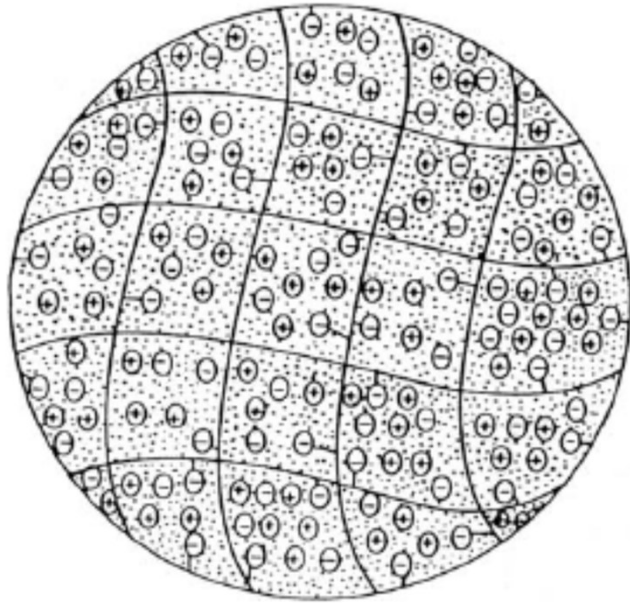


## Ion-selective membranes

An ion-exchange membrane is a polymer matrix 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<sup>3</sup>. Ion exchange capacity of the matrix is the concentration of the fixed



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

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<sup>+</sup> counter-ions. It is converted to hydrogen form by immersing it in strong acid solution, and back to sodium form with NaOH solution.

## Donnan equilibrium in an ion-exchanger

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

$$\tilde{\mu}_i^w = \tilde{\mu}_i^M \quad (10.1)$$

and for an electrolyte:

$$\mu_{12}^M = \nu_1 \tilde{\mu}_1^M + \nu_2 \tilde{\mu}_2^M = \nu_1 \tilde{\mu}_1^w + \nu_2 \tilde{\mu}_2^w = \mu_{12}^w \quad (10.2)$$

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

$$\begin{aligned} \mu_i^{0,M} + RT \ln(\gamma_i^M c_i^M) + z_i F \phi^M &= \mu_i^{0,w} + RT \ln(\gamma_i^w c_i^w) + z_i F \phi^w \\ \mu_{12}^{0,M} + RT \ln(\gamma_{12}^M c_{\pm,12}^M)^{\nu_{12}} &= \mu_{12}^{0,w} + RT \ln(\gamma_{12}^w c_{\pm,12}^w)^{\nu_{12}} \end{aligned} \quad (10.3)$$

where the mean electrolyte activity coefficient,  $\gamma_{12}$ , and mean electrolyte concentration,  $c_{\pm,12}$ , are used;  $\nu_{12} = \nu_1 + \nu_2$ . 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:

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

$$K_{12} = \frac{c_{\pm,12}^M}{c_{\pm,12}^w} = \frac{\gamma_{12}^w}{\gamma_{12}^M} \exp\left[-\frac{\mu_{12}^{0,M} - \mu_{12}^{0,w}}{\nu_{12} RT}\right]$$
(10.4)

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 than individual activity coefficients. Therefore, we reach much simpler and useful equations:

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

$$c_{\pm,12}^M = c_{\pm,12}^w$$
(10.5)

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

$$z_1 c_1^M + z_2 c_2^M + z_M c_M = 0 \Rightarrow X = \frac{z_M c_M}{z_2} = -\frac{z_1}{z_2} c_1^M - c_2^M$$
(10.6)

Note that  $X$  is always positive. For a symmetric electrolyte,  $\nu_1 = \nu_2 = \nu$ ,  $z_1 = -z_2$ ,  $X = c_1^M - c_2^M$ .  
Applying eq. (10.5),

$$c_{12}^w \left( e^{z_2 f \Delta \phi_D} - e^{-z_2 f \Delta \phi_D} \right) = 2c_{12}^w \sinh(z_2 f \Delta \phi_D) = X \Rightarrow z_2 f \Delta \phi_D = \operatorname{arcsinh} \left( \frac{X}{2c_{12}^w} \right) \quad (10.7)$$

