Transport equations via Thermodynamics of Irreversible Processes

All transport processes can be described with the formalism where a flux, $\vec{J}$, is proportional to a driving force, $\vec{X}$:

$$\vec{J} = L\vec{X} \tag{2.1}$$

The above equation is known as a **phenomenological equation** and coefficient L as a **phenomenological coefficient**. The driving force is the negative gradient of an intensive quantity, i.e. flow always takes place 'downhill'.

Diffusion:

$$\vec{J}_D = -D\nabla c \qquad\qquad \text{Fick's 1. law (not a phenomenological equation, see later)} \tag{2.2}$$

Electric current density:

$$\vec{I} = -\kappa\nabla\phi = \kappa\vec{E} \qquad\qquad \text{Ohm's law} \tag{2.3}$$

Heat flux:

$$\vec{q}' = -\lambda\nabla T \qquad\qquad \text{Fourier's law} \tag{2.4}$$

Convection:

$$\vec{J}_V = -k\nabla p \qquad\qquad \text{Darcy's law} \tag{2.5}$$

D is the diffusion coefficient, κ conductivity, λ heat conductance and k filtration coefficient. In thermodynamics transport of matter is described – in principle – only via chemical components, but ionic transport equations are usually much simpler to handle in practice. If we have only one flux and force, the dissipation function is $\theta = LX^2 > 0 \implies L > 0$.

A naive description: ball rolling downhill

Velocity is proportional to the slope: $v_2 > v_1$. Energy difference is the same in the both cases = mgh. Classical thermodynamics concerns energy differences between chemical states but does not tell anything about the velocities.
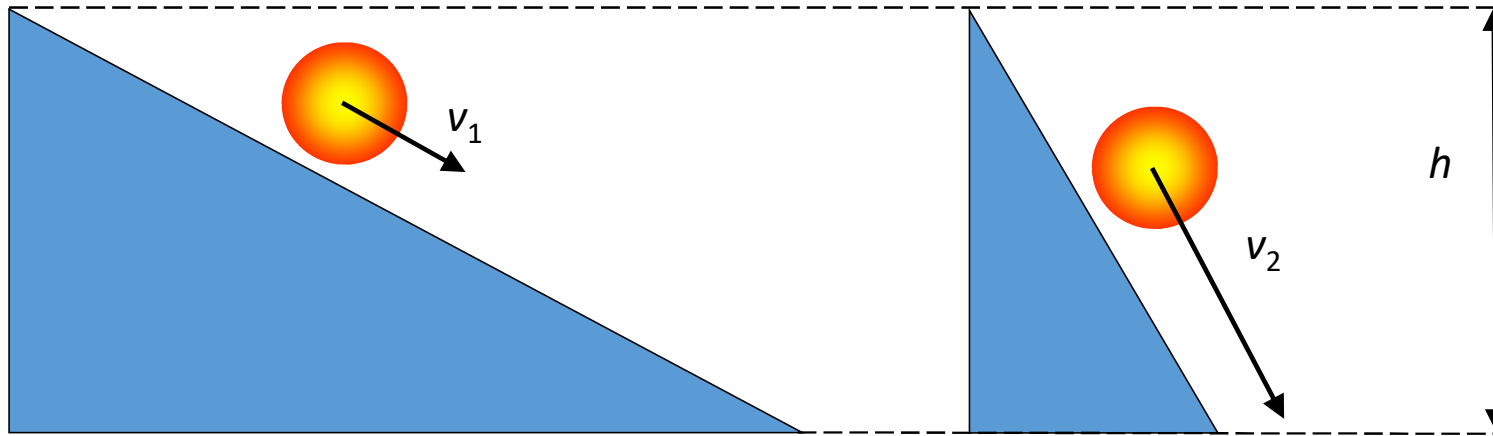
(The example above does not belong to irreversible thermodynamics but to mechanics.)

If it is assumed that the fluxes are functions of forces only,

$$\vec{J}_k = \vec{J}_k(\vec{X}_1, \vec{X}_2, ..., \vec{X}_N) \quad , \quad k = 1, 2, ..., N \tag{2.6}$$

the linear formulation of the transport equation hints that they are 1st order terms of the Taylor series, and at equilibrium where forces are zero fluxes also vanish. This means that the theory should not apply very far from equilibrium. It has been proved, however, that when electrodiffusion is concerned that is not a limitation, really.

