilute NaOH — Conc. Na$_2$SO$_4$ — Dilute H$_2$SO$_4$

BCA Configuration

d) Conc. NaOH — Dilute Na$_2$SO$_4$ — Conc. H$_2$SO$_4$

Cathode — BPM — CEM — CEM — AEM — BPM — Anode

Dilute NaOH — Conc. Na$_2$SO$_4$ — Dilute H$_2$SO$_4$

BCCA Configuration
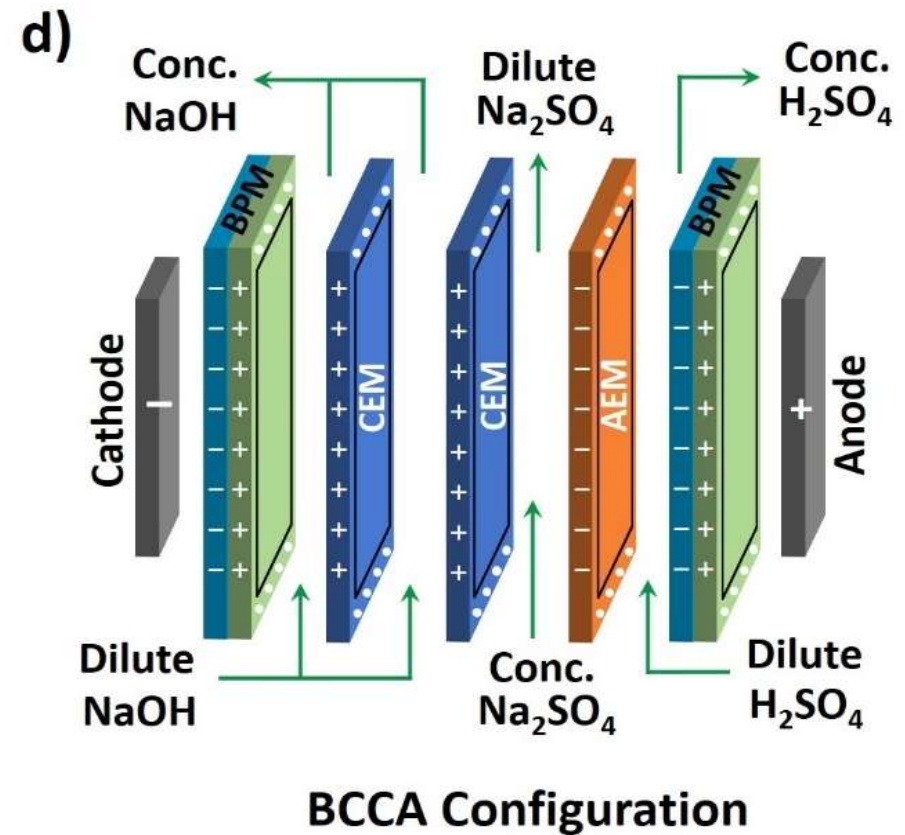
All Copper Redox Flow Battery
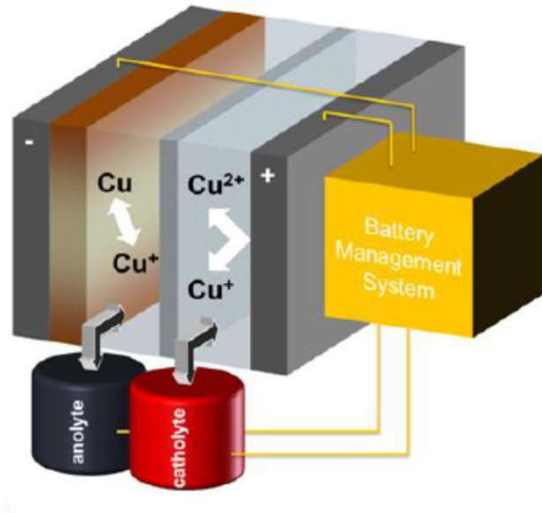
At the positive electrode (peaks 1 and 2):

(1)

$$Cu^+ \underset{Discharge}{\overset{Charge}{\rightleftarrows}} Cu^{2+} + e^-$$

(2)
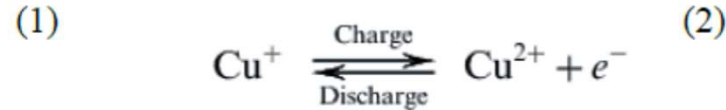
At the negative electrode (peaks 3 and 4):

(3)

