Electrokinetic Phenomena and Thermodynamics of Irreversible Processes. Saxen Relations. Electroviscosity. Relaxation Effects and Electrophoresis

CBE/NE/BME 525

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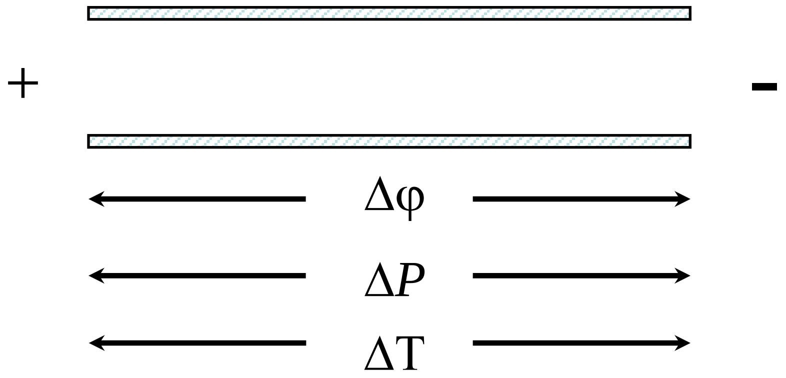
Outline

1. Linear Nonequilibrium Thermodynamics (Thermodynamics of Irreversible Processes).
2. Multiple Fluxes and Coupling. Onsager Theorem.
3. Saxen Relations. Streaming Potential and Current, Electroomosis and Electroosmotic Pressure.
4. Electroviscosity in Fluidic Channels.
5. Double Layer Polarization Effects and Ionic Relaxation in Electrophoresis

Nonequilibrium Thermodynamics and Electrokinetic Phenomena



Fluxes

$$I = L_{11}\Delta\varphi + L_{12}\Delta p + L_{13}\Delta T$$
$$U = L_{21}\Delta\varphi + L_{22}\Delta p + L_{23}\Delta T$$
$$Q = L_{31}\Delta\varphi + L_{32}\Delta p + L_{33}\Delta T$$

Onsager Theorem: for linear processes $L_{ij} = L_{ji}$

Curie Theorem: only fluxes of the same tensor rank may couple

Saxen

$$I = L_{11}\Delta\varphi + L_{12}\Delta p$$
$$U = L_{21}\Delta\varphi + L_{22}\Delta p$$
$$L_{12} = L_{21}$$

Saxen Relations

$$I = L_{11}\Delta\varphi + L_{12}\Delta p$$
$$U = L_{21}\Delta\varphi + L_{22}\Delta p$$

1. $I = 0$ $\quad \left(\frac{\Delta\varphi}{\Delta p}\right)_{I=0} = -\frac{L_{12}}{L_{11}}, \quad \Delta\varphi = -\frac{L_{12}}{L_{11}}\Delta p \text{ for } I = 0$ Streaming potential

2. $U = 0$ $\quad \left(\frac{\Delta p}{\Delta\varphi}\right)_{U=0} = -\frac{L_{21}}{L_{11}}, \quad \Delta p = -\frac{L_{21}}{L_{11}}\Delta\varphi, \text{ for } U = 0$ Electroosmotic pressure

3. $\Delta p = 0$ $\quad \left(\frac{U}{I}\right)_{\Delta P=0} = \frac{L_{21}}{L_{11}}, \quad U = \frac{L_{21}}{L_{11}} I \text{ for } \Delta p = 0$ Electroosmotic Flow

4. $\Delta\varphi = 0$ $\quad \left(\frac{I}{U}\right)_{\Delta\varphi=0} = \frac{L_{12}}{L_{22}}, \quad I = \frac{L_{12}}{L_{22}} U \text{ for } \Delta\varphi = 0$ Streaming current

Saxen Relations

Onsager theorem $$L_{12} = L_{21}$$

Then

$$\left.\begin{aligned}\left(\frac{\Delta\varphi}{\Delta p}\right)_{I=0} &= -\left(\frac{U}{I}\right)_{\Delta p=0} \\ \left(\frac{\Delta p}{\Delta\varphi}\right)_{U=0} &= -\left(\frac{I}{U}\right)_{\Delta\varphi=0}\end{aligned}\right\}$$

