Electrokinetic Phenomena in Micro- and Nanochannels

II. Electroosmosis and Current in Narrow Channels

CBE/NE/BME 525

D. N. Petsev

Outline

1. Fluid Transport in Channels with Dimensions Comparable to the Electric Double Layer
2. Electric Current Transport. Bikerman Theory.
3. Current Transport in Narrow Channels

Electroosmosis

D. Hildreth (1970)

Average fluid velocity

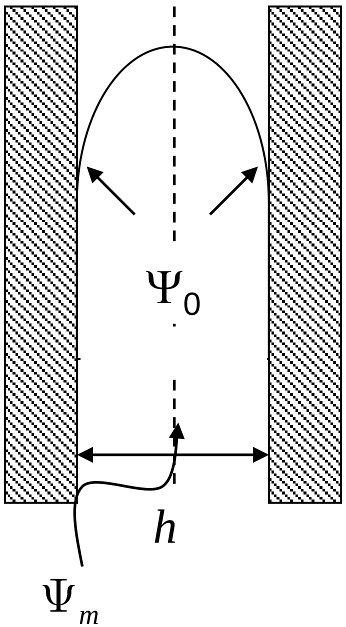
$$\mathbf{U}_{\mathrm{eo}} = \frac{1}{A}\int_A \mathbf{v}_{\mathrm{eo}}\;\;\mathbf{r}\;\; dA, \quad \mathbf{v}_{\mathrm{eo}}\;\;\mathbf{r}\;\; = -\frac{\mathbf{E}\varepsilon\varepsilon_0\zeta}{\eta}\left[1 - \frac{\Psi\;\;\mathbf{r}\;\;}{\zeta}\right]$$

$$\mathbf{U}_{\mathrm{eo}} = -\frac{1}{A}\int_A \frac{\mathbf{E}\varepsilon\varepsilon_0\zeta}{\eta}\left[1 - \frac{\Psi\;\;\mathbf{r}\;\;}{\zeta}\right] dA = -\frac{\mathbf{E}\varepsilon\varepsilon_0\zeta}{\eta}\;\; 1 - G\;\;$$

Finite Double Layer
Thickness Parameter

$$\boxed{G = \frac{1}{\zeta A}\int_A \Psi\;\;\mathbf{r}\;\; dA}$$

Electroosmosis in a Slit



$$G = \frac{1}{\zeta A}\int_A \Psi \ \mathbf{r} \ dA = \frac{1}{\zeta h}\int_0^h \Psi \ x \ dx$$

$$dx = \frac{d\tilde{\Psi}}{\kappa\sqrt{2\left[\cosh \ \tilde{\Psi} \ -\cosh \ \tilde{\Psi}_m \ \right]}}$$

$$\boxed{G = \frac{1}{\tilde{\zeta} A}\int_A \tilde{\Psi} \ \mathbf{r} \ dA = \frac{2}{\tilde{\zeta} \ \kappa h}\int_{\tilde{\zeta}}^{\tilde{\Psi}_m} \frac{\tilde{\Psi} d\tilde{\Psi}}{\sqrt{2\left[\cosh \ \tilde{\Psi} \ -\cosh \ \tilde{\Psi}_m \ \right]}}}$$