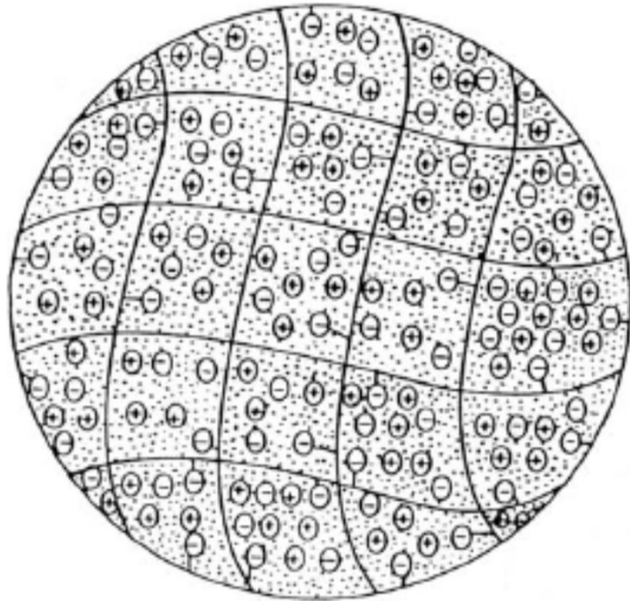$$Cu^+ + e^- \underset{Discharge}{\overset{Charge}{\rightleftarrows}} Cu^0$$

(4)
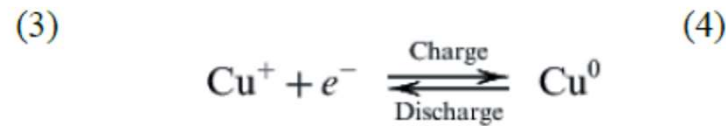
In chloride rich electrolyte the open circuit voltage of the cell is 0.65 V, as can be extracted from the peak
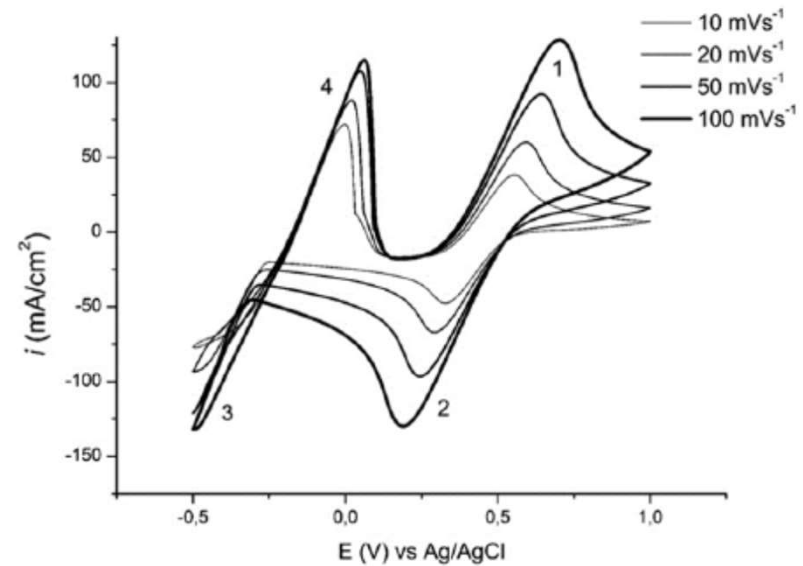
Ion-selective membranes

An ion-exchange membrane is a polymer matric containing immobilized ion exchange groups, in cation exchangers typically sulphonic acid (Nafion) and in anion exchangers amines. In Nafion it is ca. 3 mol/dm^3. Ion exchange capacity of the matrix is the concentration of the fixed concentration of the fixed groups á dry mass of the matrix because an ion exchanger swells significantly in the solution due to its high ionic strength, causing an osmotic pressure. Ions with a **charge opposite** to the fixed groups are called **counter-ions**, and ions with a **like charge co-ions**. Subscript "1" is used for the counter-ion and "2" for the co-ion.

A cation exchanger can be delivered in sodium form, i.e. with Na$^+$ counter-ions. It is converted to hydrogen form by immersing it in strong acid solution, and back to sodium form with NaOH solution.

Schematic structure of a cation exchanger. Solid lines depict for reinforcement.