In the general case with N fluxes and forces, the problem is best described in a matrix form:

$$\begin{bmatrix} \vec{J}_1 \\ \vec{J}_2 \\ \vdots \\ \vec{J}_N \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} & \cdots & L_{1N} \\ L_{21} & L_{22} & \cdots & L_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ L_{N1} & L_{N2} & \cdots & L_{NN} \end{bmatrix} \begin{bmatrix} \vec{X}_1 \\ \vec{X}_2 \\ \vdots \\ \vec{X}_N \end{bmatrix} \quad \text{or} \quad \mathbf{J} = \mathbf{LX} \qquad (2.7)$$

Onsager's reciprocal theorem states that $L_{ij} \equiv L_{ji}$. The dissipation function is written in matrix form as

$$\theta = \mathbf{X}^{\mathrm{T}}\mathbf{LX} \qquad (2.8)$$

Equation (2.8) is a **quadratic form** and in order that to be positive, the **eigenvalues** of $\mathbf{L}$ must be positive, which makes certain constrains to the phenomenological coefficients (home exercise).

Let's illustrate this with an example that has a high practical importance and proves the theory correct. Let's have two forces, $\nabla\phi$ and ∇P affecting across a charged porous membrane, and two fluxes, $\vec{I}$ (electric current density) and $\vec{J}_w$ (water flux):

$$\begin{cases} \vec{I} = -L_{11}\nabla\phi - L_{12}\nabla P \\ \vec{J}_w = -L_{21}\nabla\phi - L_{22}\nabla P \end{cases} \qquad (2.9)$$

It is obvious that L_{11} is the conductivity and L_{22} the filtration coefficient of the membrane. Yet, Eq. (2.9) claims that the pressure gradient causes also electric current and the potential gradient flux of water. This is, indeed, correct: the latter is known as electroosmosis and the former as streaming current; they are both **electrokinetic** phenomena. Their molecular origin is the interplay of the electric double layer with the flux of an electrolyte solution. Electroosmosis is actually the basis of capillary electrophoresis (CE). According to Onsager

$$\left(\frac{\vec{J}_w}{\vec{I}}\right)_{\nabla P=0} = \frac{L_{21}}{L_{11}} = \frac{L_{12}}{L_{11}} = -\left(\frac{\nabla\phi}{\nabla p}\right)_{\vec{I}=0} = \upsilon \tag{2.10}$$

According to Eq. (2.10) the coefficient $L_{12} = L_{21}$ can be determined measuring either the electroosmotic flux or **streaming potential, υ**; the latter is easier. Electrokinetic phenomena can be linked to the charge density and pore size applying a microscopic model, solving simultaneously Navier-Stokes and Poisson-Boltzmann equations in the pore. It is "easily" doable in, e.g. a thin capillary with a fixed charge density on its walls. These models are considered in the textbook pp. 205-214.
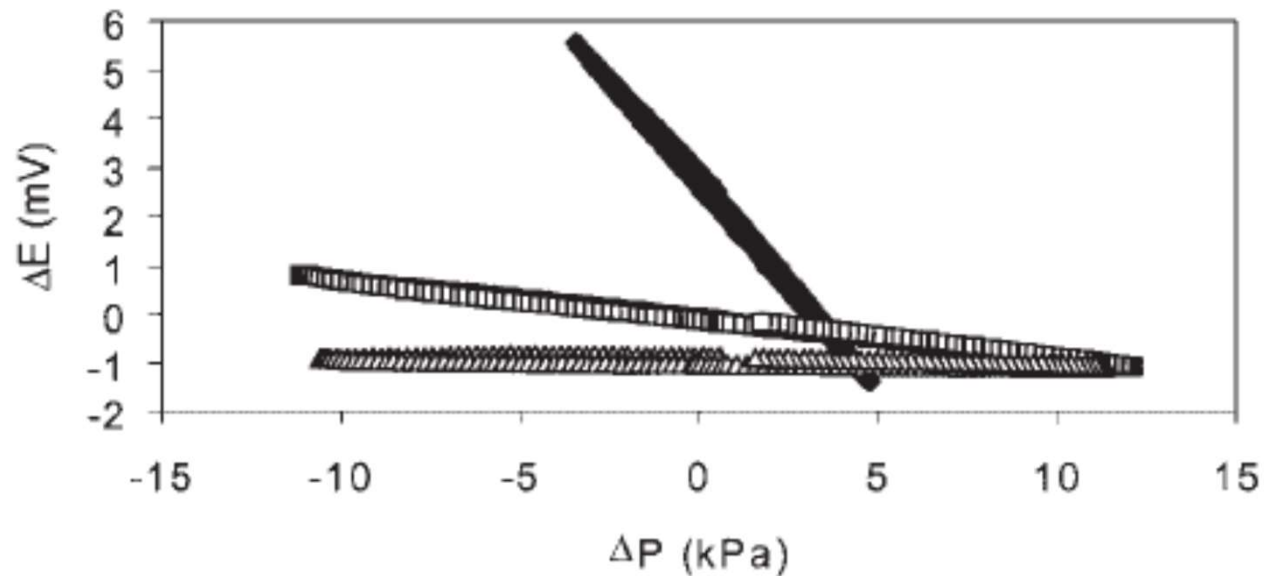
Streaming potential measurement in a synthetic membrane in 1.0, 10 ja 100 mM NaCl solution. J. Raiman et al., "Drug adsorption in human skin: a streaming potential study", *J.Pharm.Sci.* **92** (2003) 2366.

