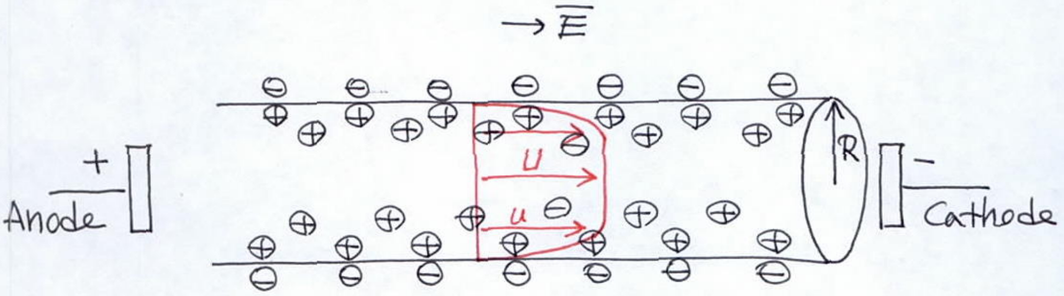
Electroosmosis

- Basic concept

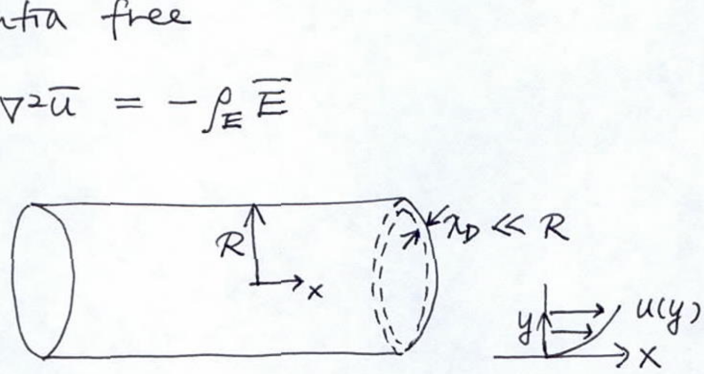


Momentum equation

$$\rho \frac{D\bar{u}}{Dt} = -\nabla p + \mu \nabla^2 \bar{u} + \rho \bar{g} + \underbrace{\rho_E \bar{E}}_{\text{electric body force per unit volume}}$$

- [no pressure gradient
  inertia free

$$\mu \nabla^2 \bar{u} = -\rho_E \bar{E}$$



In diffuse layer

$$\mu \frac{\partial^2 u}{\partial y^2} = -\rho_E E_x \underset{\substack{\uparrow \\ \text{Poisson's eq. } (\nabla^2 \phi = -\frac{\rho_E}{\epsilon})}}{=} \epsilon \frac{\partial^2 \phi}{\partial y^2} E_x$$

$$\mu \frac{\partial u}{\partial y} = \epsilon \frac{\partial \phi}{\partial y} E_x$$

at the edge of diffuse layer ($y \to \infty$)

$$\frac{\partial u}{\partial y} = \frac{\partial \phi}{\partial y} = 0.$$

- $\cancel{\mu u = \epsilon \phi E_x + C}$

$$\mu \int_0^\infty \frac{\partial u}{\partial y} dy = \epsilon E_x \int_0^\infty \frac{\partial \phi}{\partial y} dy$$

$$\mu(U-0) = \epsilon E_x (0-\zeta)$$

$$\therefore U = -\frac{\epsilon \zeta E_x}{\mu} \quad : \text{Helmholtz–Smoluchowski eq.}$$

Outside the diffuse layer.

$$\cancel{\frac{\mu}{r}}\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right) = 0$$

$$r\frac{\partial u}{\partial r} = \text{const} = a$$

$$\frac{\partial u}{\partial r} = \frac{a}{r}$$

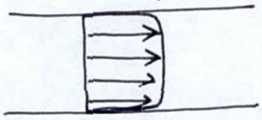
$$u = a\ln r + b$$

$$u(r=0) = \text{finite} : \quad a=0$$

$$u = \text{const} = U.$$

looks like the liquid slipping

$\therefore$ plug flow



U independent of R

e.g. $\zeta_{typical} \approx 0.1\ V$, $\quad E_x = 10^3\ V/m$

$U = ?$

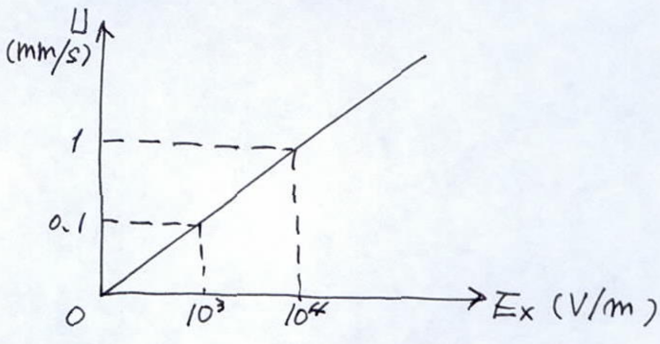
$$\epsilon_{water} = \epsilon_0(1+79.1) = 8.854\times10^{-12}\times 80 \ \ F/m$$