Donnan equilibrium in an ion-exchanger

The general equilibrium condition between any phases is the equality of the electrochemical potential. Hence, for an ion:

$$\tilde{\mu}_i^w = \tilde{\mu}_i^M \tag{9.1}$$

and for an electrolyte:

$$\mu_{12}^M = \upsilon_1 \tilde{\mu}_1^M + \upsilon_2 \tilde{\mu}_2^M = \upsilon_1 \tilde{\mu}_1^w + \upsilon_2 \tilde{\mu}_2^w = \mu_{12}^w \tag{9.2}$$

Remembering the expression of the electrochemical potential, $\tilde{\mu}_i = \mu_i^0 + RT\ln\left(\gamma_i c_i\right) + z_i F\phi$ the equilibrium conditions become

$$\mu_i^{0,M} + RT\ln\left(\gamma_i^M c_i^M\right) + z_i F\phi^M = \mu_i^{0,w} + RT\ln\left(\gamma_i^w c_i^w\right) + z_i F\phi^w$$

$$\mu_{12}^{0,M} + RT\ln\left(\gamma_{12}^M c_{\pm,12}^M\right)^{\upsilon_{12}} = \mu_{12}^{0,w} + RT\ln\left(\gamma_{12}^w c_{\pm,12}^w\right)^{\upsilon_{12}} \tag{9.3}$$

where the mean electrolyte activity coefficient, γ_{12}, and mean electrolyte concentration, $c_{\pm,12}$, are used; $\upsilon_{12} = \upsilon_1 + \upsilon_2$. Check Lecture 1 for their definitions (or textbook p. 154). Note that due to electroneutrality the Galvani potential terms are canceled out.

Solving for the partitioning of an ion between an aqueous phase and a membrane it is obtained:

$$K_i = \frac{c_i^M}{c_i^w} = \frac{\gamma_i^w}{\gamma_i^M} \exp\left[-\frac{\mu_i^{0,M} - \mu_i^{0,w}}{RT}\right] \exp\left[-z_i f \Delta\phi_D\right]$$

(9.4)

$$K_{12} = \frac{c_{\pm,12}^M}{c_{\pm,12}^w} = \frac{\gamma_{12}^w}{\gamma_{12}^M} \exp\left[-\frac{\mu_{12}^{0,M} - \mu_{12}^{0,w}}{\upsilon_{12} RT}\right]$$

where $\Delta\phi_D = \phi^M - \phi^w$ is the Donnan potential (that cannot be measured) and $f = F/RT$. Because membranes usually contain quite a lot of water, the difference between the standard chemical potentials is ignored. Also, the activity coefficient ratio approaches unity much faster that individual activity coefficients. Therefore, we reach much simpler and useful equations:

$$c_i^M = c_i^w e^{-z_i f \Delta\phi_D}$$

$$c_{\pm,12}^M = c_{\pm,12}^w$$

(9.5)

Note that the **mean electrolyte concentration is continuous** across a phase boundary. As discussed in textbook pp. 154-155, in water the electrolyte concentration c_{12} is related to the ionic concentrations via Eqs. (4.112-113) but in a membrane via Eq. (4.114), which is the reason for using the mean electrolyte concentration instead. Considering one electrolyte, electroneutrality in a membrane reads

$$z_1 c_1^M + z_2 c_2^M + z_M c_M = 0 \quad \Rightarrow \quad X = \frac{z_M c_M}{z_2} = -\frac{z_1}{z_2} c_1^M - c_2^M$$

(9.6)

Note that X is always positive. For a symmetric electrolyte, $\upsilon_1 = \upsilon_2 = \upsilon$, $z_1 = -z_2$, $X = c_1^M - c_2^M$. Applying eq. (9.5),

$$c_{12}^w\left(e^{z_2 f \Delta \phi_D} - e^{-z_2 f \Delta \phi_D}\right) = 2c_{12}^w \sinh(z_2 f \Delta \phi_D) = X \quad \Rightarrow \quad z_2 f \Delta \phi_D = \mathrm{arcsinh}\left(\frac{X}{2c_{12}^w}\right) \tag{9.7}$$

Because $\mathrm{asinh}(x) = \ln\left(x + \sqrt{x^2 + 1}\right)$,

$$c_1^M = c_{12}^w\left(\frac{X}{2c_{12}^w} + \sqrt{\left(\frac{X}{2c_{12}^w}\right)^2 + 1}\right) = \frac{X}{2} + \sqrt{\left(\frac{X}{2}\right)^2 + \left(c_{12}^w\right)^2}$$

$$\tag{9.8}$$

$$c_2^M = c_{12}^w\left(\frac{X}{2c_{12}^w} + \sqrt{\left(\frac{X}{2c_{12}^w}\right)^2 + 1}\right)^{-1} = -\frac{X}{2} + \sqrt{\left(\frac{X}{2}\right)^2 + \left(c_{12}^w\right)^2}$$

Multiplying the above equations with each other it is seen that $c_1^M c_2^M = \left(c_{12}^w\right)^2$, as expected. This result would have been obtained more simply by solving the 2nd order equation