Saxen relations

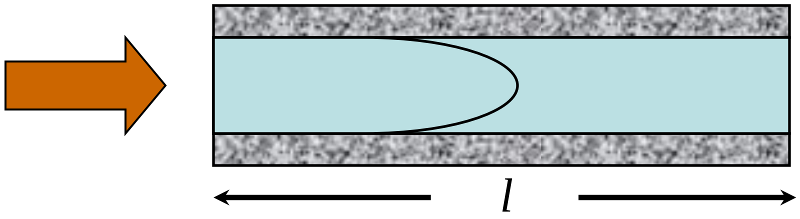
If we take into account heat flux, more possibilities

$$\begin{aligned}I &= L_{11}\Delta\varphi + L_{12}\Delta p + L_{13}\Delta T \\ U &= L_{21}\Delta\varphi + L_{22}\Delta p + L_{23}\Delta T \\ J &= L_{31}\Delta\varphi + L_{32}\Delta p + L_{33}\Delta T\end{aligned}$$

Electroviscosity in a Straight Capillary

$$I = L_{11}\Delta\varphi + L_{12}\Delta p$$
$$U = L_{21}\Delta\varphi + L_{22}\Delta p$$

$$0 = L_{11}\Delta\varphi + L_{12}\Delta p$$
$$U = L_{21}\Delta\varphi + L_{22}\Delta p$$



$$L_{12} = L_{21}$$

$$\Delta\varphi = -\frac{L_{12}}{L_{11}}\Delta p \quad \Rightarrow \quad U = L_{22}\left(1 - \frac{L_{12}^2}{L_{11}L_{22}}\right)\Delta p$$

Electroviscosity in a Straight Capillary

$$v_{\mathrm{eo}}\;\mathbf{r}\; = g\;\mathbf{r}\;\frac{\Delta p}{l} - \frac{\varepsilon\varepsilon_0}{\eta}\left[\zeta - \Psi\;\mathbf{r}\;\right]\frac{\Delta\varphi}{l}$$

For cylindrical capillary $$g\;\mathbf{r}\; = \frac{R^2 - r^2}{4\mu}$$

$$U = \iint_A v\;\mathbf{r}\;dA = \underbrace{\frac{1}{l}\iint_A g\;\mathbf{r}\;dA}_{L_{22}}\Delta p - \underbrace{\frac{1}{l}\iint_A \frac{\varepsilon\varepsilon_0}{\eta}\left[\zeta - \Psi\;\mathbf{r}\;\right]dA}_{L_{12}}\Delta\varphi$$

$$I = \underbrace{\frac{1}{l}\iint_A \left[K_{\mathrm{mig}}\;\mathbf{r}\; - \frac{\varepsilon\varepsilon_0}{\eta}\left[\zeta - \Psi\;\mathbf{r}\;\right]\right]dA}_{L_{11}}\Delta\varphi$$

Straight Cylindrical Capillary. Thin EDL

$$L_{11} = \frac{\pi R^2 K_{\mathrm{tot}}}{l}, \quad L_{12} = \frac{\pi R^2 \varepsilon\varepsilon_0 \zeta}{\eta l}, \quad L_{22=} \frac{\pi R^4}{8\eta l}$$

$$U = L_{22}\left(1 - \frac{L_{12}^2}{L_{11}L_{22}}\right)\Delta p = \frac{\pi R^4}{8\eta l}\left(1 - \frac{8\ \varepsilon\varepsilon_0\ ^2\zeta^2}{\eta K_{\mathrm{tot}} R^2}\right), \quad K_{\mathrm{tot}} = K_{\mathrm{s}} + K_{\mathrm{b}} = \lambda_0$$