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

$$c_1^M = c_{12}^w \left( \frac{X}{2c_{12}^w} + \sqrt{\left( \frac{X}{2c_{12}^w} \right)^2 + 1} \right) = \frac{X}{2} + \sqrt{\left( \frac{X}{2} \right)^2 + (c_{12}^w)^2} \quad (10.8)$$

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

Multiplying the above equations with each other it is seen that  $c_1^M c_2^M = (c_{12}^w)^2$ , as expected.

This result would have been obtained more simply by solving the 2<sup>nd</sup> order equation

$$(c_{12}^w)^2 = (c_2^M + X) c_2^M \quad (10.10)$$

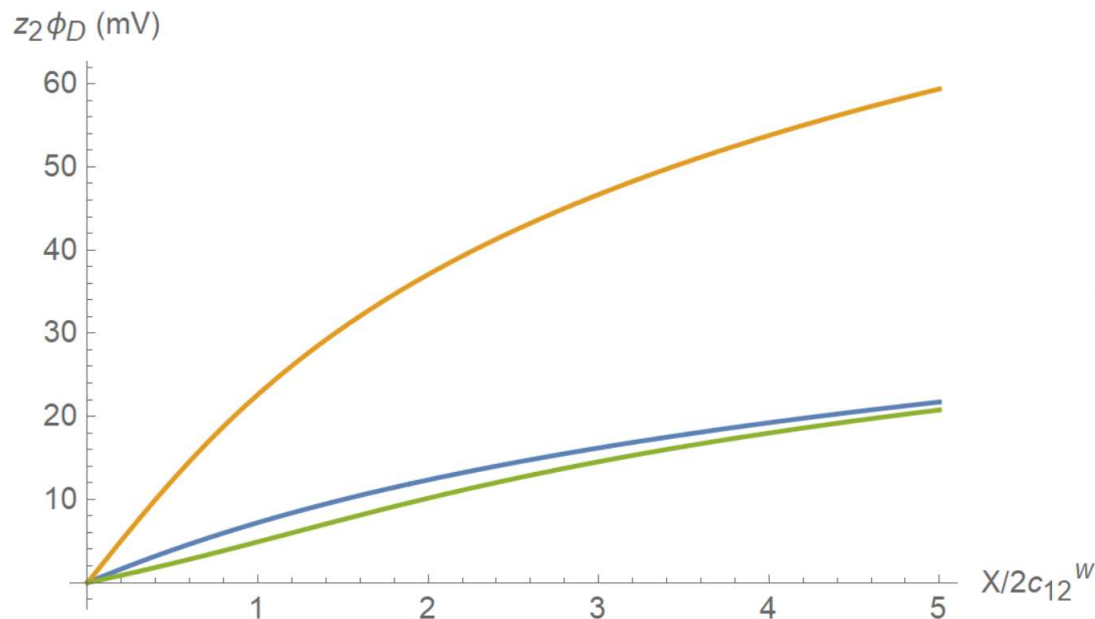
For asymmetric electrolytes Donnan potential must be solved numerically, or as a root of a 3<sup>rd</sup> order polynomial with respect of  $e^{zf\Delta\phi_D}$ .