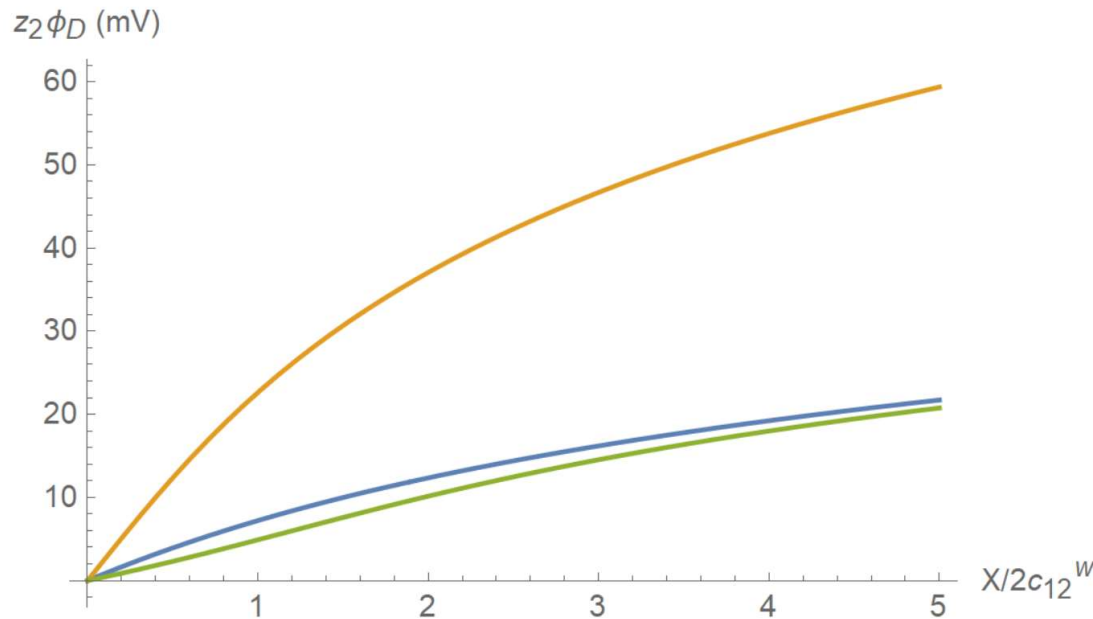$$\left(c_{12}^w\right)^2 = \left(c_2^M + X\right)c_2^M \tag{9.10}$$

For asymmetric electrolytes Donnan potential must be solved numerically, or as a root of a 3rd order polynomial with respect of $e^{zf\Delta\phi_D}$.

2:1 electrolyte, $z_1 = -2z_2$, $\upsilon_1 = 1$, $\upsilon_2 = 2$:

$$2c_{12}^w \left(e^{2z_2 f\Delta\phi_D} - e^{-z_2 f\Delta\phi_D} \right) = X \quad \Leftrightarrow \quad \frac{X}{2c_{12}^w} = e^{2z_2 f\Delta\phi_D} - e^{-z_2 f\Delta\phi_D} \tag{9.11}$$

1:2 electrolyte, $2z_1 = -z_2$, $\upsilon_1 = 2$, $\upsilon_2 = 1$:

$$2c_{12}^w \left(e^{-z_1 f\Delta\phi_D} - e^{2z_1 f\Delta\phi_D} \right) = X \quad \Leftrightarrow \quad \frac{X}{2c_{12}^w} = e^{-z_1 f\Delta\phi_D} - e^{2z_1 f\Delta\phi_D} \tag{9.12}$$
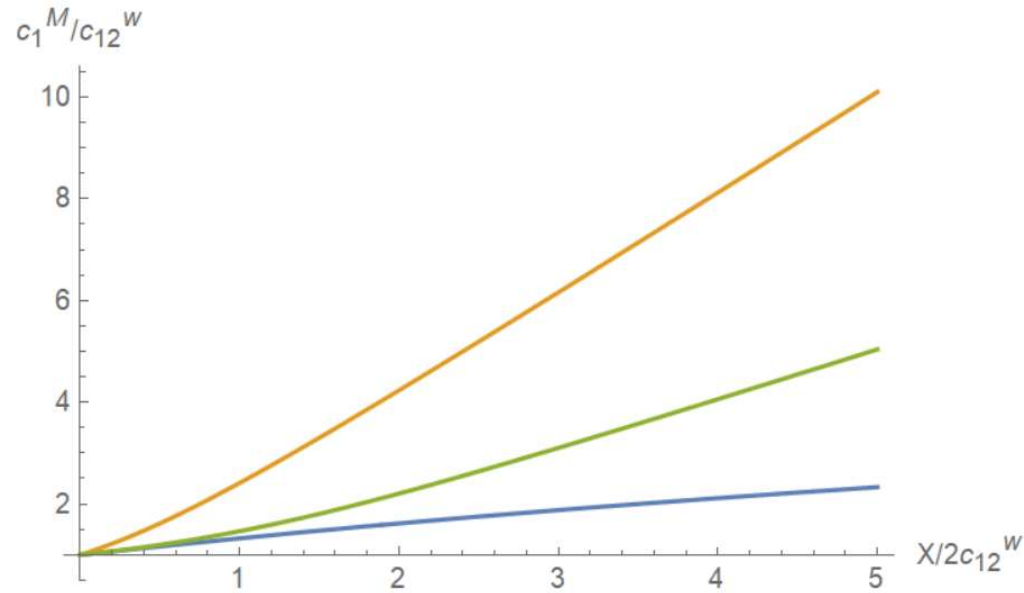

