EXTENDED CHARGE ELECTRO-OSMOSIS AND ELECTRO-CONVECTIVE INSTABILITY

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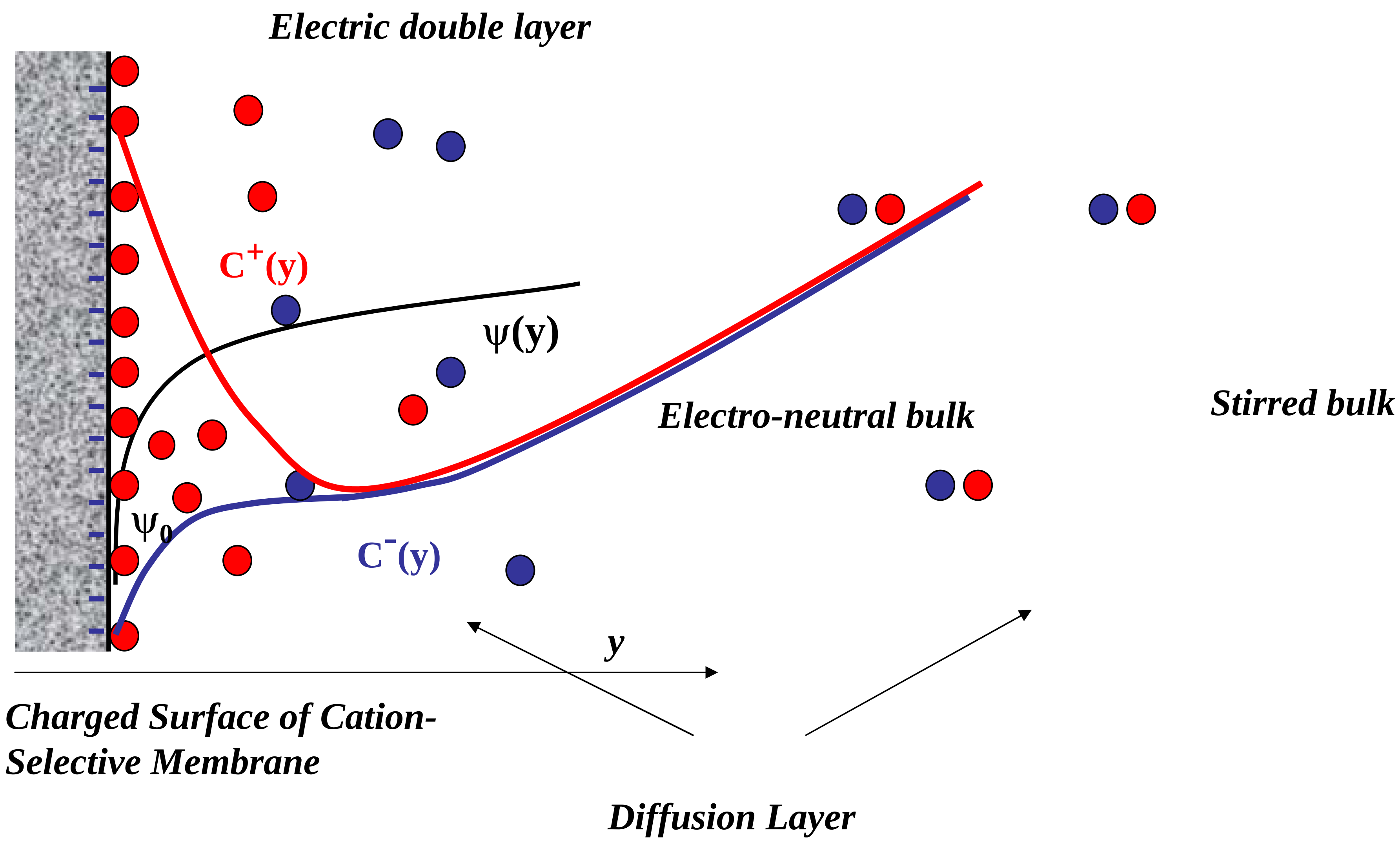
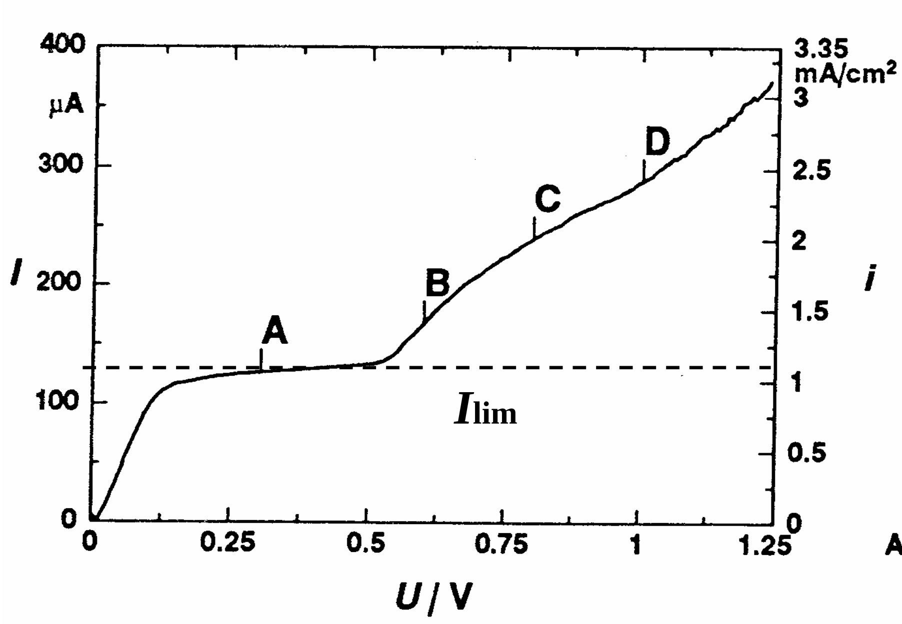
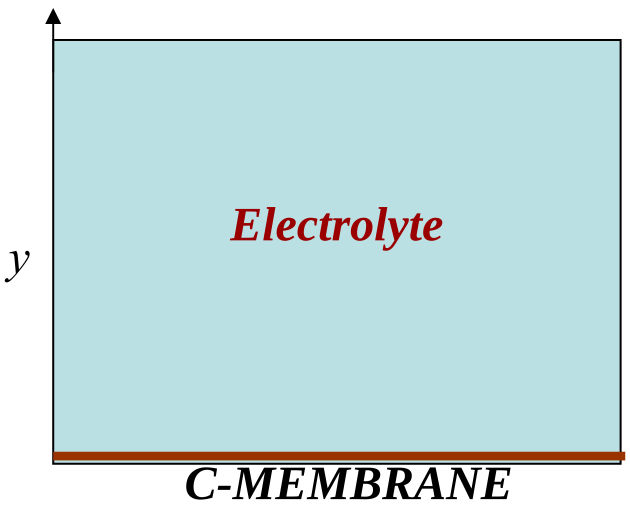
Conduction from an electrolyte into a charge-selective solid (ion exchange membrane or metal electrode)