$$L_{12} = \pi r_0^2 \frac{\lambda \sigma}{\eta}\left(\frac{2}{R} - \frac{I_0(R_0)}{I_1(R_0)}\right) \qquad \lambda = \left(\frac{\varepsilon RT}{F^2 \sum_i z_i^2 \bar{c}_i^0}\right) \; ; \text{ thickness of the electric double layer; } R_0 = r_0 / \lambda$$

$$L_{11} = \pi r_0^2 \left\{ \frac{\varepsilon}{2\lambda^2}(D_1 + D_2)\left[1 - \frac{D_1 - D_2}{D_1 + D_2}\frac{F\lambda\sigma}{\varepsilon RT}\left(\frac{2}{R_0} - \frac{1}{I_1(R_0)}\right)\right] + \frac{\sigma^2}{\eta}\left[1 + \frac{I_0(R_0)}{I_1(R_0)}\left(\frac{2}{R_0} - \frac{I_0(R_0)}{I_1(R_0)}\right)\right]\right\}$$
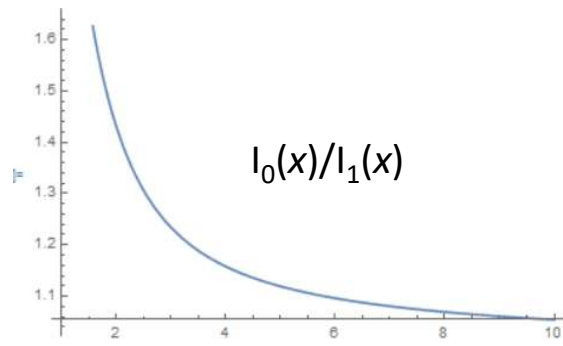
r_0 = pore radius
σ = surface charge density of the pore
η = solution viscosity
ε = solution relative permittivity (= $\varepsilon_0 \varepsilon_r$)
D_1, D_2 = diffusion coefficients of the cation and anion
I_0, I_1 = modified Bessel functions of the zeroth and first order