Donnan potentials:

1:1 electrolyte (orange),

2:1 electrolyte (blue),
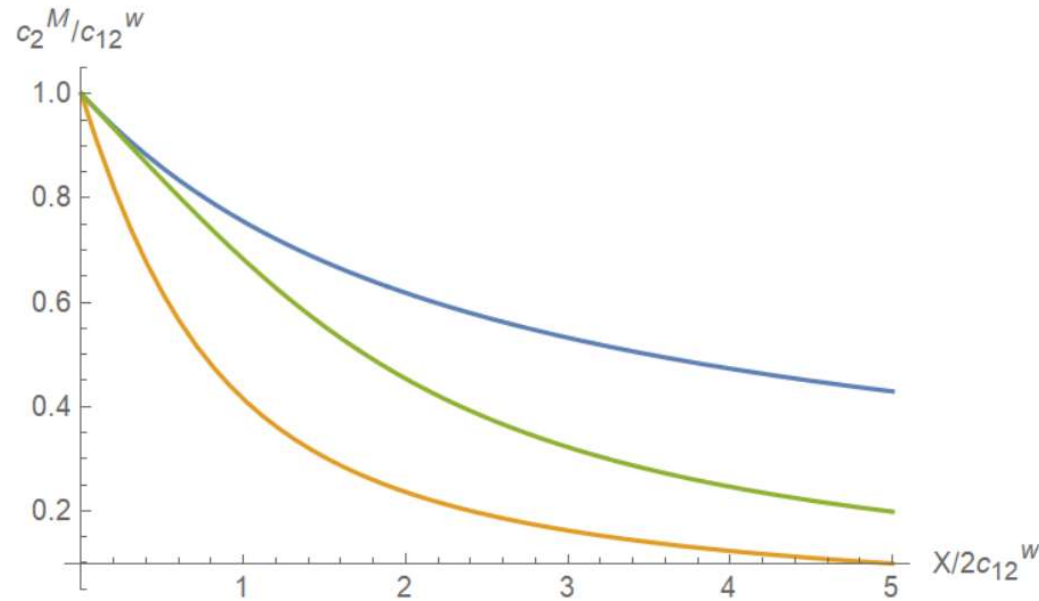
1:2 electrolyte (green).

Counter-ion concentrations:

1:1 electrolyte (orange),

2:1 electrolyte (blue),

1:2 electrolyte (green).

Co-ion concentrations:

1:1 electrolyte (orange),

2:1 electrolyte (blue),

1:2 electrolyte (green).

Potential profile in the solution close to the charged membrane surface

Potential can be solved from the Poisson-Boltzmann equation

$$\frac{d^2\phi}{dx^2} = -\frac{\rho}{\varepsilon_r\varepsilon_0} = -\frac{F}{\varepsilon_r\varepsilon_0}\sum_i z_i c_i^w \exp\left(-\frac{z_i F\phi}{RT}\right) \qquad (9.13)$$

where ρ = charge density. Boundary conditions: $\phi(\infty) = (d\phi/dx)_\infty = 0$. An analytical solution is available for symmetric $z{:}z$ electrolytes:

$$\frac{\tanh(zF\phi/4RT)}{\tanh(zF\phi_0/4RT)} = \exp(-\kappa x) \qquad (9.14)$$

$$\kappa = \left(\frac{2c_{12}^w z^2 F^2}{\varepsilon_r\varepsilon_0 RT}\right)^{1/2} \qquad (9.15)$$