2:1 electrolyte,  $z_1 = -2z_2$ ,  $\nu_1 = 1$ ,  $\nu_2 = 2$ :

$$2c_{12}^w \left( e^{2z_2 f \Delta\phi_D} - e^{-z_2 f \Delta\phi_D} \right) = X \Leftrightarrow \frac{X}{2c_{12}^w} = e^{2z_2 f \Delta\phi_D} - e^{-z_2 f \Delta\phi_D} \quad (10.10)$$

1:2 electrolyte,  $2z_1 = -z_2$ ,  $\nu_1 = 2$ ,  $\nu_2 = 1$ :

$$2c_{12}^w \left( e^{-z_1 f \Delta\phi_D} - e^{2z_1 f \Delta\phi_D} \right) = X \Leftrightarrow \frac{X}{2c_{12}^w} = e^{-z_1 f \Delta\phi_D} - e^{2z_1 f \Delta\phi_D} \quad (10.10)$$

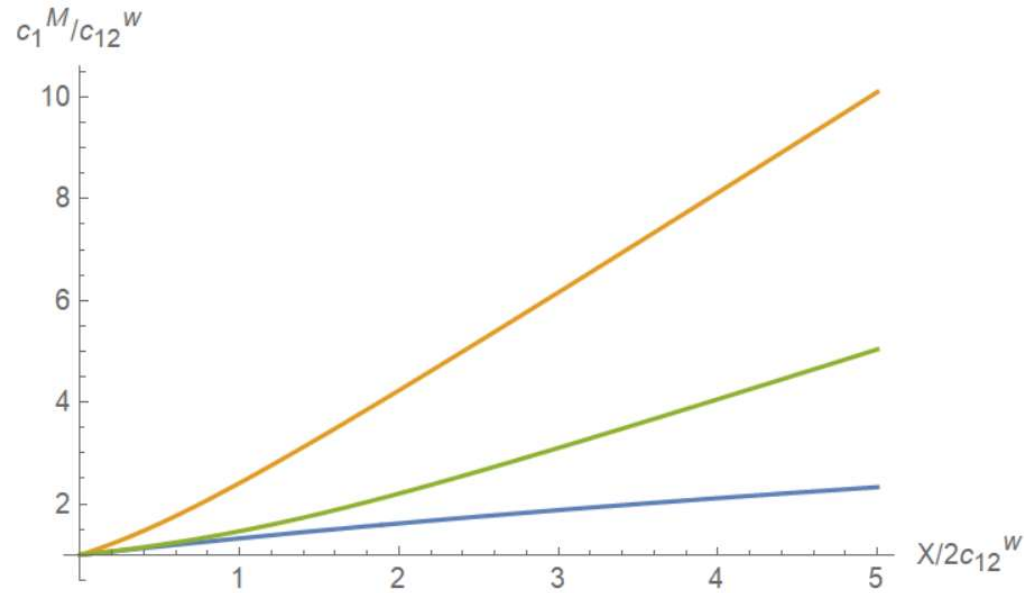


Donnan potentials:

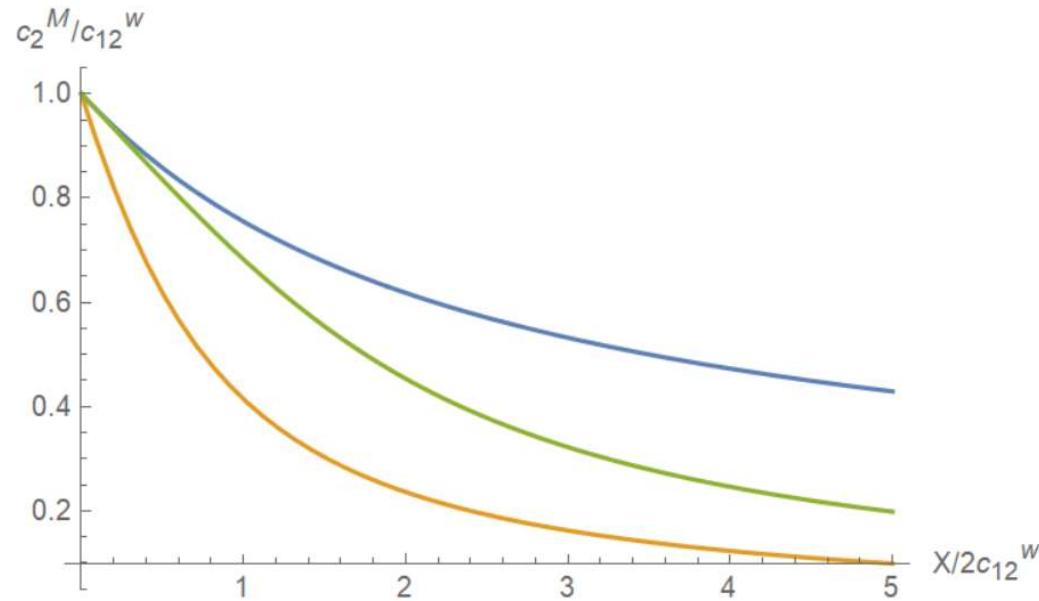
1:1 electrolyte (orange),

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

$$\frac{d^2\phi}{dx^2} = -\frac{\rho}{\epsilon_r\epsilon_0} = -\frac{F}{\epsilon_r\epsilon_0} \sum_i z_i c_i^w \exp\left(-\frac{z_i F \phi}{RT}\right) \quad (10.11)$$