$I_0(x)/I_1(x)$

Estimation of the pore size and charge density in human cadaver skin
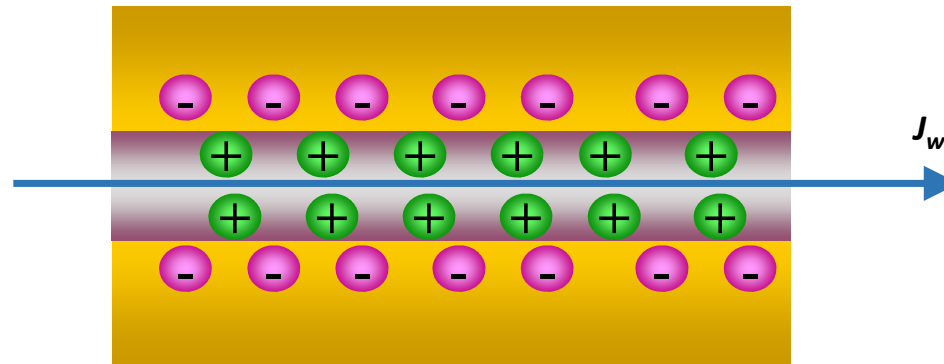
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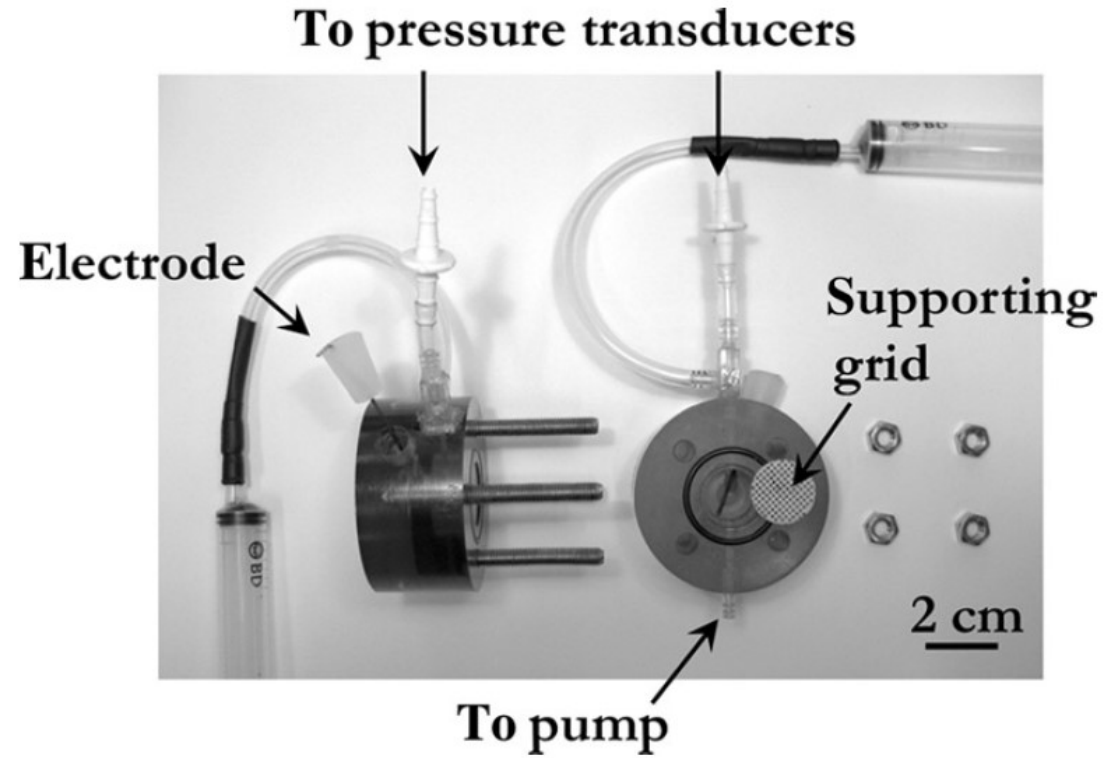
Micropore and electric double layer
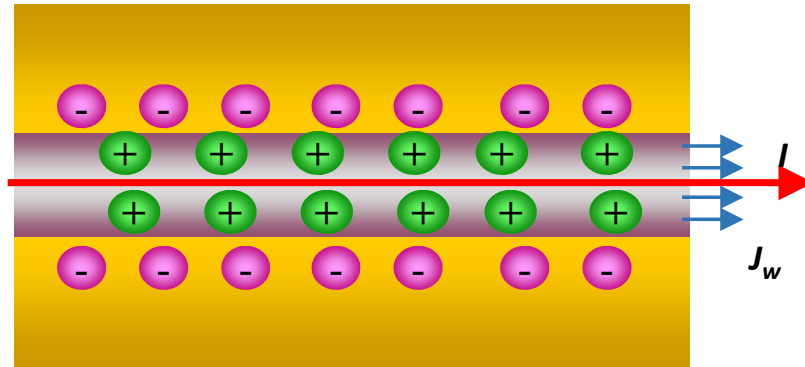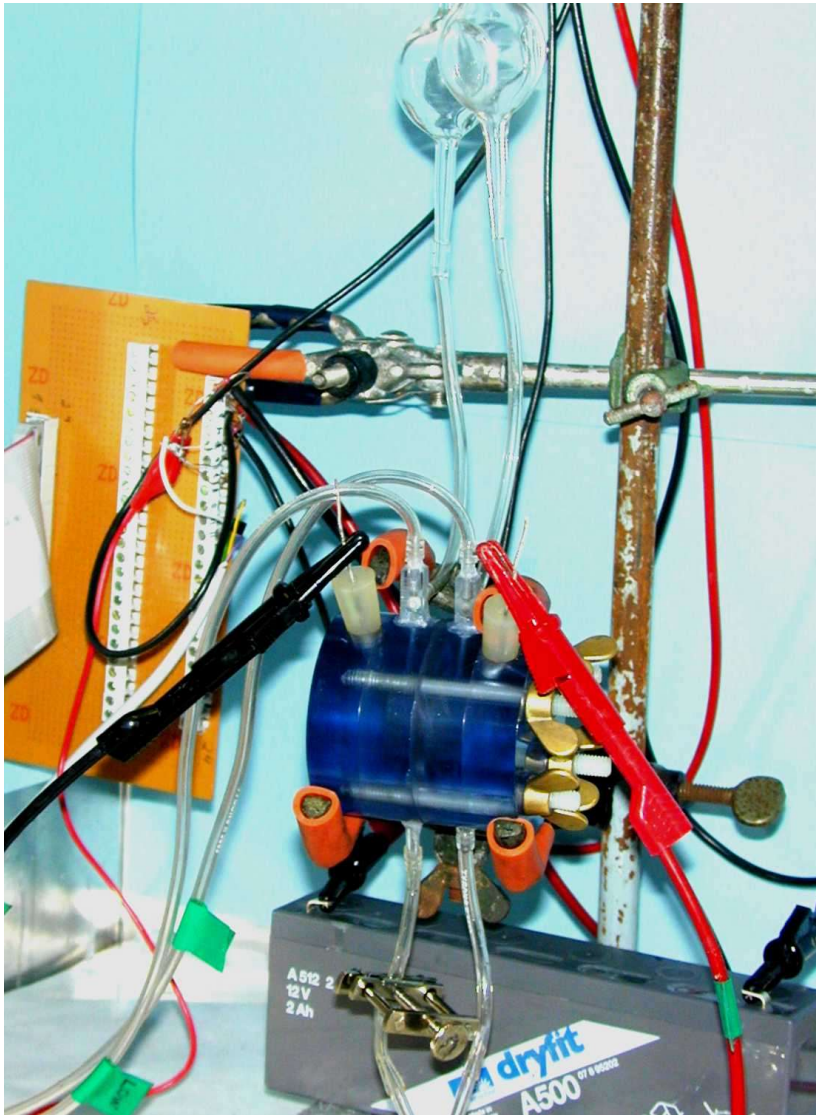