From Bikerman theory

$$K_{\mathrm{s}} = \frac{2e^2 n_0 L}{kT\kappa}\left\{D_1\left[\exp\left(-\frac{\tilde{\zeta}}{2}\right) - 1\right]\ 1 + 3m_1\ \ + D_2\left[\exp\left(\frac{\tilde{\zeta}}{2}\right) - 1\right]\ 1 + 3m_2\ \right\}$$

$$K_{\mathrm{b}} = \frac{e^2 n_0 h L}{kT}\ D_1 + D_2$$

Straight Cylindrical Capillary. Thin EDL

For $K_b << K_s$ and $e\zeta/kT << 1$

$$K_s = \frac{e^2 \tilde{\zeta} n_0 L}{kT\kappa}\left[-D_1\left(1+3m_1\right)+D_2\left(1+3m_2\right)\right]$$

For KCl, $D_1 = D_2 = D$ $\qquad K_s = 0$

The enhanced surface conductivity is most important for high surface (or ζ) potentials

Effect of the Double Layer Polarization on the Electrophoresis

Overbeek & Booth

$$\boxed{\nabla^2\Psi = -\frac{\rho_e}{\varepsilon\varepsilon_0}, \quad \text{for binary electrolyte: } \rho_e = e\ \ z_1 n_1 - z_2 n_2}$$

In the case of DL polarization the Boltzmann distribution for the ions is no longer valid!

The bulk charge is then derived from:

$$\nabla \cdot \left[-D_{1,2}\nabla n_{1,2} \mp \left(\frac{D_{1,2} z_{1,2} n_{1,2} e}{kT} \right) \nabla\Psi + n_{1,2}\mathbf{v} \right] = 0$$

Steady state

The fluid velocity, $\mathbf{v}$

$$\eta\nabla^2\mathbf{v} = \nabla p - \rho_e \nabla\Psi, \quad \nabla\cdot\mathbf{v} = 0$$

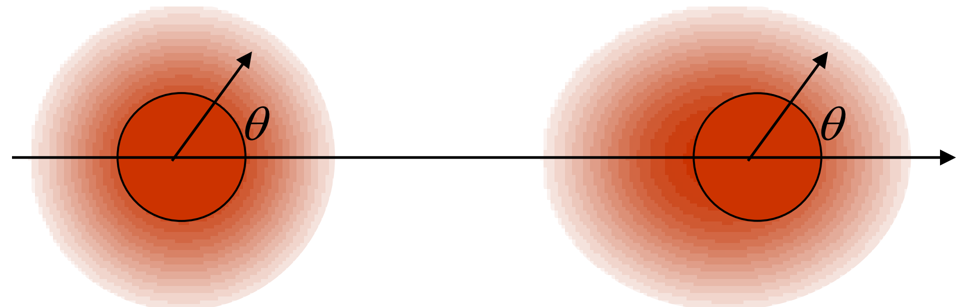
Effect of the Double Layer Polarization on the Electrophoresis

Spherical insulating particle

$$\Psi \to \Psi(r,\theta)$$

$$n_{1,2} \to n_{1,2}(r,\theta)$$

$$\mathbf{v} \to \mathbf{v}(r,\theta)$$



$$v_{\mathrm{ep}} = \frac{\varepsilon\varepsilon_0}{6\pi\eta}\int_{\infty}^{R}\left[\frac{\mathfrak{R}}{r}\frac{d\Psi_{\mathrm{eq}}}{dr} - 2r\int_{\infty}^{r}\left(\frac{1}{r^2}\frac{d\mathfrak{R}}{dr} - \frac{\mathfrak{R}}{r^3}\right)\frac{d\Psi_{\mathrm{eq}}}{dr}\,dr\right]dr$$

$$\hat{\Psi}(r,\theta) = \Psi(r,\theta) - \Psi_{\mathrm{eq}}(r,\theta) = \mathfrak{R}(r)\cos(\theta)$$