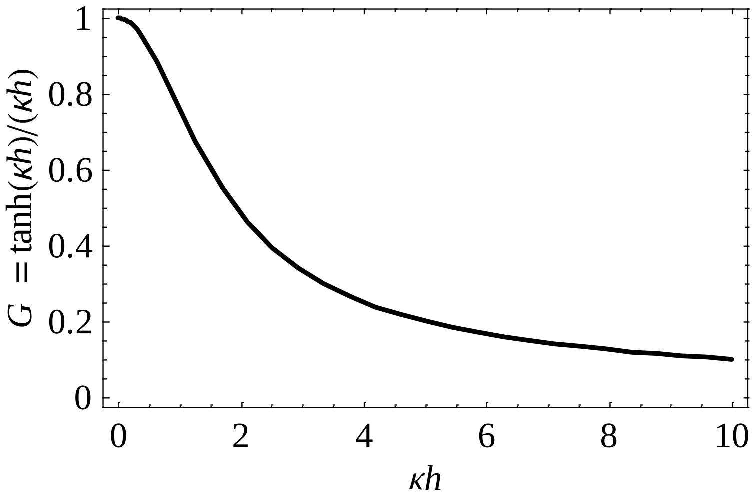
D. Hildreth – numerical solution

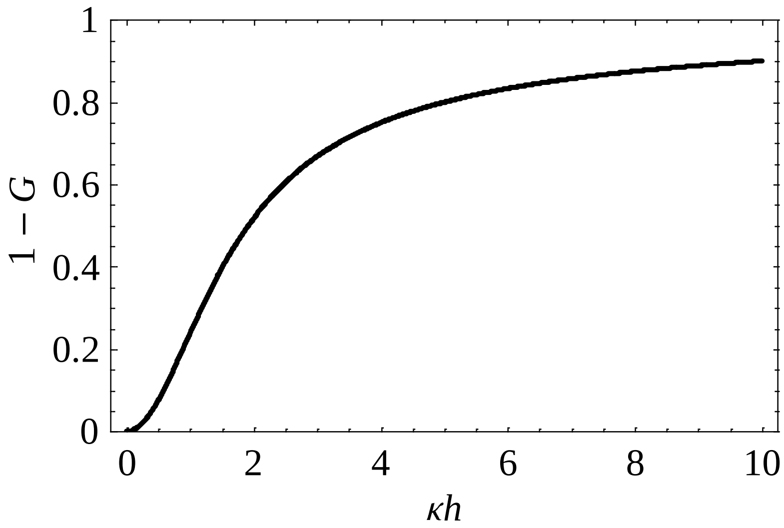
Electroosmosis in a Slit: Low Surface Potential

S. Levine *et al.*, 1975

$$\Psi = \Psi_0 \frac{\cosh[\kappa(h-x)]}{\cosh(\kappa h)} \approx \zeta \frac{\cosh[\kappa(h-x)]}{\cosh(\kappa h)}$$

$$\boxed{G \approx \frac{\tanh(\kappa h)}{\kappa h}}$$





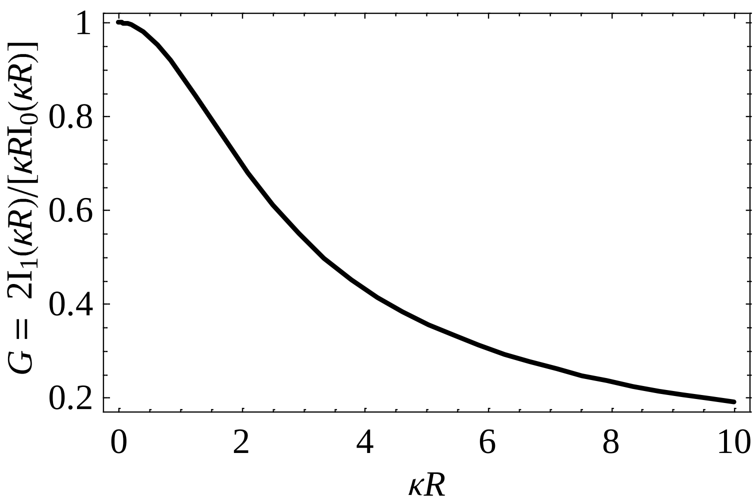
$$\mathbf{U}_{eo} = -\frac{\mathbf{E}\varepsilon\varepsilon_0\zeta}{\eta}(1-G)$$

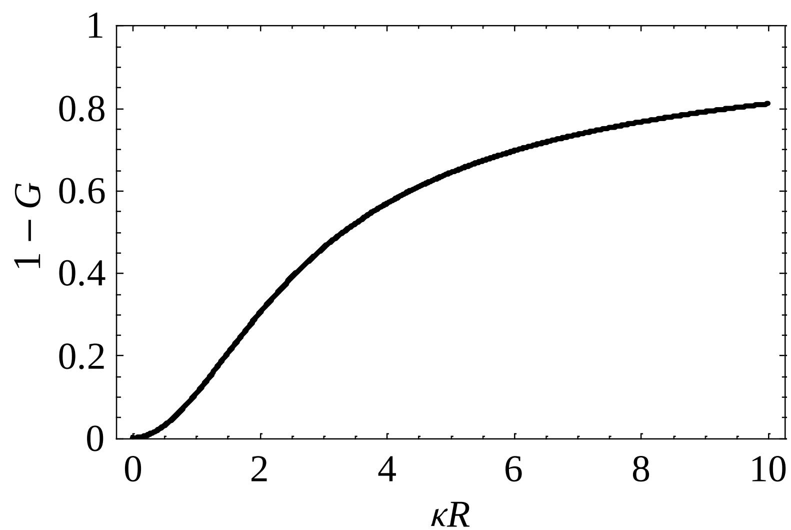
Electroosmosis in a Cylindrical Capillary: Low Surface Potential