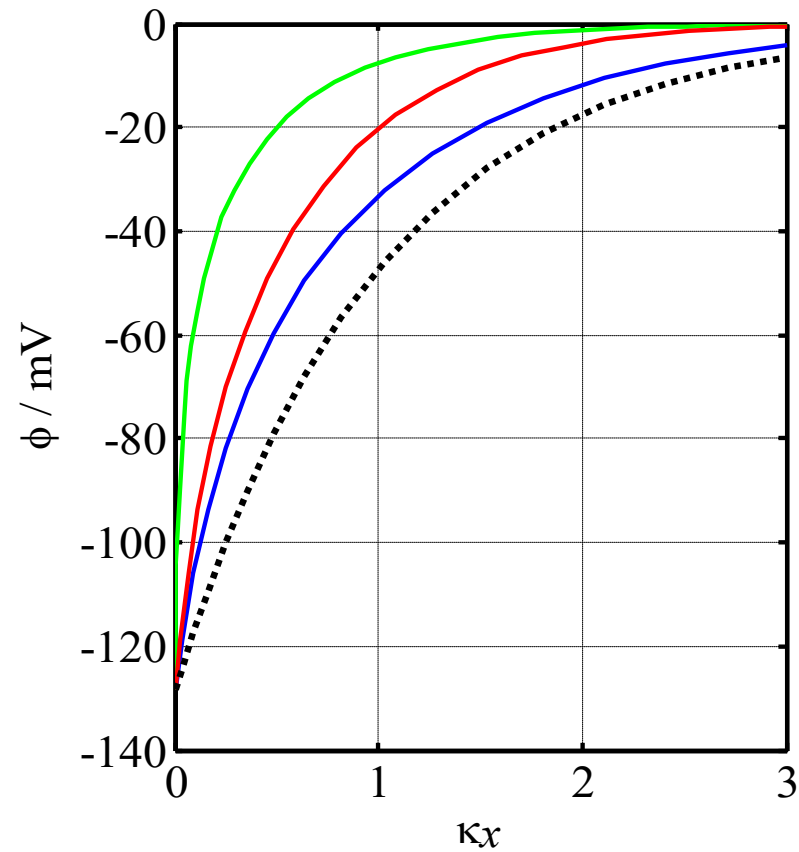
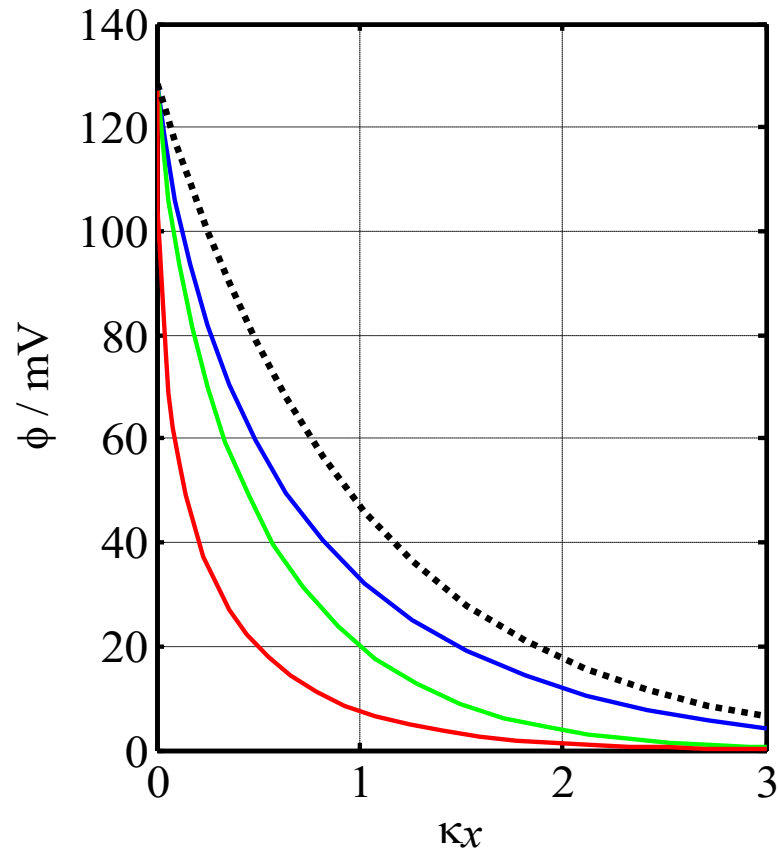
where  $\rho$  = charge density. Boundary conditions:  $\phi(\infty) = (d\phi/dx)_{\infty} = 0$ . An analytical solution is available for symmetric z:z electrolytes:

$$\frac{\tanh(zF\phi / 4RT)}{\tanh(zF\phi_0 / 4RT)} = \exp(-\kappa x) \quad (10.12)$$

$$\kappa = \left( \frac{2c_{12}^w z^2 F^2}{\epsilon_r \epsilon_0 RT} \right)^{1/2} \quad (10.13)$$

The quantity  $\kappa^{-1}$  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. (10.12) is ( $\tanh(x) \approx x$ ),

$$\phi(x) = \phi_0 e^{-\kappa x}. \quad (10.14)$$



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 (10.14). 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  $\phi_0$ .



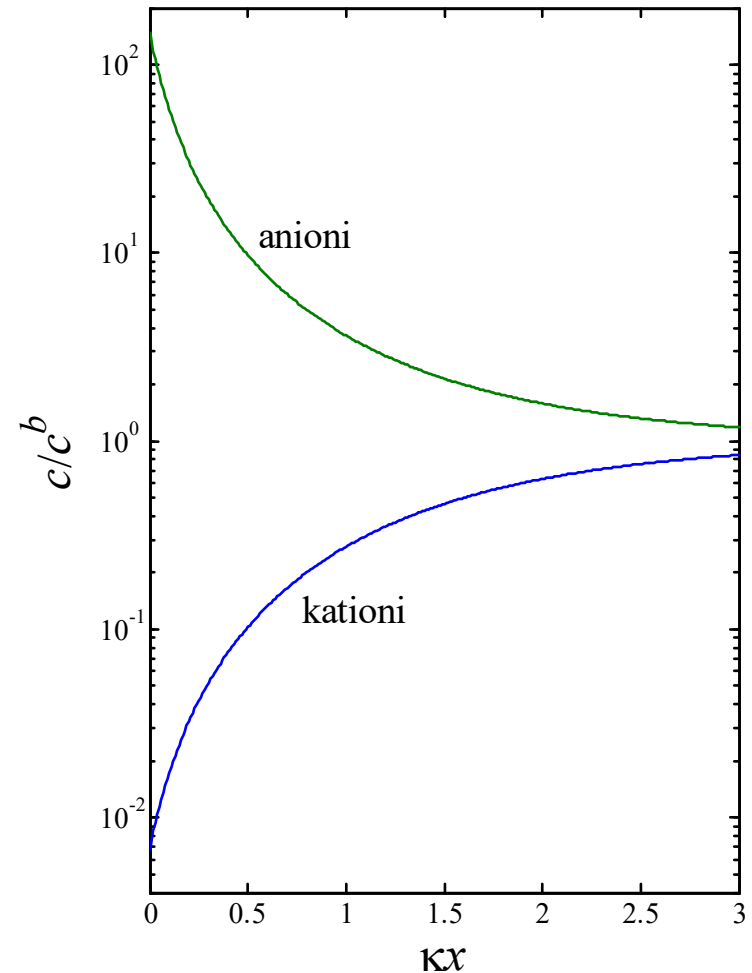
The surface charge  $\sigma$  (C/cm<sup>2</sup>) and potential  $\phi_0$  are connected by