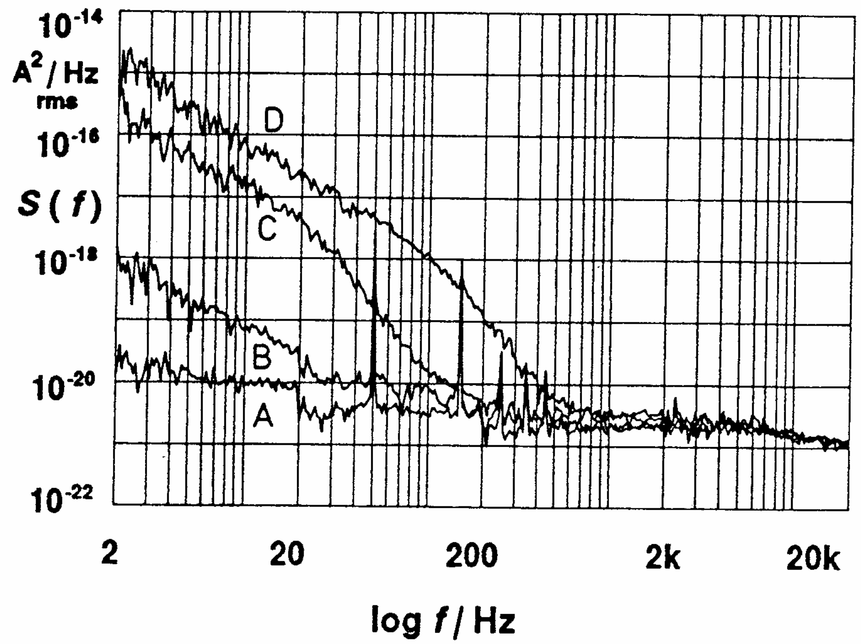


F. Maletzki et al 1992



Voltage-current curve of a C-membrane





Current power spectra

Classical picture of concentration polarization

membrane: y=0   outer edge of diffusion layer: y=1

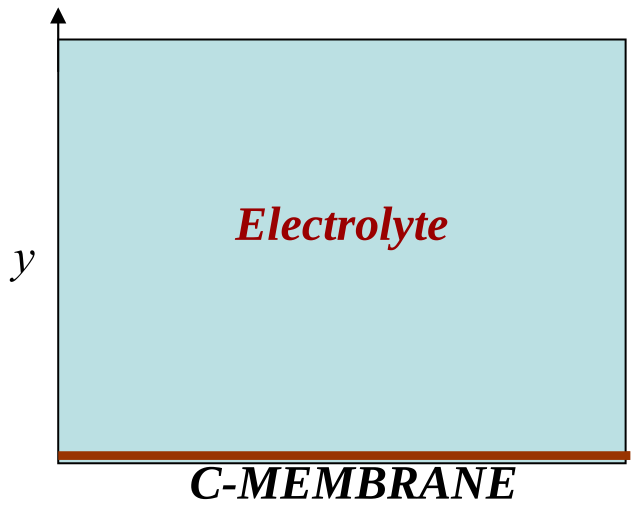
$$c^{+} = c^{-} = \bar{c}, \quad 0 < y < 1.$$