Double Layer Polarization and Electrophoretic Mobility

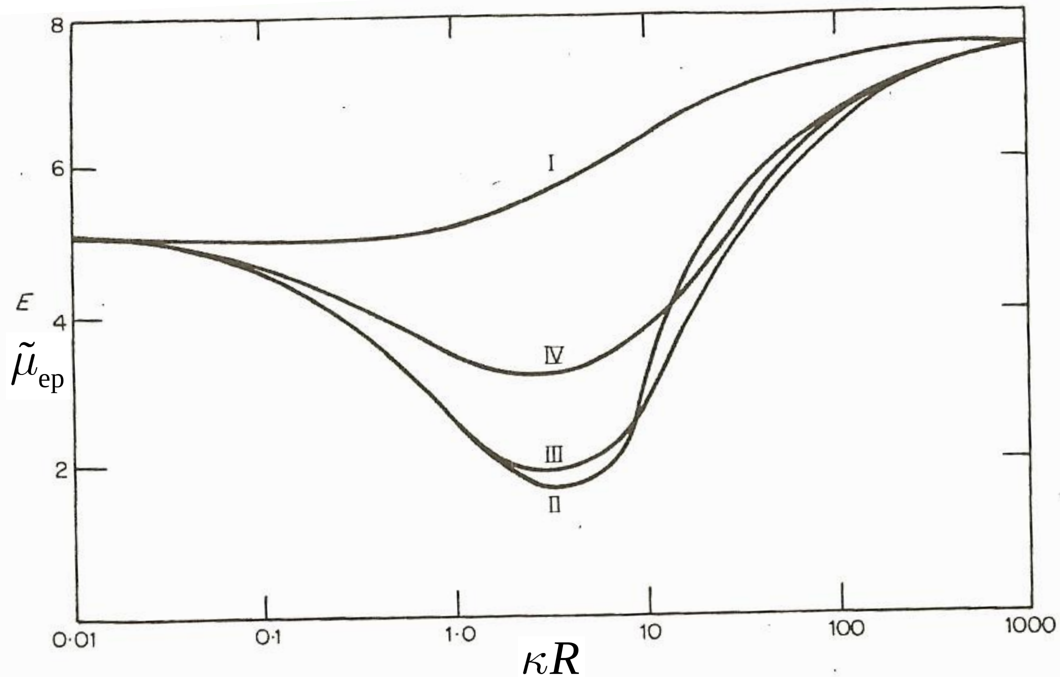


Fig. 3.16. The dimensionless mobility function, *E*, from eq (3.7.3), as a function of κa according to I: Henry (1931); II: Overbeek (1943); III: Booth (1950) and IV: The computed solution of Wiersema *et al.* (1966). Calculations are for $\tilde{\zeta} = 5$ and $m_{\pm} = 0{\cdot}184$.

$$\tilde{\mu}_{ep} = \frac{3\eta e}{2\varepsilon\varepsilon_0 kT}\mu_{ep}$$

Huckel $\quad \tilde{\mu}_{ep} = \tilde{\zeta}$

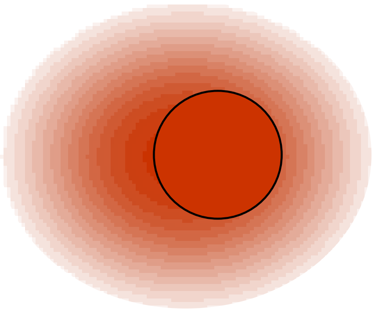
Smoluchowski $\quad \tilde{\mu}_{ep} = \dfrac{3\tilde{\zeta}}{2}$

Overbeek

$$\tilde{\mu}_{ep} = \frac{3}{2}\tilde{\zeta} - \frac{z^2}{2\kappa R}\tilde{\zeta}^3 - \frac{3\varepsilon\varepsilon_0}{16\pi\eta}\left(\frac{kT}{e}\right)^2\frac{1}{\kappa R}\tilde{\zeta}^3$$

for $\kappa R >> 1$

Quantifying the Ionic Relaxation



The DL polarization and then relaxation depends on the mobilities of the ions in the diffuse atmosphere

$$m_{1,2} = \frac{2\varepsilon\varepsilon_0 RT}{3\eta}\frac{z_{1,2}^2}{\Lambda_{1,2}^0}, \quad R = N_A k \leftarrow \text{gas constant}, \left[\Lambda_{1,2}^0\right] \text{ m}^2\text{ohm}^{-1}\text{mol}^{-1}$$