$$\sigma = -\varepsilon_r \varepsilon_0 \left( \frac{d\phi}{dx} \right)_0 = \left\{ 2RT \varepsilon_r \varepsilon_0 \sum_i c_i^w \left[ \exp\left( -\frac{z_i F \phi}{RT} \right) - 1 \right] \right\}^{1/2} \quad (10.15)$$

For a symmetric z:z electrolyte it is obtained:

$$\sigma = \left( 8RT c_{12}^w \varepsilon_r \varepsilon_0 \right)^{1/2} \sinh\left( \frac{zF\phi_0}{2RT} \right) \quad (10.16)$$

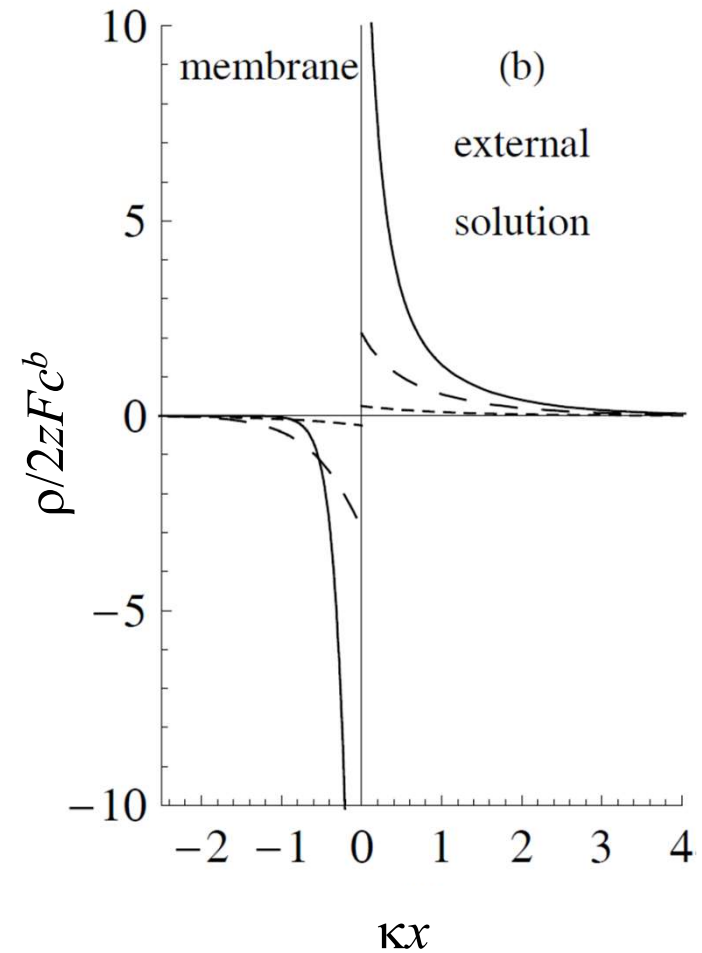
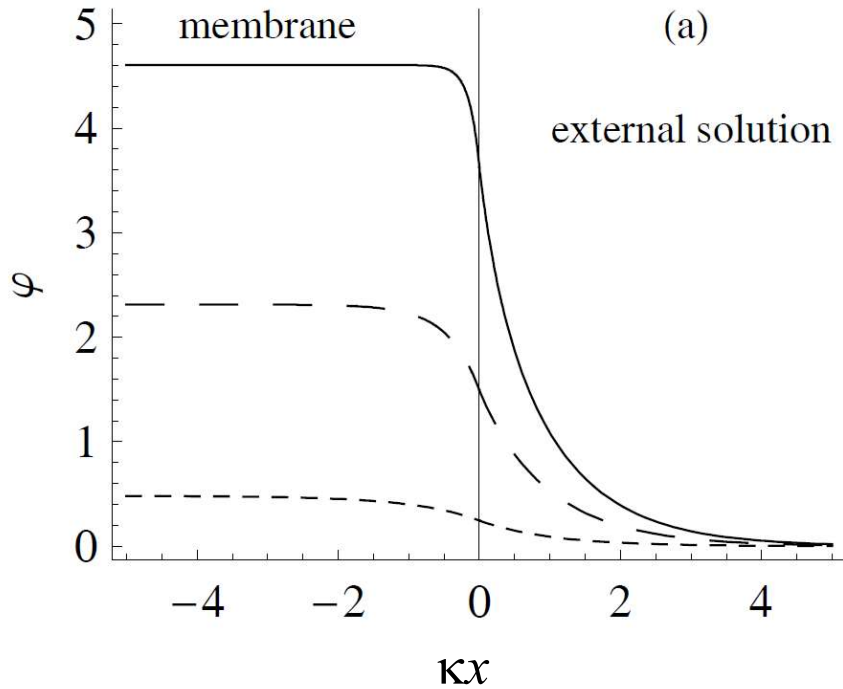
Due to the potential profile the concentration of counter-ions increases and the concentration of co-ions decreases by the amount  $\exp(zF\phi_0/RT)$  at the surface. Aside: simulated conc. profiles for a 1:1 electrolyte, when  $z\phi_0/RT = +5$ , i.e.  $\phi_0 \approx 130$  mV. If  $c_{12}^w = 10$  mM,  $\sigma \approx 7$   $\mu$ C/cm<sup>2</sup> and  $\kappa^{-1} \approx 3$  nm. This surface charge corresponds to  $7.4 \times 10^{-11}$  mol/cm<sup>2</sup> ( $z = +1$ ) which in turn corresponds to the solution charge  $\sim 0.62$  M.



Inside of an ion exchange membrane the potential profile is

$$f\phi(x) = f\phi_D - \tanh(f\phi_D / 2) e^{\kappa x} \quad x < 0 \quad (10.17)$$

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. (10.17) it is possible to calculate the connection between the charge density of an ion exchanger and the surface potential  $\phi_0$ :

$$f\phi_0 = f\Delta\phi_D - \tanh(f\Delta\phi_D/2) = f\Delta\phi_D - \frac{e^{f\Delta\phi_D/2} - e^{-f\Delta\phi_D/2}}{e^{f\Delta\phi_D/2} + e^{-f\Delta\phi_D/2}} = f\phi_D - \frac{e^{f\Delta\phi_D} - 1}{e^{f\Delta\phi_D} + 1} \quad (10.18)$$

$$f\phi_0 = a \sinh\left(\frac{X}{2c_{12}^w}\right) - \frac{\left(\frac{X}{2c_{12}^w} + \sqrt{\left(\frac{X}{2c_{12}^w}\right)^2 + 1}\right) - 1}{\left(\frac{X}{2c_{12}^w} + \sqrt{\left(\frac{X}{2c_{12}^w}\right)^2 + 1}\right) + 1} \quad (10.19)$$