Electroosmosis

Streaming potential

Equipment

Drug adsorption on bovine and porcine sclera studied with streaming potential, Lasse Murtomäki, Tuomas Vainikka, Silvia Pescina, Sara Nicoli, *J. Pharm. Sci.* **102**, (2013) 2264-2272.

to pressure sensors

solution flow

Ag/AgCl electrodes

Solution

Supporting frits

Membrane (skin)

o-rings
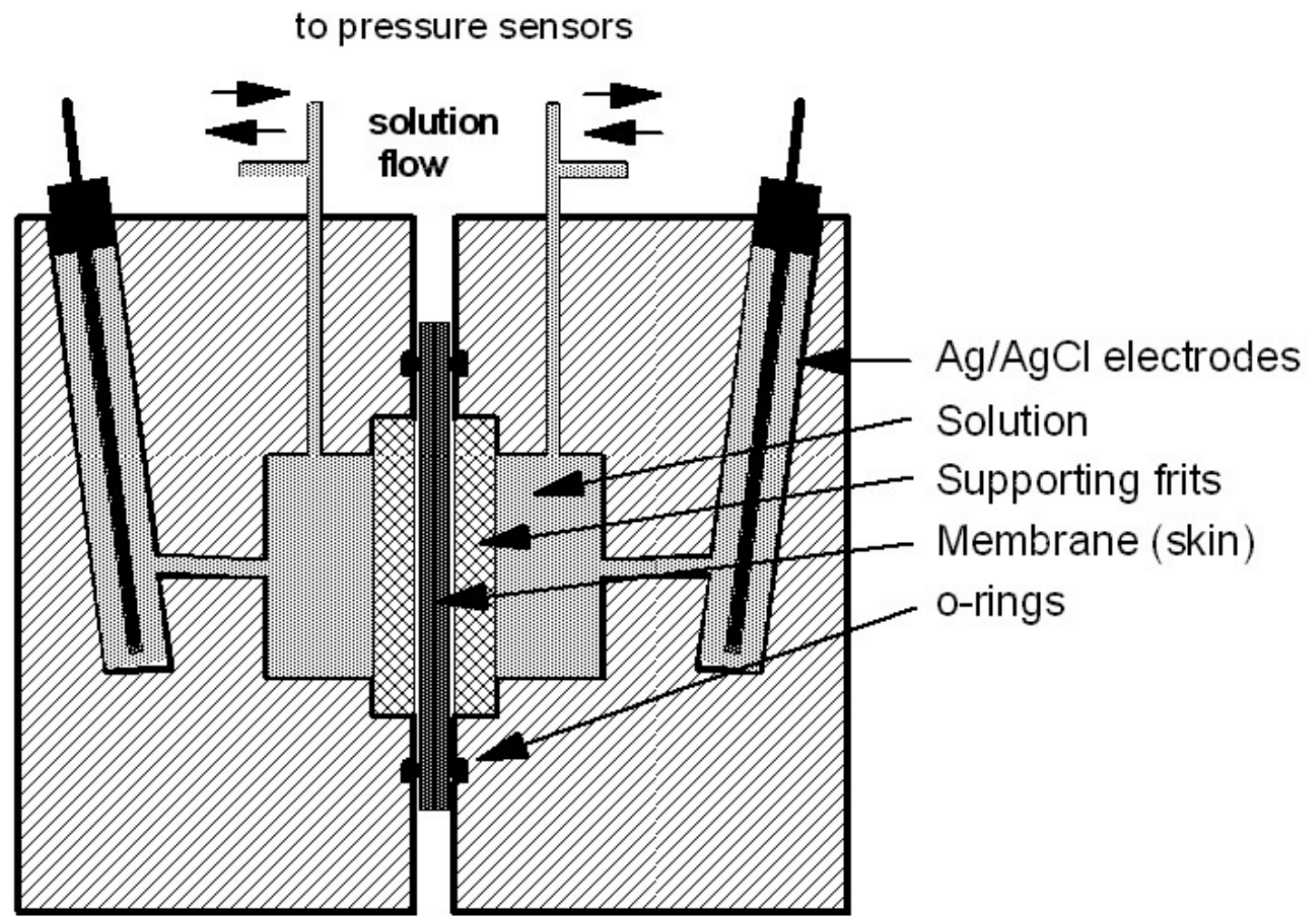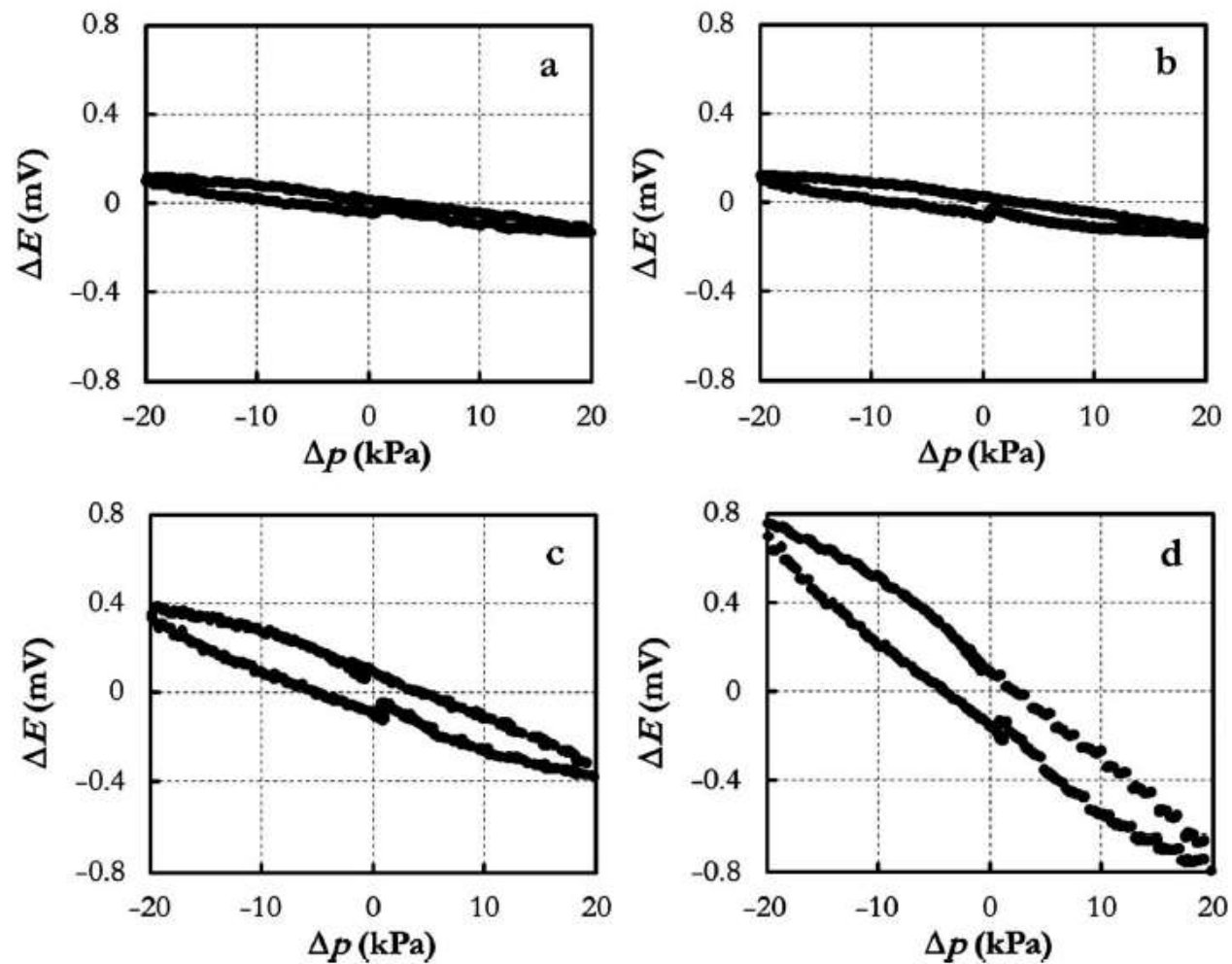
Figure 5. Streaming potential in porcine sclera at various concentrations of MPSS: 0 (a), 1 (b), 5 (c), and 9 mM (d). MPSS = methylprednisolone sodium succinate (anionic)

It has to be realized that the coupling of electric current and water flux does not take place in a solution, but it requires a charged membrane with pores of the same order of magnitude as the thickness of the electric double layer. In other words, the membrane is a thermodynamic component of the system; we return to this question later on.

But coupling of electrolytes diffusion does take place in a solution. The phenomenological driving force of diffusion is the gradient of the chemical potential,

$$\vec{J}_i = -\sum_k L_{ik} \nabla \mu_k \qquad\qquad (2.11)$$

Let's consider a mixture of two electrolytes with the concentrations c_1 and c_2. Using Fickian formalism,

$$\begin{bmatrix} \vec{J}_1 \\ \vec{J}_2 \end{bmatrix} = -\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \begin{bmatrix} \nabla c_1 \\ \nabla c_2 \end{bmatrix} \qquad (2.12)$$

On the diagonal of the diffusion coefficient matrix are the diffusion coefficients of the electrolytes with respect to water, and the off-diagonal elements are the cross-coefficients. Note that because eq. (2.12) is not a phenomenological equation, $D_{12} \neq D_{21}$.