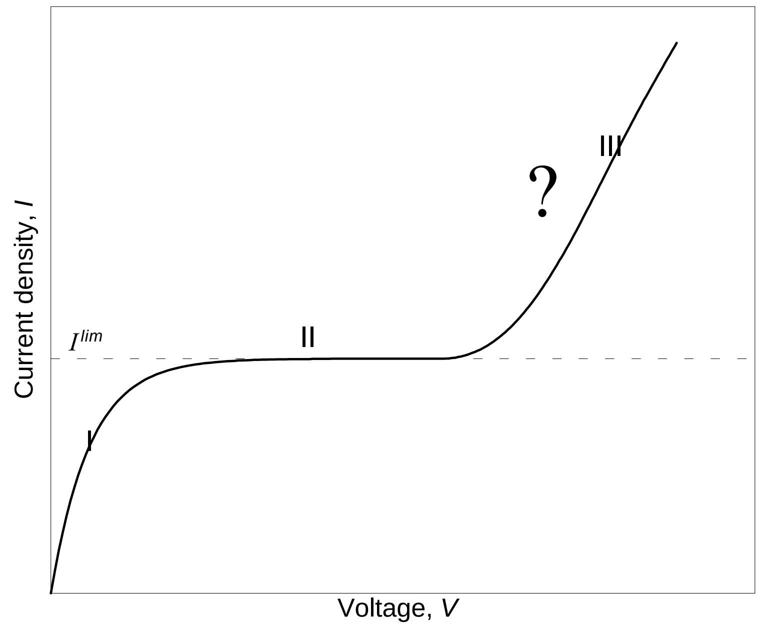
$$\bar{c}_y - \bar{c}\,\bar{\varphi}_y = 0, \; \bar{c}_y + \bar{c}\,\bar{\varphi}_y = I$$

and $\bar{c}(1) = 1, \; \bar{\varphi}(1) = 0, \; \bar{\varphi}(0) = -V$.

$$\bar{c} = \frac{I}{2}(y-1)+1, \; \bar{\varphi} = \ln \bar{c}, I = 2\left(1-e^{-V}\right)$$

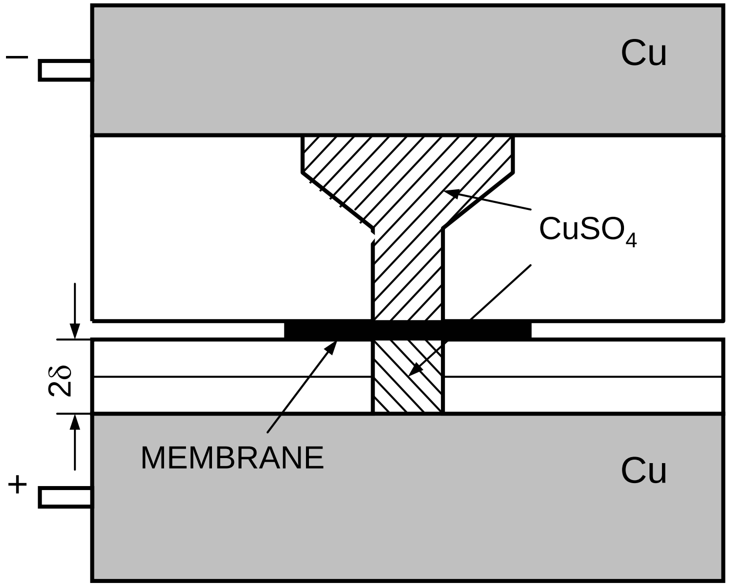
$$V \to \infty \Rightarrow \quad \bar{c}(0) = 0, \; I \to I^{\lim} = 2$$

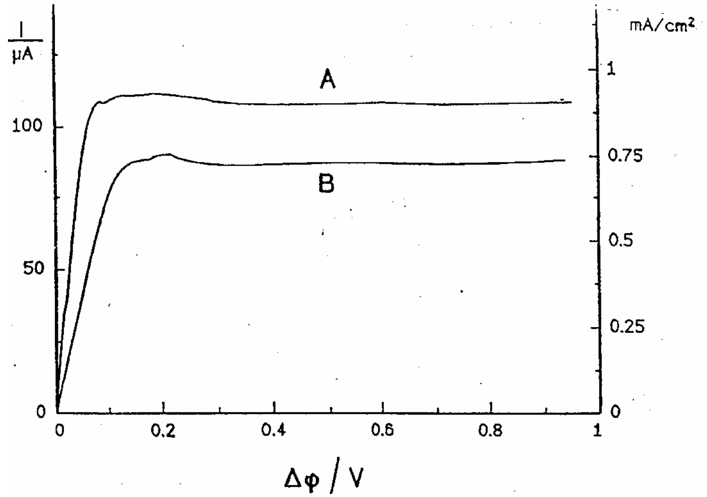




Voltage-current characteristic for amalgamated copper cathode (A) and membrane (B) with electrolyte immobilized by agar-agar, F. Maletzki et al 1992