S. Levine *et al.*, 1975

$$\Psi = \Psi_0 \frac{I_0(\kappa r)}{I_0(\kappa R)} \approx \zeta \frac{I_0(\kappa r)}{I_0(\kappa R)}$$

$$\boxed{G = \frac{2 I_1(\kappa R)}{\kappa R\, I_0(\kappa R)}}$$

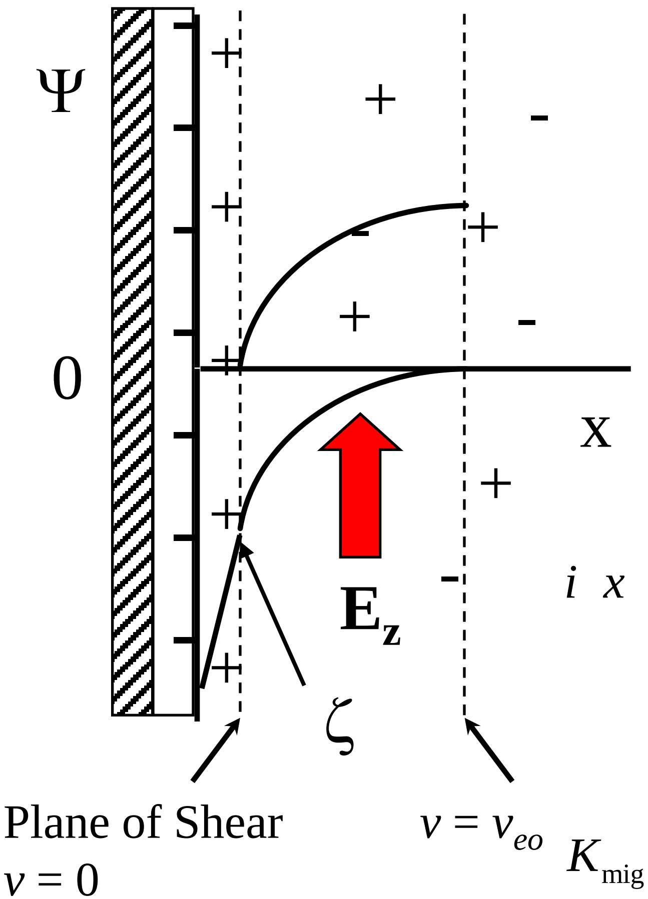




$$\mathbf{U}_{eo} = -\frac{\mathbf{E}\varepsilon\varepsilon_0\zeta}{\eta}(1 - G)$$

$$\frac{2 I_1(\kappa R)}{\kappa R\, I_0(\kappa R)} \approx 1 - \frac{(\kappa R)^2}{8} + O\left[(\kappa R)^3\right]$$

Transport of Current in a Single Flat Double Layer: Theory of Bikerman



Total current in a single double layer

$$I_{\mathrm{tot}} = LE\int_0^\infty i(x)\,dx$$

$$i(x) = \left(\underbrace{K_{\mathrm{mig}}(x)}_{\text{Migration}} - \underbrace{\frac{\rho_{\mathrm{e}}\varepsilon\varepsilon_0\left[\zeta - \Psi(x)\right]}{\eta}}_{\text{EO Convection}}\right)E, \quad \rho_{\mathrm{e}} = e\sum_i z_i n_i^0 \exp\left(-\frac{z_i e\Psi}{kT}\right)$$

$$K_{\mathrm{mig}}(x) = \frac{e^2}{kT}\left(z_1^2 D_1 n_1^0 \exp\left[-z_i\tilde{\Psi}(x)\right] + z_2^2 D_2 n_2^0 \exp\left[-z_i\tilde{\Psi}(x)\right]\right)$$

Double Layer Contribution to the Conductivity

Far from the Double Layer

(Bulk)

$$I_{\mathrm{b}} = \frac{e^2 z_1 z_2 n E}{kT} \; z_1 D_1 + z_2 D_2$$

$$z_1 n_1^0 = z_2 n_2^0 \quad \Rightarrow \quad \frac{n_1^0}{z_1} = \frac{n_2^0}{z_2} = n$$