Aside data from Albright et al. (*J. Phys Chem.* **93** (1989) 2176-2180) where $C_1 = [NaCl]$ and $C_2 = [MgCl_2]$. As can be seen D_{21} remains quite small at all concentrations whereas D_{12} is even higher than D_{11} and D_{22} at high concentrations. In some cases the cross-coefficient has also been found to be negative. That is not violating the positive dissipation function as the other terms are compensating it.
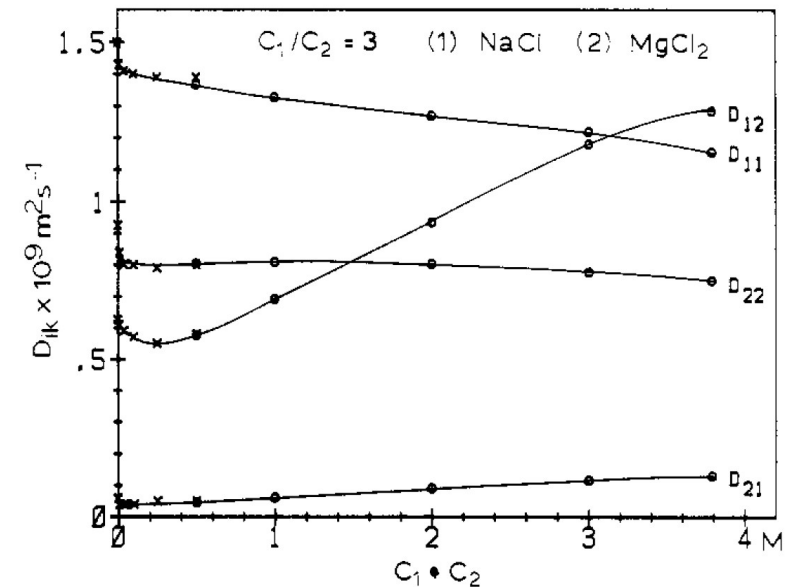
It has to be emphasized that writing the transport equation with phenomenological equations,

$$\begin{bmatrix} \vec{J}_1 \\ \vec{J}_2 \end{bmatrix} = -\begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix}\begin{bmatrix} \nabla\mu_1 \\ \nabla\mu_2 \end{bmatrix} \tag{2.13}$$

does not mean that $L_{ik}\nabla\mu_k = D_{ik}\nabla c_k$. Only in a binary (e.g. water-salt) solution

$$-\vec{J}_1 = D_1\nabla c_1 = L_1\nabla\mu_1 \quad \Leftrightarrow \quad L_1 = \frac{D_1 c_1}{RT} \tag{2.14}$$

The general relation between the phenomenological and the (Fickian) diffusion coefficients is in the textbook eq. (2.52):

$$D_{ij} = \sum_k L_{ik}\frac{\partial\mu_k}{\partial c_j} \tag{2.15}$$

Because the phenomenological coefficients are complicated functions of the local concentrations, they are not practical to use: the integration of $-\vec{J}_1 = L_{11}\nabla\mu_1$ is not possible without explicit information of the dependence of L_{11} or μ_1 on c_1. On the contrary, D_1 can assumed to be constant (at least within a reasonable range of c_1) which makes the integration of $-\vec{J}_1 = D_1\nabla c_1$ rather simple. The value of the phenomenological approach is, however, in the notice that, in general, fluxes are coupled, giving the explanation to, e.g. electrokinetic or thermoelectric phenomena (Peltier, Seebeck effects).

Ionic phenomenological equations can be defined in an analogous manner:

$$\vec{j}_i = -\sum_k \ell_{ik} \nabla \tilde{\mu}_k \quad ; \quad \ell_{ik} = \ell_{ki} \qquad (2.16)$$

Note that instead of the chemical potential μ the electrochemical potential $\tilde{\mu}$ is used. In the textbook pp. 40-41 it is shown that when the flux is expressed in the Hittorf reference the dissipation function takes the form

$$\theta_{ed} = -\sum_{i \neq 0} \vec{j}_i^H \cdot \nabla \tilde{\mu}_i \qquad (2.17)$$