$$= 7.08\times10^{-10} \ \ F/m$$

$$\mu_{water} = 10^{-3}\ kg/m\cdot s$$

$$U = \frac{(7.08\times10^{-10})(0.1)(10^3)}{10^{-3}} = 10^{-9-1+3+3} = 10^{-4}\ m/s$$

$$= 100\ \mu m/s$$



· Comparison with pressure-driven flow

$$Q_{\Delta p} = \frac{\pi}{8\mu} R^4 \left(\frac{\Delta p}{L}\right) \quad \sim R^4$$

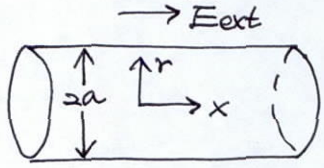
$$Q_{EOF} = U \pi R^2 \qquad \sim R^2 \qquad \left(\frac{\lambda_D}{R} \ll 1 \right)$$

as $R \downarrow$ – electroosmosis increasingly effective

Effects of $\frac{\lambda_D}{R}$

· pressure gradient exists

· binary dilute solution



Momentum equation :

$$0 = -\nabla p + \mu \nabla^2 \bar{u} + \underbrace{\rho_E \bar{E}}_{\substack{\| \\ -F(z_+ c_+ + z_- c_-)\nabla\phi}}$$

· symmetrical salt : $z_+ = z_- = z$

$$\frac{\mu}{r}\frac{\partial}{\partial r}\left(r \frac{\partial u}{\partial r}\right) = \frac{\partial p}{\partial x} + Fz\,(c_+ - c_-)\frac{\partial \phi}{\partial x}$$

ion concentration ~ electric field.

$$\nabla^2 \phi = -\frac{\rho_E}{\epsilon}$$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \phi}{\partial r}\right) + \cancel{\frac{\partial^2 \phi}{\partial x^2}} = -\frac{Fz}{\epsilon}(c_+ - c_-)$$

without assuming thin EDL

long capillary

$$\phi(x, r) = \Phi(x) + \psi(x, r)$$

(~~externally applied~~ $\cancel{\frac{d\Phi}{dx} = -E_{ext}}$)

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \psi}{\partial r}\right) = -\frac{Fz}{\epsilon}(c_+ - c_-)$$

Nernst-Planck equation → Boltzmann distribution of c

$$c_{\pm}(x,r) = c_0(x)\exp\left(\mp\frac{zF\psi}{RT}\right)$$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\psi}{\partial r}\right) = -\frac{Fz}{\epsilon}c_0\left[\exp\left(-\frac{zF\psi}{RT}\right) - \exp\left(\frac{zF\psi}{RT}\right)\right]$$

$$= \frac{Fzc_0}{\epsilon}\cdot 2\sinh\left(\frac{zF\psi}{RT}\right)$$

Nondimensionalization

$$r^* = \frac{r}{a}, \quad \lambda^* = \frac{\lambda_D}{a}, \quad \psi^* = \frac{zF\psi}{RT}$$

$$\lambda_D = \left(\frac{\epsilon RT}{2F^2z^2c}\right)^{1/2}$$

$$\frac{1}{ar^*}\frac{1}{a}\frac{\partial}{\partial r^*}\left(ar^*\frac{1}{a}\frac{\partial\psi^*}{\partial r^*}\cdot\frac{RT}{zF}\right) = \frac{FzC}{\epsilon}\cdot 2\sinh(\psi^*)$$