$$m_{1,2} = 12.86\times 10^{-4}\left(\frac{z_{1,2}^2}{\Lambda_{1,2}^0}\right)$$

For KCl $m_{1,2} = 0.184$

Double Layer Polarization and Electrophoretic Mobility

Wiersema, numerical procedure

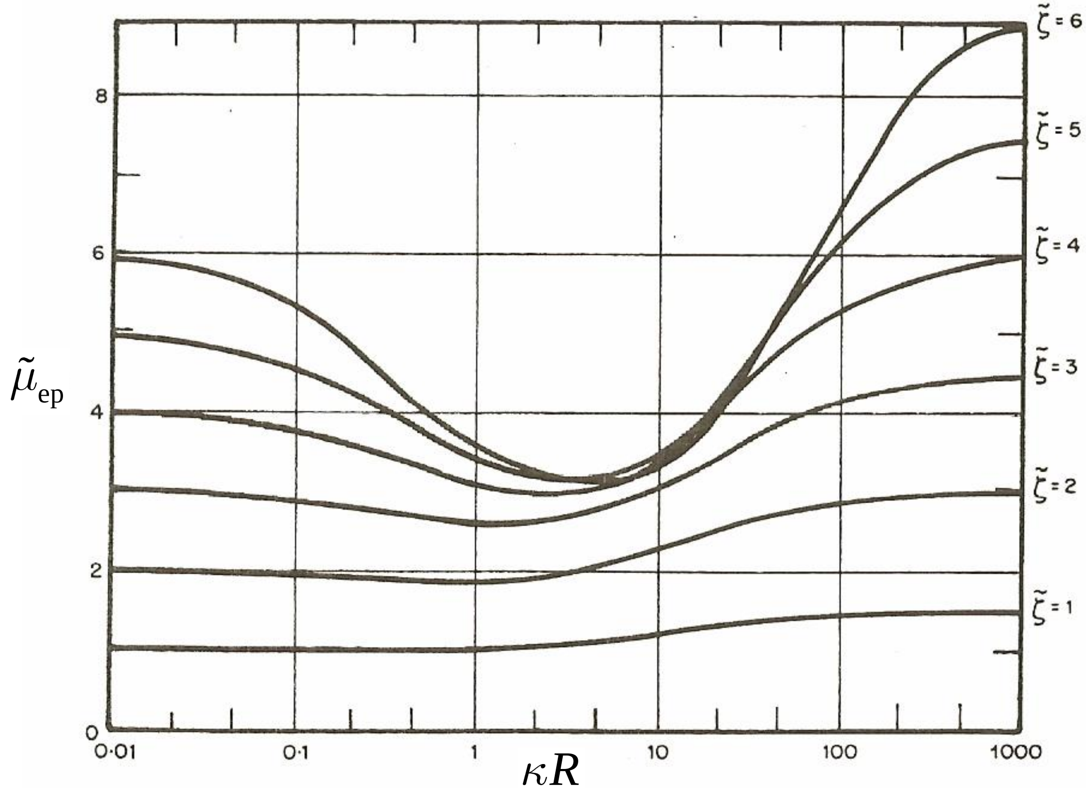
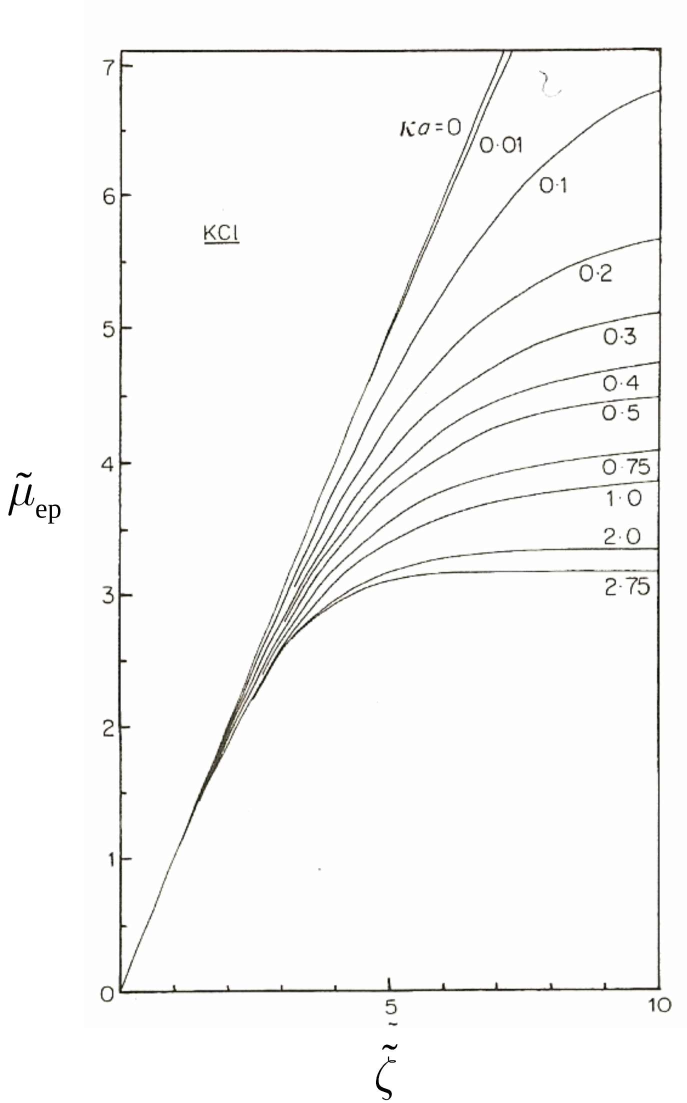
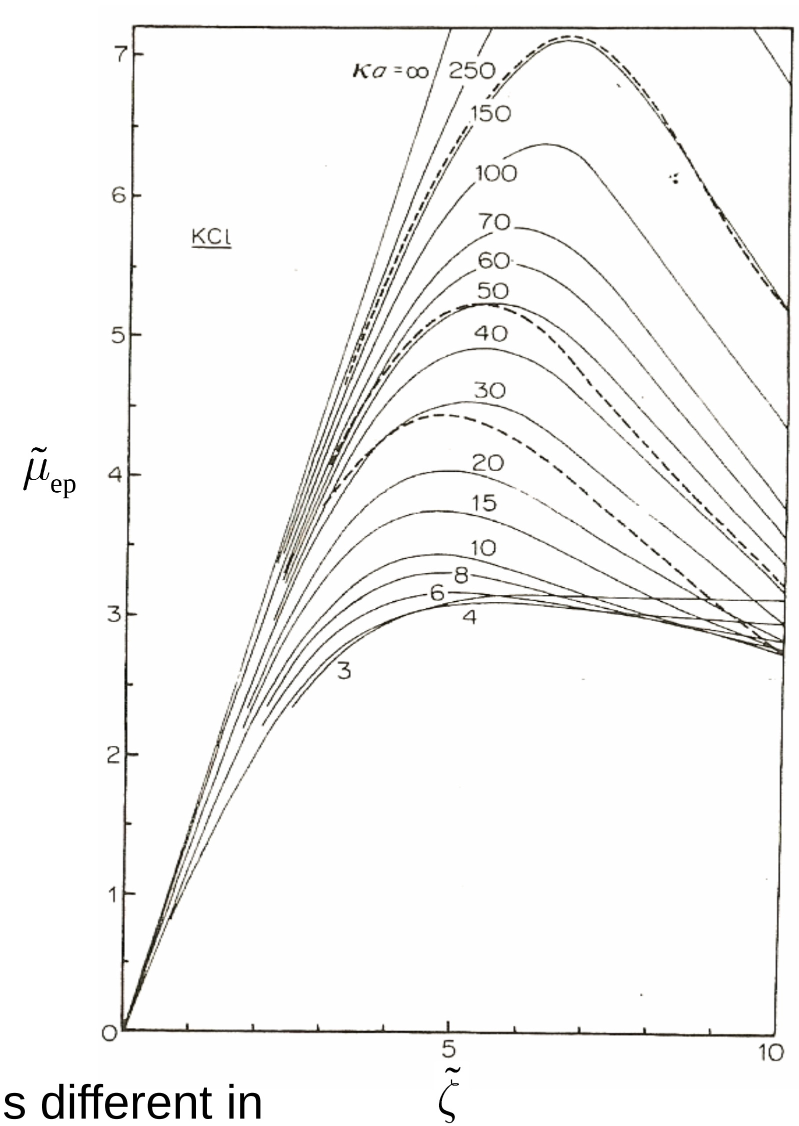