But as mentioned earlier, in moderately dilute solutions all the reference frames are practically the same and we omit their superscripts. Let's consider a binary solution, i.e. one salt and a solvent (water). An electrolyte $A_{\upsilon_1} B_{\upsilon_2}$ is assumed to be dissociated completely to ions A^{z_1} and B^{z_2}. Electroneutrality thus requires that $z_1 \upsilon_1 + z_2 \upsilon_2 = 0$. The dissipation function is

$$\theta_{ed} = -\left(\vec{j}_1 \cdot \nabla \tilde{\mu}_1 + \vec{j}_2 \cdot \nabla \tilde{\mu}_2 \right) \qquad (2.18)$$

and the phenomenological equations are

$$\begin{bmatrix} \vec{j}_1 \\ \vec{j}_2 \end{bmatrix} = -\begin{bmatrix} \ell_{11} & \ell_{12} \\ \ell_{21} & \ell_{22} \end{bmatrix} \begin{bmatrix} \nabla \tilde{\mu}_1 \\ \nabla \tilde{\mu}_2 \end{bmatrix} \qquad (2.19)$$

The dissipation function can also be written as

$$\theta_{ed} = -\left(\vec{J}_{12} \cdot \nabla \mu_{12} + \vec{I} \cdot \nabla \phi_{ohm} \right) \qquad (2.20)$$

where ϕ_{ohm} is the ohmic part of the Galvani potential in the solution (will be discussed later on).

The phenomenological equations related to Eq. (2.20) are

$$\begin{bmatrix} \vec{J}_1 \\ \vec{I} \end{bmatrix} = -\begin{bmatrix} L_{12,12} & L_{12,\phi} \\ L_{12,\phi} & L_{\phi,\phi} \end{bmatrix}\begin{bmatrix} \nabla\mu_{12} \\ \nabla\phi_{ohm} \end{bmatrix} \qquad (2.21)$$

As shown on the textbook p. 43, the equivalence of the dissipation function requires that $L_{12,\phi} = 0$. Hence, the component presentation takes the form

$$\begin{cases} \vec{J}_{12} = -L_{12,12}\nabla\mu_{12} \\ \vec{I} = -\kappa\nabla\phi_{ohm} \end{cases} \qquad (2.22)$$

where the conductivity $\kappa = L_{\phi,\phi} = F^2\left(z_1^2\ell_{11} + 2z_1z_2\ell_{12} + z_2^2\ell_{22}\right)$. This exercise of calculus proves the intuitively evident fact that the flux of a neutral component cannot depend on the ohmic potential gradient, neither electric current can depend on the chemical potential (concentration) gradient of a neutral component.

Fickian approach

Strictly speaking, only components can diffuse and ions carry current. Ionic fluxes can be expressed in terms of component fluxes and electric current as

$$\vec{j}_i = \sum_K \upsilon_{ik}\vec{J}_K + \frac{t_i\vec{I}}{z_iF} \qquad (2.23)$$

where υ_{ik} is the stoichiometric coefficient of ion i in component K and t_i is its transport number. Transport number is the fraction of current carried by ion i.

Example: KCl-HCl, K$^+$ = "1", H$^+$ = "2", Cl$^-$ = "3"; KCl = "13", HCl = "23".

$$\vec{j}_1 = J_{13} + \frac{t_1 i}{F} \quad ; \quad \vec{j}_2 = J_{23} + \frac{t_2 i}{F} \quad ; \quad \vec{j}_3 = J_{13} + J_{23} - \frac{t_3 i}{F}$$

Remember the following definitions:

$$\vec{I} = F\sum_i z_i\vec{j}_i \qquad (2.24)$$

$$t_i = \frac{z_i^2 D_i c_i}{\sum_m z_m^2 D_m c_m} \quad ; \quad \sum_i t_i = 1 \qquad (2.25)$$

Inserting the component fluxes in Fickian format the flux is given as

$$\vec{j}_i = -\sum_J \sum_K \upsilon_{iK} D_{KJ} \nabla c_J + \frac{t_i \vec{I}}{z_i F} \qquad (2.26)$$

The above equation is, however, rather impractical because in multicomponent solutions the transport numbers depend on the local composition of the solution, and because the cross-diffusion coefficients and their concentration dependence are usually not known. Only in a binary solution transport numbers are constant, and we get

$$\vec{j}_i = -\upsilon_i D_{12} \nabla c_{12} + \frac{t_i \vec{I}}{z_i F} \quad ; \quad i = 1,2 \qquad (2.27)$$

Example: KCl, K^+ = "1", Cl^- = "2"; KCl = "12".

$$\vec{j}_1 = -D_{12} \nabla c_{12} + \frac{t_1 \vec{I}}{F} \quad ; \quad \vec{j}_2 = -D_{12} \nabla c_{12} - \frac{(1-t_1)\vec{I}}{F} \quad ; \quad t_1 = \frac{D_1}{D_1 + D_2}$$

For the diffusion of neutral (z_i = 0) solutes the coupling of fluxes is very weak, and the flux is well described with the Fick's law

$$\vec{J}_K = -D_K \nabla c_K \qquad (2.28)$$

The practical way of analyzing ionic transport is via the **Nernst-Planck** approximation to which we will concentrate next.