The quantity κ^{-1} is known as the **Debye length**, because it has the unit of length, describing the thickness of the electric double layer. In an aqueous solution with $c = 1.0$ mM, at $T = 298$ K, $\kappa^{-1} \approx 10$ nm. The linearized form of eq. (9.14) is ($\tanh(x) \approx x$),

$$\phi(x) = \phi_0 e^{-\kappa x}. \qquad (9.16)$$
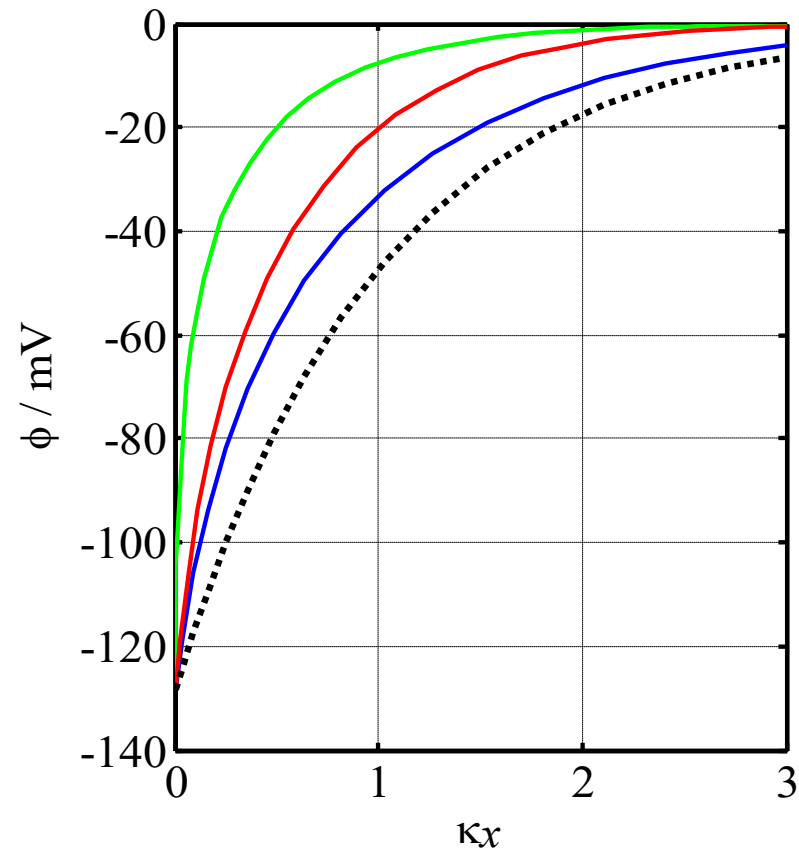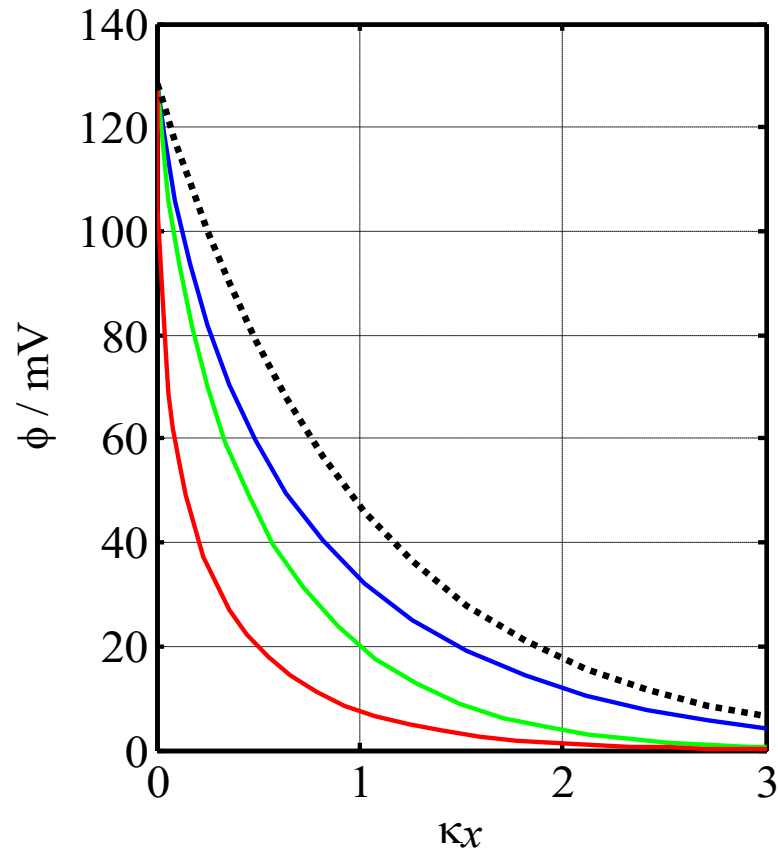
Simulated potential profiles, $F\phi_0/RT = \pm 5$: 1:1 electrolyte (blue), 2:1 electrolyte (green), 1:2 electrolyte (red). Black dotted line depicts the linearized equation (9.16). When $\phi_0 > 0$, 2:2 electrolyte curve almost coincides with the 1:2 electrolyte curve (red), and when $\phi_0 < 0$, 2:1 electrolyte curve (green). Note how the order of curves is changed with ϕ_0.