The contribution form the Double Layer only will be

$$I_{\mathrm{tot}} - I_{\mathrm{b}} = LE \left\{ \frac{e^2}{kT} \; z_1^2 D_1 \int_0^\infty \left[n_1 \; x \; - n_1^0 \right] dx + z_2^2 D_2 \int_0^\infty \left[n_2 \; x \; - n_2^0 \right] dx \; + \right.$$

$$\left. \frac{\varepsilon \varepsilon_0}{\eta} \int_0^\infty \rho_{\mathrm{e}} \; x \; \left[\zeta - \Psi \; x \; \right] dx \right\}$$

Surface Conductivity

Symmetric *z*:*z* electrolyte

Integration variable substitution

$$dx = -\frac{d\tilde{\Psi}}{2\kappa \sinh\left(\frac{\tilde{\Psi}}{2}\right)}$$

$$K_s = \frac{e^2 z^2 n_0}{kT\kappa}\left[D_1 \int_0^{\tilde{\zeta}} \frac{\exp\left(-\tilde{\Psi}\right)-1}{2\sinh\left(\tilde{\Psi}/2\right)} d\tilde{\Psi} + D_2 \int_0^{\tilde{\zeta}} \frac{\exp\left(\tilde{\Psi}\right)-1}{2\sinh\left(\tilde{\Psi}/2\right)} d\tilde{\Psi} + \right.$$

$$\left. \frac{\varepsilon\varepsilon_0}{\eta}\left(\frac{kT}{ze}\right)^2 \int_0^{\tilde{\zeta}} \frac{\left[\exp\left(\tilde{\Psi}\right)-\exp\left(-\tilde{\Psi}\right)\right]\left(\tilde{\zeta}-\tilde{\Psi}\right)}{2\sinh\left(\tilde{\Psi}/2\right)} d\tilde{\Psi}\right]$$

Bikerman Formula for z = 1

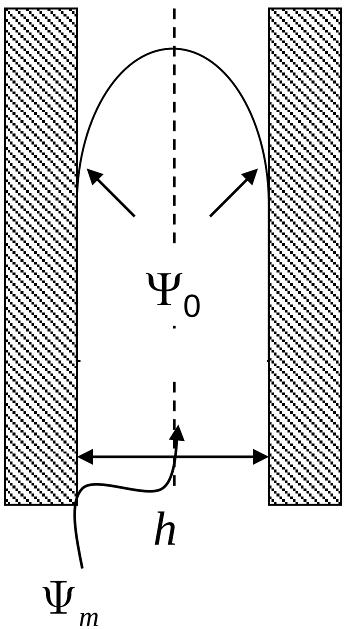
$$K_s = \frac{2e^2 n_0}{kT\kappa}\left\{D_1\left[\exp\left(-\frac{\tilde{\zeta}}{2}\right)-1\right] 1+3m_1 \; + D_2\left[\exp\left(\frac{\tilde{\zeta}}{2}\right)-1\right] 1+3m_2 \;\right\}$$

$$m_{1,2} = \left(\frac{kT}{e}\right)^2 \frac{\varepsilon\varepsilon_0}{6\pi\eta D_{1,2}}$$

For KCl $\quad m_{1,2} = 0.186$

Transport of Current in Channels with Overlapping Double Layers

Slit shaped Channel (Hildreth,)



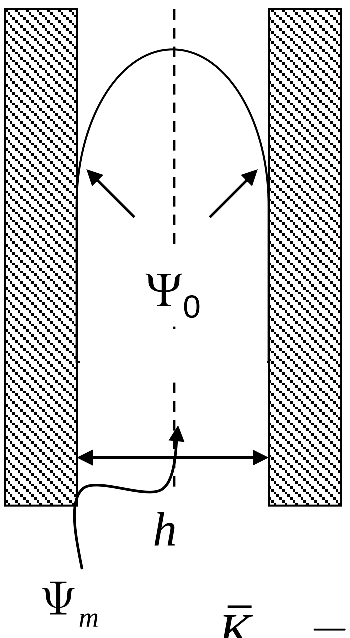
$$\bar{K}_{\mathrm{mig}} = \frac{1}{h}\int_0^h \frac{K_{\mathrm{mig}}\quad x}{K^0_{\mathrm{mig}}}\,dx$$

$$\bar{K}_{\mathrm{mig}} = 1 + \frac{4}{\kappa h}\int_{\tilde{\zeta}}^{\tilde{\Psi}_{\mathrm{m}}} \frac{\sinh\quad \tilde{\Psi}\quad d\tilde{\Psi}}{\sqrt{2\left[\cosh\quad \tilde{\zeta}\quad - \cosh\quad \tilde{\Psi}_m\quad\right]}}$$

$$\bar{K}_{\mathrm{eo}} = \frac{\varepsilon\varepsilon_0}{K^0_{\mathrm{mig}}\eta}\left(\frac{kT}{ze}\right)^2 \int_0^\infty \frac{\rho_{\mathrm{e}}\quad \tilde{\Psi}\quad \tilde{\zeta} - \tilde{\Psi}\quad d\tilde{\Psi}}{\sqrt{2\left[\cosh\quad \tilde{\zeta}\quad - \cosh\quad \tilde{\Psi}\quad\right]}}$$