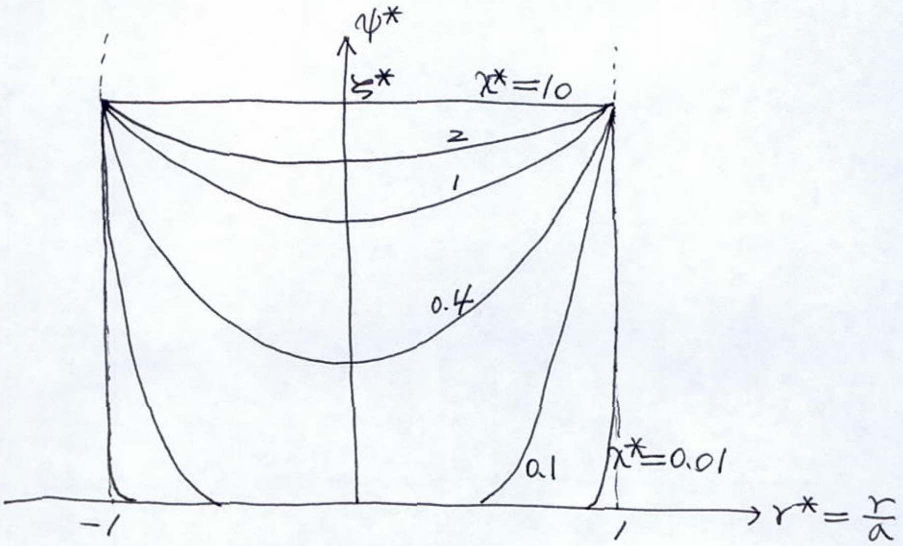
$$\frac{1}{a^2}\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial\psi^*}{\partial r^*}\right)\frac{\epsilon RT}{2F^2z^2C} = \sinh\psi^*$$

$$\lambda^{*2}\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial\psi^*}{\partial r^*}\right) = \sinh\psi^*$$

B.C. $r^*=0$: $\frac{\partial\psi^*}{\partial r^*} = 0$

$r^*=1$: $\psi^* = \psi_w^* = \zeta^*$

numerical solution



Combining the momentum eq and the Poisson eq.

$$\frac{\mu}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right) = -\frac{\epsilon}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \psi}{\partial r}\right)\frac{d\Phi}{dx} + \frac{dp}{dx}$$

BC $\quad \frac{\partial u}{\partial r} = 0$ and $\frac{\partial \psi}{\partial r} = 0 \quad$ at $r = 0$

$\qquad u = 0 \,.\; \psi = \zeta \quad$ at $r = a$

Integrating,

$$\mu r \frac{\partial u}{\partial r} = -\epsilon r \frac{\partial \psi}{\partial r}\frac{d\Phi}{dx} + \frac{1}{2}r^2\frac{dp}{dx} + \cancel{c_1}^{\,0}$$

$$\mu u = -\epsilon \psi \frac{d\Phi}{dx} + \frac{1}{4}r^2\frac{dp}{dx} + c_2$$

$$0 = -\epsilon \zeta \frac{d\Phi}{dx} + \frac{1}{4}a^2\frac{dp}{dx} + c_2$$

$$c_2 = \epsilon\zeta\frac{d\Phi}{dx} - \frac{1}{4}a^2\frac{dp}{dx}$$

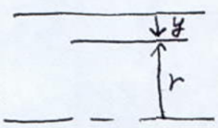
$$\begin{cases} u = -\dfrac{\epsilon(\overset{(r)}{\psi}-\zeta)}{\mu}\dfrac{d\Phi}{dx} + \dfrac{r^2-a^2}{4\mu}\dfrac{dp}{dx} \\[2ex] Q = \displaystyle\int_0^a u(2\pi r)\,dr = -\int_0^a \frac{\epsilon(\psi-\zeta)}{\mu}\frac{d\Phi}{dx}2\pi r\,dr - \frac{\pi a^4}{8\mu}\frac{dp}{dx} \end{cases}$$

$$\psi(r) = ?$$

(1) Limiting case $\frac{\lambda_D}{a} \ll 1$

neglect curvature effect

$$\frac{\partial^2 \psi^*}{\partial y^2} = \sinh \psi^* . \qquad y^* = \frac{y}{\lambda_D}$$



$y = a - r$

$$\psi^* = \frac{zF\psi}{RT} \ll 1$$

$$\frac{\partial^2 \psi^*}{\partial y^{*2}} - \psi^* = 0$$

$$\psi^* = c_1 e^{y^*} + c_2 e^{-y^*}$$

$y^* = 0 \; : \; \psi^* = \zeta^*$

$y^* \to \infty \; : \; \psi^* \to 0$

$$\psi^* = \zeta^* e^{-y^*}$$

$$\psi = \zeta e^{-(a-r)/\lambda_D}$$

$$\therefore \quad u = \frac{\epsilon \zeta}{\mu}\left[1 - e^{-(a-r)/\lambda_D}\right]\frac{d\Phi}{dx} + \frac{r^2 - a^2}{4\mu}\frac{dp}{dx}$$

$$Q = \frac{\epsilon\zeta}{\mu}\frac{d\Phi}{dx}\pi a^2\left[1 - \frac{2\lambda_D}{a} + \underbrace{\cancel{\frac{2\lambda_D^2}{a^2}}}_{H.O.T} - \underbrace{\cancel{\frac{2\lambda_D^2}{a^2}e^{-\frac{a}{\lambda_D}}}}_{H.O.T.}\right] - \frac{\pi a^4}{8\mu}\frac{dp}{dx}$$