The surface charge σ (C/cm²) and potential ϕ_0 are connected by

$$\sigma = -\varepsilon_r \varepsilon_0 \left(\frac{d\phi}{dx} \right)_0 = \left\{ 2RT\varepsilon_r \varepsilon_0 \sum_i c_i^w \left[\exp\left(-\frac{z_i F\phi}{RT} \right) - 1 \right] \right\}^{1/2} \qquad (9.17)$$

For a symmetric $z{:}z$ electrolyte it is obtained:

$$\sigma = \left(8RTc_{12}^w \varepsilon_r \varepsilon_0 \right)^{1/2} \sinh\left(\frac{zF\phi_0}{2RT} \right) \qquad (9.18)$$

Due to the potential profile the concentration of counter-ions increases and the concentration of co-ions decreases by the amount $\exp(zF\phi_0/RT)$ at the surface. Aside: simulated conc. profiles for a 1:1 electrolyte, when $z\phi_0/RT = +5$, i.e. $\phi_0 \approx 130$ mV. If $c_{12}^w = 10$ mM, $\sigma \approx 7$ µC/cm² and $\kappa^{-1} \approx 3$ nm. This surface charge corresponds to 7.4×10^{-11} mol/cm² ($z = +1$) which in turn corresponds to the solution charge $\sim$0.62 M.
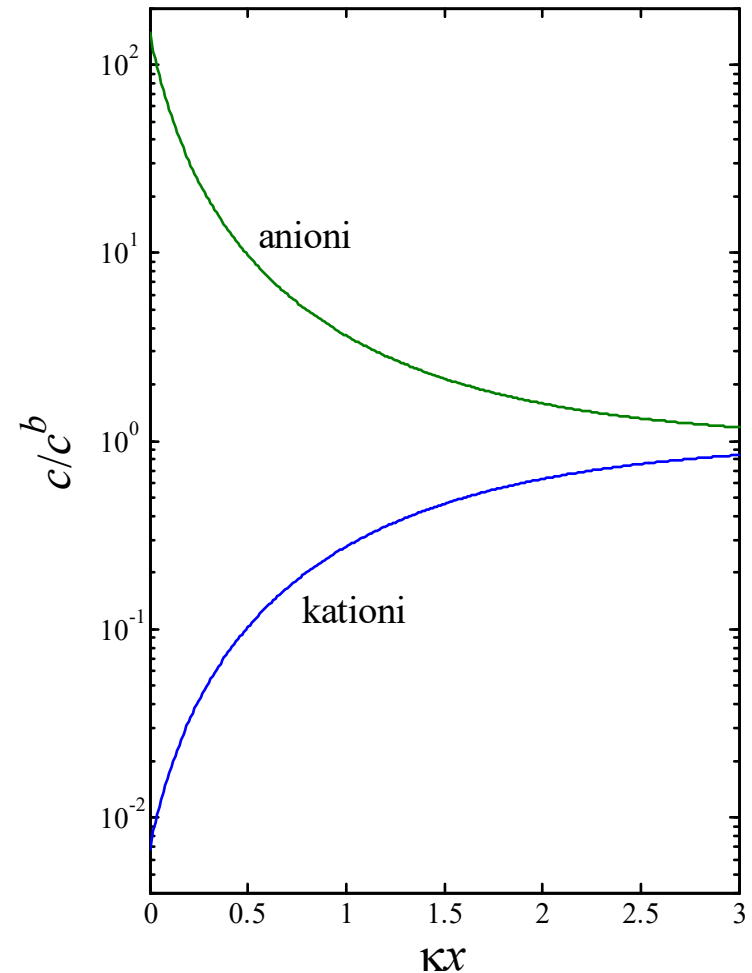
Inside of an ion exchange membrane the potential profile is

$$f\phi(x) = f\phi_D - \tanh(f\phi_D/2)e^{\kappa x} \quad x < 0 \qquad\qquad (9.19)$$