Fig. 3.17. $E(\kappa a)$ for various values of the reduced zeta potential according to Wiersema *et al.* (1966). Note that E approaches $\tilde{\zeta}$ for small κa (the Hückel solution) and that unambiguous assignments of ζ-potential become impossible for high ζ-potentials in the neighbourhood of $\kappa a = 10$.

Double Layer Polarization and Electrophoretic Mobility





The linear slope is different in the two figures

Double Layer Polarization and Electrophoretic Mobility.

Analytical Theories

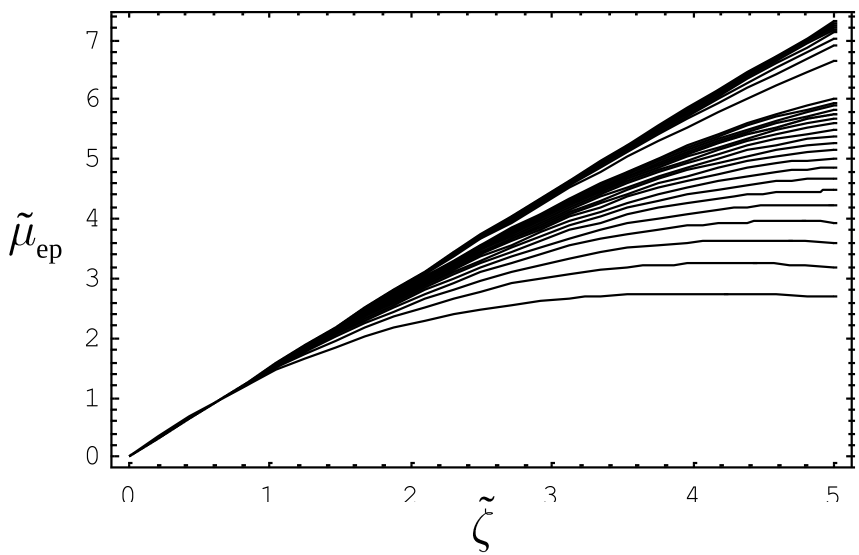
Dukhin and Derjaguin, in E. Matijevic (Ed.), *Surface and Colloid Science*, Vol. 7: 49. New York: Wiley Interscience

$$\tilde{\mu}_{\text{ep}} = \frac{3\tilde{\zeta}}{2} - 6\left[\frac{\tilde{\zeta} M \sinh^2 \ Z \ + \ 2z^{-1} M \sinh \ 2Z \ - 3m\tilde{\zeta} \ \ln \ \cosh \ Z}{\kappa R + 8M \sinh^2 \ Z \ - \ 24m/z^2 \ \ln \ \cosh \ Z}\right]$$

$$M = 1 + \frac{3m}{z^2}, \quad Z = \frac{z\tilde{\zeta}}{4}, \quad \tilde{\zeta} = \frac{e\zeta}{kT}$$

O’Brien and Hunter, for $\kappa R >> 1$

$$\tilde{\mu}_{\text{ep}} = \frac{3\tilde{\zeta}}{2} - \frac{6\left[\frac{\tilde{\zeta}}{2} - \frac{\ln 2}{z} \ 1 - \exp \ -z\tilde{\zeta}\right]}{2 + \frac{\kappa R}{M}\exp\left(-\frac{z\tilde{\zeta}}{2}\right)}$$



Summary

1. The transport of fluid and current in a channel are coupled.
2. Thermodynamics of irreversible processes is presents a convenient tool for analysis of electrokinetic phenomena.
3. The apparent hydrodynamic resistance of a channel increases due to double layer effects.
4. The DL polarization and relaxation have a strong effect on the elecrtophoretic mobility and it relation to the ζ-potential.