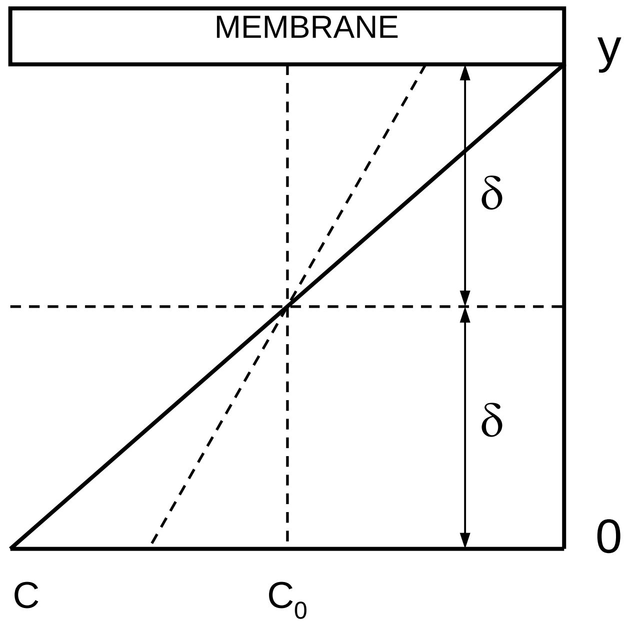
Prototypical experiment, I. Rubinstein 70-th





Convective mixing

$$0.01 < C < 0.1N, 100 < \delta < 200\mu,\ 10 < \mathrm{Ra} < 100$$



No Gravitational Convection

No Free Surface

No Marangoni Convection

Electro-Convection

TWO TYPES OF ELECTRO-CONVECTION IN STRONG ELECTROLYTES

Bulk electro-convection | **Electro-osmosis**

$$c_t^+ + \mathrm{Pe}\,\vec{v}\,\nabla c^+ = D\nabla(\nabla c^+ + c^+\nabla\varphi) \quad 0<y<1,\ -\infty<x<\infty$$

$$c_t^- + \mathrm{Pe}\,\vec{v}\,\nabla c^- = \nabla(\nabla c^- - c^-\nabla\varphi)$$

$$\varepsilon^2\Delta\varphi = c^- - c^+$$

$$\frac{1}{\mathrm{Sc}}\vec{v}_t = \Delta\vec{v} + \Delta\varphi\nabla\varphi - \nabla p$$

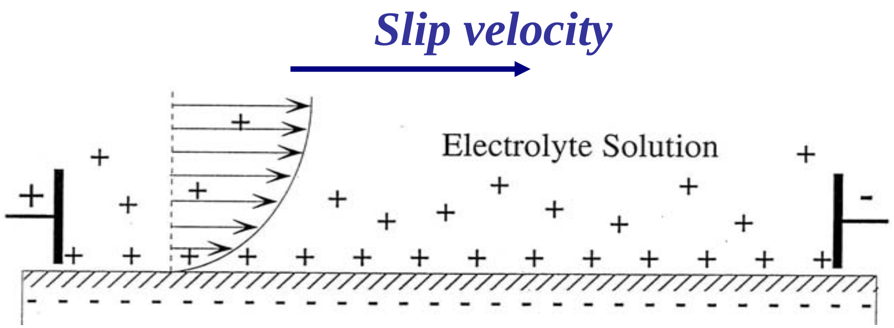
$$\nabla\vec{v} = 0$$

$$y=0:\ \ \vec{v}=0,\ c^+ = p_1,\ \varphi = -V,\ c_y^- - c^-\varphi_y = 0$$

$$\mathrm{Pe} = \frac{v_0 L}{D_-} = \left(\frac{RT}{F}\right)^2 \frac{d}{4\pi\eta D_-} \approx 0.5,\ \ \mathrm{Sc} = \frac{\nu}{D_-},\ D = \frac{D_+}{D_-}$$

$$\varepsilon = \frac{(dRT)^{1/2}}{2F(\pi c_0)^{1/2}},\ 10^{-12} < \varepsilon^2 < 10^{-5}$$