Dimensionless potential profile (a) and charge density (b). $X/c_{12}^w = 100$ (——), 10 (– –) ja 1 (- - -). z is the charge number of the counter-ion.
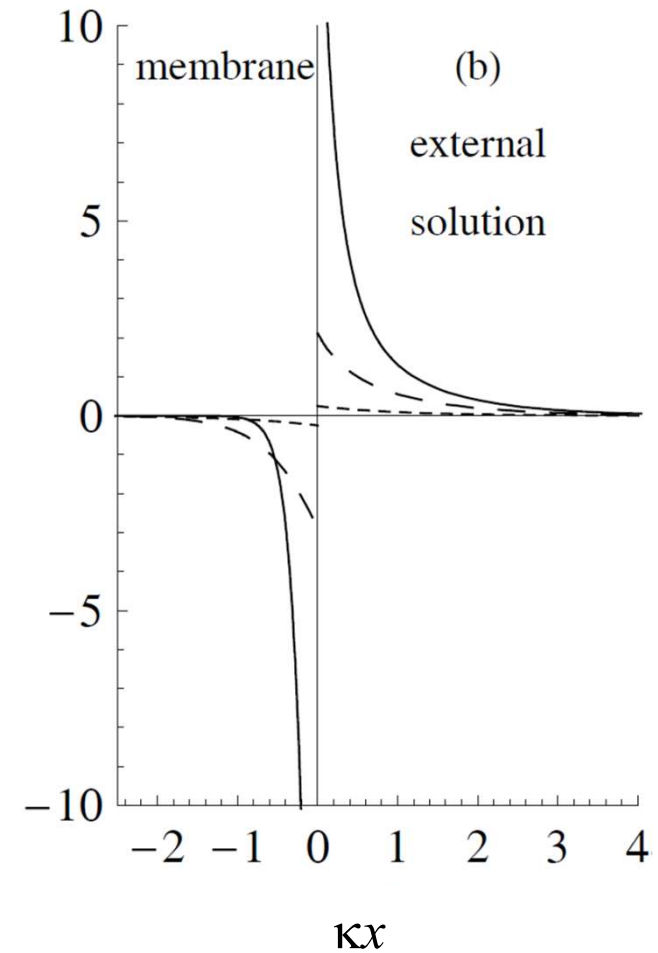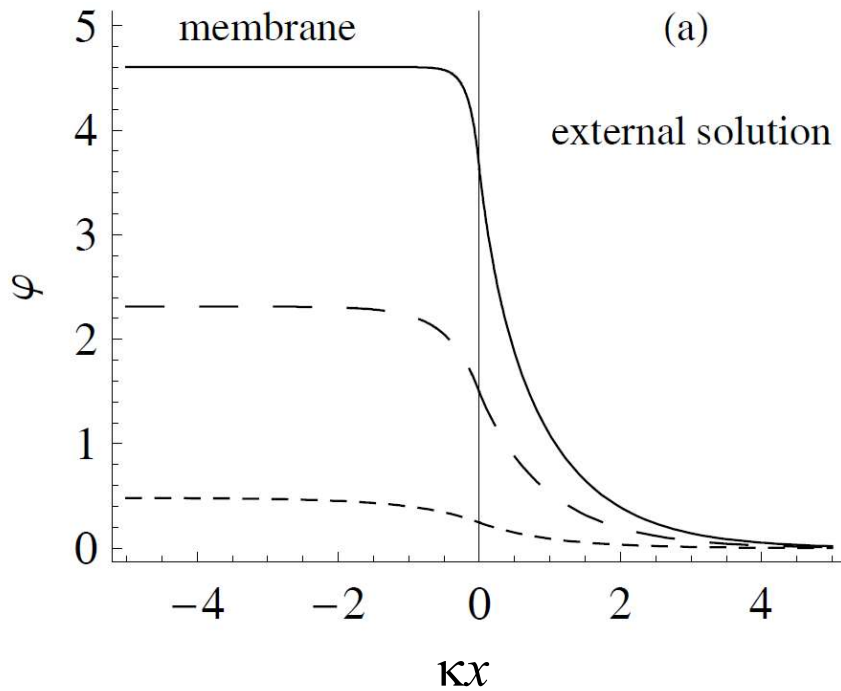
From eq. (9.19) it is possible to calculate the connection between the charge density of an ion exchanger and the surface potential ϕ_0:

$$f\phi_0 = f\Delta\phi_D - \tanh(f\Delta\phi_D/2) = f\Delta\phi_D - \frac{e^{f\Delta\phi_D/2} - e^{-f\Delta\phi_D/2}}{e^{f\Delta\phi_D/2} + e^{-f\Delta\phi_D/2}} = f\phi_D - \frac{e^{f\Delta\phi_D} - 1}{e^{f\Delta\phi_D} + 1} \tag{9.20}$$

$$f\phi_0 = \operatorname{asinh}\left(\frac{X}{2c_{12}^w}\right) - \frac{\left(\dfrac{X}{2c_{12}^w} + \sqrt{\left(\dfrac{X}{2c_{12}^w}\right)^2 + 1}\,\right) - 1}{\left(\dfrac{X}{2c_{12}^w} + \sqrt{\left(\dfrac{X}{2c_{12}^w}\right)^2 + 1}\,\right) + 1} \tag{9.21}$$