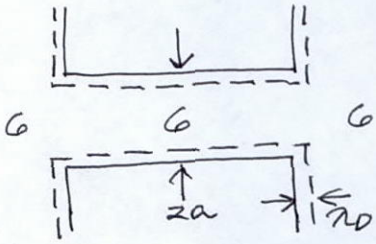
For $\frac{dp}{dx} = 0$, $\frac{a}{\lambda_D} \to \infty$. $(\gg 100)$

$$u \approx \frac{\epsilon\zeta}{\mu}\frac{d\Phi}{dx} \quad : \text{Helmholtz-Smoluchowski eq.}$$

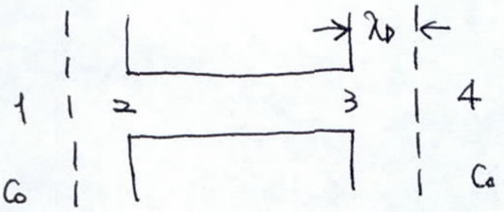
(1) $\lambda^* \ll 1$, $\lambda_D \ll a$

$\psi = 0$ in most region

$c_+ = c_- = c_0$



(2) λ^* large . $\lambda_D \gtrsim \overset{10}{a}$ $\psi = \zeta$ throughout . Fig. 6.5.2.



At equilibrium with no flow ($u=0$) & no flux ($j_i^*=0$),

$\psi_1 = \psi_4 = 0$

$\psi_2 = \psi_3 = \zeta$

Boltzmann distribution

$$c_{\pm 2} = c_{\pm 3} = c_0 \exp\left(\mp \frac{zF\zeta}{RT}\right)$$

At small Peclet number. $Pe = \dfrac{U\lambda_D}{D} \ll 1$,

diffusion and electromigration dominate over convection:

Boltzmann distribution still holds

Momentum equation:

$$\frac{\mu}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right) = \frac{\partial p}{\partial x} + Fz(c_+ - c_-)\frac{\partial \phi}{\partial x}$$

$$c_+ - c_- = -c_0 \sinh\left(\frac{zF\zeta}{RT}\right)$$

B.C. $u = 0$ at $r = a$

$\dfrac{\partial u}{\partial r} = 0$ at $r = 0$.

$$u = -\frac{a^2 - r^2}{4\mu}\frac{d}{dx}\left[p - 2zFc_0\Phi \sinh\left(\frac{zF\zeta}{RT}\right)\right]$$

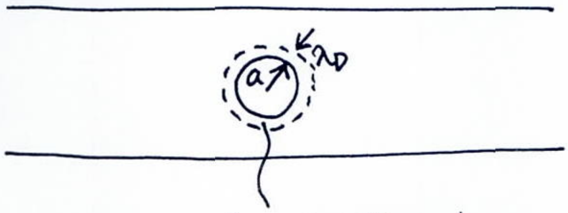
$$Q = -\frac{\pi a^4}{8\mu}\frac{d}{dx}\left[p - 2zFc_0\Phi \sinh\left(\frac{zF\zeta}{RT}\right)\right]$$

when $\lambda_D \gg a$

$Q \sim a^4$: same as pressure-driven flow

ELECTROPHORESIS

- The charge of macromolecules and particles



$$dq = 4\pi r^2 \rho_E \, dr$$

Poisson eq in spherical coordinates

$$\nabla^2 \phi = -\frac{\rho_E}{\epsilon}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial^2}{\partial \phi^2}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi}{\partial r}\right) = -\frac{\rho_E}{\epsilon}$$

$$q = \int dq = -\int_a^\infty 4\pi r^2 \epsilon \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi}{\partial r}\right) dr$$

$$= -\int_a^\infty 4\pi\epsilon \frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi}{\partial r}\right) dr$$

$$= -4\pi\epsilon \left(r^2 \frac{\partial \phi}{\partial r}\Big|_{r\to\infty} - r^2 \frac{\partial \phi}{\partial r}\Big|_{r=a} \right)$$

$$= 4\pi\epsilon a^2 \left(\frac{\partial \phi}{\partial r}\right)_{r=a} \quad [C]$$: charge in the double layer

Surface charge density $\quad q_s = -\frac{q}{4\pi a^2} = -\epsilon \left(\frac{\partial \phi}{\partial r}\right)_{r=a} \quad [C/m^2]$

$\frac{\partial \phi}{\partial r}\Big|_{r=a} \sim q_s$