Bulk



$\varepsilon \ll 1 \Rightarrow$ OUTER SOLUTION: BULK ELECTRO-CONVECTION

INNER SOLUTION: ELECTRO-OSMOTIC SLIP

"BULK" ELECTRO-CONVECTION (NO SLIP)

$$c = c^- = c^+ ,\ 0 < y < 1$$

$$c_t + \mathrm{Pe}\,\vec{v}\,\nabla c = D\nabla(\nabla c + c\nabla\varphi)$$

$$c_t + \mathrm{Pe}\,\vec{v}\,\nabla c = \nabla(\nabla c - c\nabla\varphi)$$

$$\frac{1}{\mathrm{Sc}}\vec{v}_t = \Delta\vec{v} - \nabla p + \Delta\varphi\nabla\varphi$$

$$\nabla\vec{v} = 0$$

$$y = 0{,}1:\ c_y + c\varphi_y = I,\ c_y - c\varphi_y = 0,\quad \vec{v} = 0$$

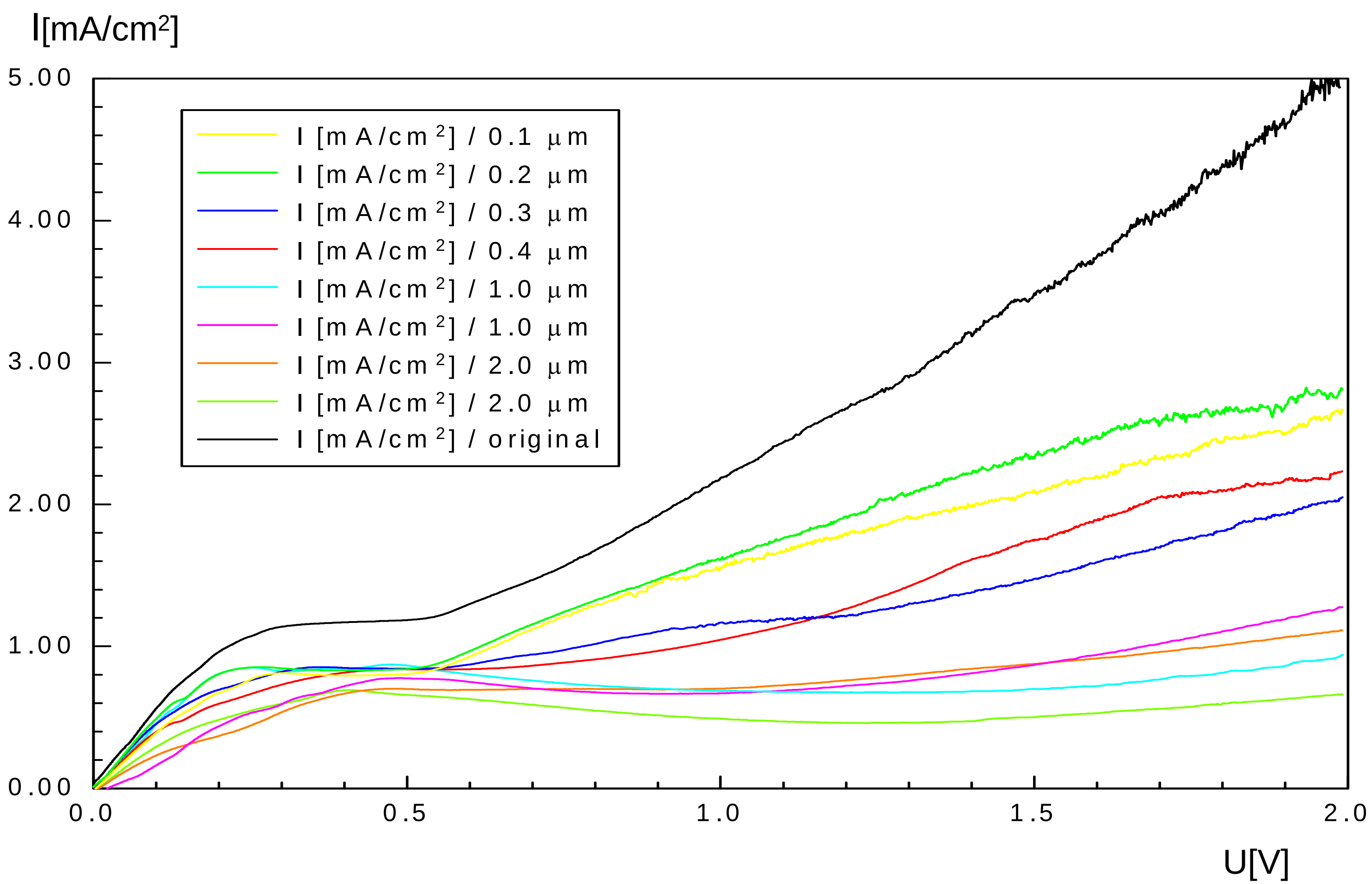
$$c_0(y) = \frac{I}{2}(y-1)+1,\ \varphi_0 = \ln c_0, \vec{v}_0 = 0$$

For low-molecular electrolytes:

1. Conduction - stable,

2. Electric force - stabilizes like gravitation for stable stratification.

Rubinstein, Zaltzman, Pretz, Linder

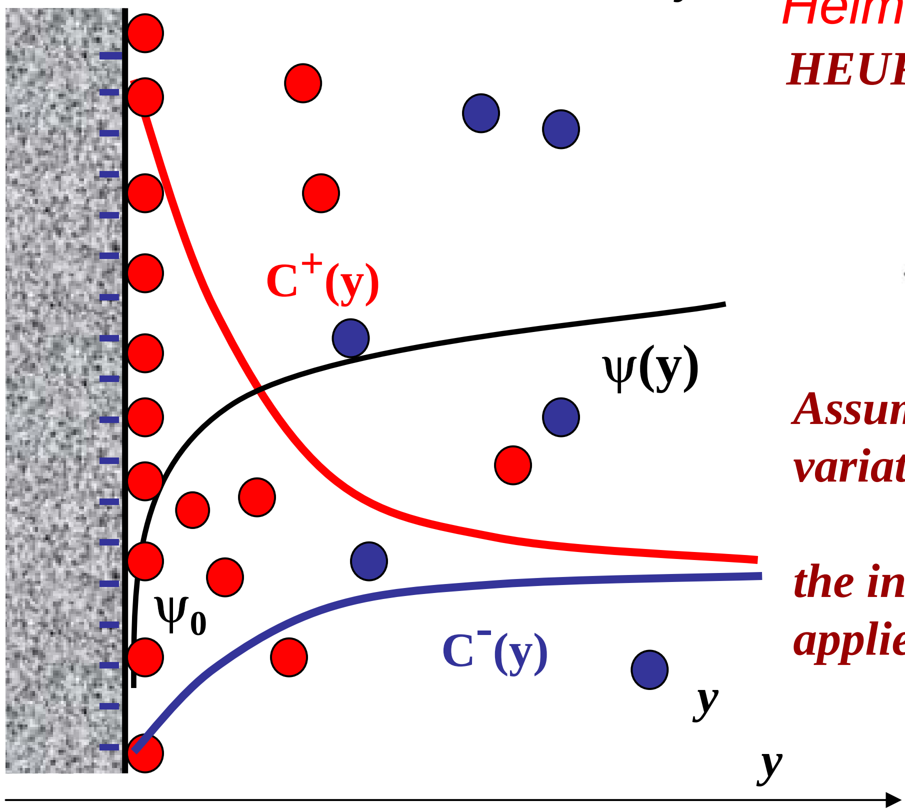


Current-voltage curves of a C-membrane modified by a thin layer of cross-linked polyvinyl alcohol

Theory of Electric Double Layer and Electro-Osmotic Slip

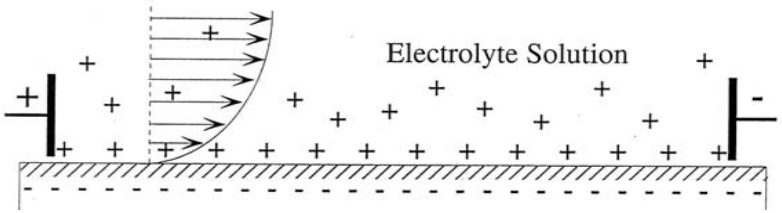
Helmholtz (1879), Guoy-Chapman (1914), Stern (1924)

Electric double layer



Helmholtz-Smoluchowski 1879, 1903, 1921

HEURISTIC THEORY OF ELECTRO-OSMOTIC SLIP



Assumptions: 1. Lateral hydrostatic pressure variation is negligible.

2. Electric field = superposition of the intrinsic field of EDL and weak constant applied tangential field

$$u_{yy} + \varphi_{yy} E = 0$$

$$u\,|_{\Sigma} = -\varsigma E, \quad E = -\varphi_x$$

ς *– potential drop between the interface and EN Bulk*

Matched asymptotic expansions (Dukhin 60s – 70s)

$$z=\frac{y}{\varepsilon},\ c^{\pm}(x,z),\ \varphi(x,z)$$

$$\vec{v}=u\vec{i}+w\vec{j},\, w=0\Rightarrow p_z=\frac{1}{\varepsilon^2}\varphi_{zz}\varphi_z\Rightarrow p=\frac{1}{2\varepsilon^2}\varphi_x{}^2$$

$$u_{zz}=\frac{1}{2}\left(\varphi_z{}^2\right)_x-\varphi_{zz}\varphi_x$$

$$c_z^+ + c^+\varphi_z=0\Rightarrow c^+=\overline{c}(x,0)e^{-(\varphi(x,z)-\overline{\varphi}(x,0))}$$

$$c_z^- - c^-\varphi_z=0\Rightarrow c^-=\overline{c}(x,0)e^{\varphi(x,z)-\overline{\varphi}(x,0)}$$

$$\varphi_{zz}=c^- - c^+=\overline{c}\left(e^{\varphi-\overline{\varphi}}-e^{\overline{\varphi}-\varphi}\right)\Rightarrow \varphi(x,z)=\overline{\varphi}(x)+2\ln\frac{e^{\varsigma/2}+1+\left(e^{\varsigma/2}-1\right)e^{-\sqrt{2\overline{c}}z}}{e^{\varsigma/2}+1-\left(e^{\varsigma/2}-1\right)e^{-\sqrt{2\overline{c}}z}}$$

$$\varsigma=-V-\overline{\varphi}(0) \qquad \overline{u}(x)=u(x,\infty)=\varsigma\left(\ln\overline{c}+\overline{\varphi}\right)_x-4\left(\ln\overline{c}\right)_x\ln\frac{1+e^{\varsigma/2}}{2}$$