Transport of Current in Channels with Weakly Overlapping Double Layers

Symmetric z:z electrolyte



In the bulk solution

$$K^0_{\mathrm{mig}} = \frac{(ze)^2 n_0}{kT}(D_1 + D_2)\,, \quad n_0 \text{ -- bulk electrolyte concentration}$$

Relative conductivity of a slit-shaped channel

$$\bar{K}_{\mathrm{mig}} = \frac{1}{h}\int_0^h \frac{K_{\mathrm{mig}}(x)}{K^0_{\mathrm{mig}}}dx, \quad \bar{K}_{\mathrm{eo}} = \frac{1}{h}\int_0^h \frac{K_{\mathrm{eo}}(x)}{K^0_{\mathrm{mig}}}dx$$

$$\bar{K}_{\mathrm{mig}} = 1 + \frac{4}{(D_1+D_2)\kappa h}\left\{D_1\left[\exp\left(-\frac{\tilde{\zeta}}{2}\right) - \exp\left(-\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right] + D_2\left[\exp\left(\frac{\tilde{\zeta}}{2}\right) - \exp\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right]\right\}$$

$$\bar{K}_{\mathrm{eo}} = \frac{8\varepsilon\varepsilon_0}{\eta\kappa h(D_1+D_2)}\left(\frac{kT}{e}\right)^2\left\{2\left[\cosh\left(\frac{\tilde{\zeta}}{2}\right) - \cosh\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right] - (\tilde{\zeta} - \tilde{\Psi}_{\mathrm{m}})\sinh\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right\}$$

Transport of Current in Channels with Weakly Overlapping Double Layers

A special case: KCl ($D_1 = D_2 = D$)

$$\bar{K}_{\mathrm{mig}} = 1 + \frac{4}{\kappa h}\left[\cosh\left(\frac{\tilde{\zeta}}{2}\right) - \cosh\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right]$$

$$\bar{K}_{\mathrm{eo}} = \frac{4\varepsilon\varepsilon_0}{\eta\kappa h}\left(\frac{kT}{e}\right)^2 \frac{1}{D}\left\{2\left[\cosh\left(\frac{\tilde{\zeta}}{2}\right) - \cosh\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right] - \ \tilde{\zeta} - \tilde{\Psi}_{\mathrm{m}} \ \sinh\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right\}$$

Electric Current in Fluidic Channels

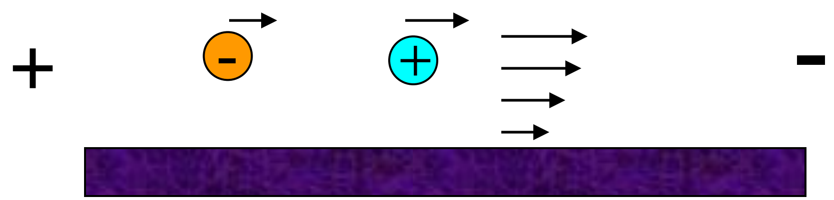
Total current

(from Nernst-Planck)

$$K_{\text{tot}} = \frac{1}{h}\int_0^h \left\{ -\rho_e(x)\frac{\varepsilon\varepsilon_0\left[\zeta - \Psi(x)\right]}{\eta} + K_{\text{mig}}(x) \right\} dx$$