Classical approach $-\ \varsigma\ -$ *material constant; Induced charge osmosis* $-\ \varsigma$ *depends on the applied field*

Quasi-Equilibrium Electro-Osmotic Slip.

$$\bar{u}(x) = u(x,\infty) = \varsigma\left(\ln\bar{c} + \bar{\varphi}\right)_x - 4\left(\ln\bar{c}\right)_x \ln\frac{1+e^{\varsigma/2}}{2}$$

1. ***Impermable Charged Surface***

$$\bar{c} = const,\ \bar{u} = \varsigma\bar{\varphi}_x$$

2. ***Charge-Selective Solid (Cation-Selective Membrane)***

$$Concentration\ Polarization$$

$$V \to \infty \Rightarrow \quad \bar{c}(0) = 0,\ I \to I^{\lim} = 2$$

$$\ln\bar{c} + \bar{\varphi} = \ln p_1 - V = const \Rightarrow \bar{u} = 4\ln\frac{1+e^{\varsigma/2}}{2}\bar{\varphi}_x$$

$$V \to \infty \Rightarrow \varsigma \to -\infty \Rightarrow \bar{u} = -\left(4\ln 2\right)\bar{\varphi}_x$$

1D Conduction stable: *Zholkovskij, Vorotynsev, Staude (1996)*

Breakdown of Quasi-Equilibrium at the Limiting Current

$$c^+ = \bar{c}(x,0)e^{-(\varphi(x,z)-\bar{\varphi}(x,0))}, \; c^- = \bar{c}(x,0)e^{\varphi(x,z)-\bar{\varphi}(x,0)}$$

Valid for $\bar{c}(x,0) > 0, \; |\; \bar{\varphi}(x,0) \;| < \infty$, fails at the limiting current.

Rubinstein, Shtilman 1979

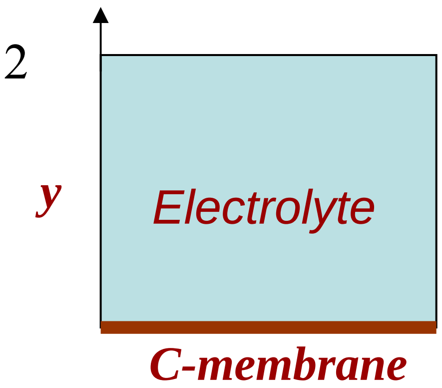
$$(c_y^+ + c^+\varphi_y)_y = 0, \;\; (c_y^- - c^-\varphi_y)_y = 0, \;\; \varepsilon^2\varphi_{yy} = c^- - c^+, \;\; 0 < y < 2$$

Depleted membrane s urface:

$$\varphi(0) = -V, \;\; c^+(0) = p_1, \;\; c_y^-(0) - c^-(0)\varphi_y(0) = 0$$

Enriched membrane surface:

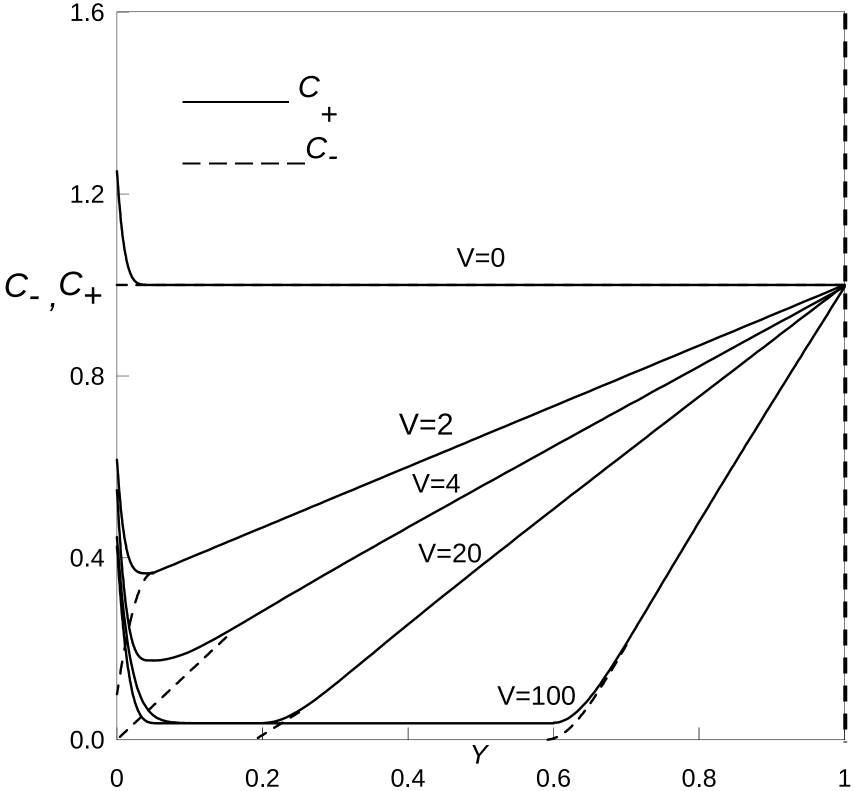
$$\varphi(2) = 0, \;\; c^+(2) = p_1, \;\; c_y^-(2) - c^-(2)\varphi_y(2) = 0\,.$$