EO current   Migration

The **EO current** is carried by the convective EO flow



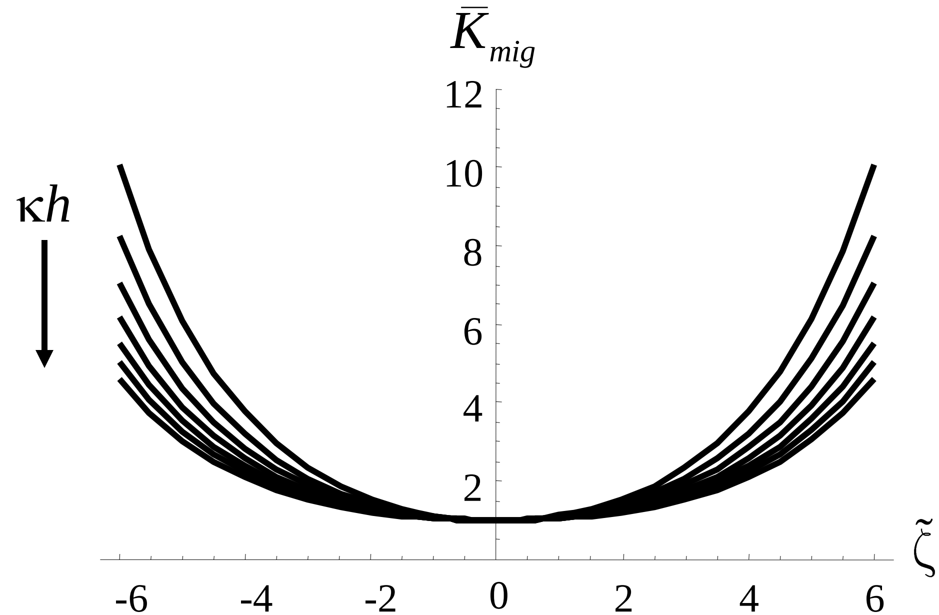
The **migration current** is due to transport of the ions toward the electrodes with opposite polarity as in the bulk

Electric Current Symmetric (1:1) Electrolyte

For $D^{+} = D^{-} = D$ (KCl)

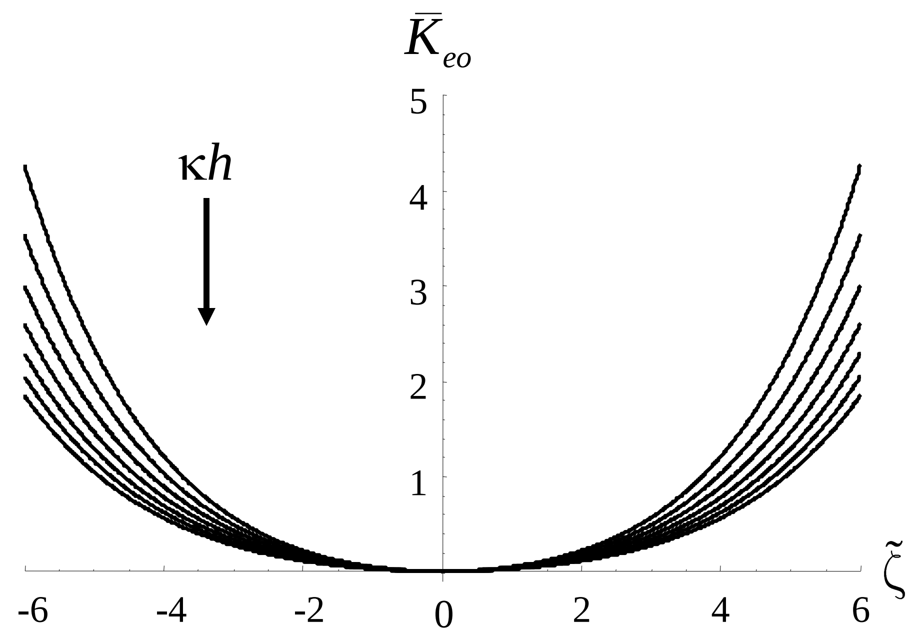
Relative to the bulk

$$\bar{K}_{\mathrm{mig}} = 1 + \frac{4}{\kappa h}\left[\cosh\left(\frac{\tilde{\zeta}}{2}\right) - \cosh\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right]$$



$$\bar{K}_{\mathrm{eo}} = \frac{4\varepsilon\varepsilon_0}{\eta\kappa h}\left(\frac{kT}{e}\right)^2 \frac{1}{D} \times$$

$$\left\{2\left[\cosh\left(\frac{\tilde{\zeta}}{2}\right) - \cosh\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right] - \quad \tilde{\zeta} - \tilde{\Psi}_{\mathrm{m}} \quad \sinh\left(\frac{\tilde{\Psi}_{\mathrm{m}}}{2}\right)\right\}$$



From the top: κh = 4, 5, 6, 7, 8, 9, 10

The University of New Mexico

Summary

1. The potential distribution in a fluidic channel determines the shape of the flow velocity profile. For very thin double layers the flow is plug-shaped.
2. The double layers may have an important effect on the total current in fluidic channels even when they are much thinner than the channel width.
3. The current in channels have a convective component wich is not present in systems without double layer wall effects.