Transition from Quasi-Equilibrium to Non-Equilibrium Regime

Ionic concentration profiles

ε=.01, V=0, V=2, V=4, V=20, V=100



O(ε^{2/3}) - the critical length scale for *V*=*O*(4/3|ln(*ε*)|) - the transition from QE-EDL to NE-EDL.
For *V*> *O*(4/3|ln(*ε*)|), a whole range of scales appears for the extent of the space charge, anything from *O*(ε^{2/3}) to *O*(1). For such voltages, *O(ε^{2/3})* is the length scale of the transition zone from the extended non-equilibrium space charge region to the quasi-electro-neutral bulk

Levich 1959

Grafov, Chernenko 1962-1964, Newman, Smyrl 1965-1967, Buck 1975, Rubinstein, Shtilman 1979,Listovnichy 1989 , Nikonenko, Zabolotsky, Gnusin, 1989, Bruinsma, Alexander 1990, Chazalviel 1990, Mafe, Manzanares, Murphy, Reiss 1993, Urtenov 1999, Chu, Bazant 2005

Dukhin (1989) : NE-EDL ⇨ Electrokinetic Phenomena of the Second Kind

BASIC 1D PROBLEM IN TERMS OF PAINLEVÉ EQUATION

$$F = -\varepsilon^{2/3} I^{-1/3} \varphi_y, \quad F - Electric \;\; field$$

$$z = \frac{y}{\varepsilon^{2/3}} I^{1/3} \text{ - } Inner \;\; variable$$

$$F'' = \frac{1}{2} F^3 + (z - z_0) F + 1,$$

$$\left. \left(F' + \frac{1}{2} F^2 \right) \right|_{z=0} = 2 I^{-2/3} \varepsilon^{-2/3} p_1 + z_0 \; ,$$

$$F(\infty) = 0$$

z_0 – *increasing function of* $V(-\zeta)$

$z_0 << -1$ - *QE-EDL,*

$z_0 = O(1)$ - *Transition ,*

$z_0 >> 1$ - *Extended Space Charge*

Extreme Non-Equilibrium Electro-osmosis

$$\bar{u}(x,0) = \lim_{z\to\infty} u(x,z) = -\frac{V^2}{8}\frac{I_x}{I}$$

$z_0 >> 1\ (V >> \tfrac{4}{3}|\ln\varepsilon|)$ - *NE-EDL, Extended Space Charge Dominance*

$$F \approx -\sqrt{2(z_0 - z)},\ 0 < z < z_0$$

$$\int F dz = \zeta \approx -V \quad \Rightarrow\ z_0 \approx \frac{(3V)^{2/3}}{2}$$

$$u_{zz} = \frac{1}{2}\left(\varphi_z{}^2\right)_x - \varphi_{zz}\varphi_x,\ 0 < z < \infty$$

$$u(0) = 0, \qquad \lim_{z\to\infty} u_z = 0$$

Instability of Quiescent Conduction

$$\varepsilon = 0,\quad c = c^- = c^+$$

$$0 < y < 1,\ -\infty < x < \infty$$

$$c_t + \mathrm{Pe}\vec{v}\,\nabla c = D\nabla(\nabla c + c\nabla\varphi)$$

$$c_t + \mathrm{Pe}\vec{v}\,\nabla c = \nabla(\nabla c - c\nabla\varphi) \Longrightarrow$$

$$\tfrac{1}{\mathrm{Sc}}\vec{v}_t = \Delta\vec{v} + \cancel{\Delta\varphi\nabla}\varphi - \nabla p$$

$$\nabla\vec{v} = 0$$

$$c_t + \mathrm{Pe}\,\vec{v}\,\nabla c = \frac{2D}{D+1}\Delta c,$$

$$\tfrac{1}{\mathrm{Sc}}\vec{v}_t = \Delta\vec{v} - \nabla p,\quad \nabla\vec{v} = 0$$

$$y = 0:\quad c = 0,\ u = -\frac{V^2}{8}\frac{c_{yx}}{c_y},\ w = 0.$$

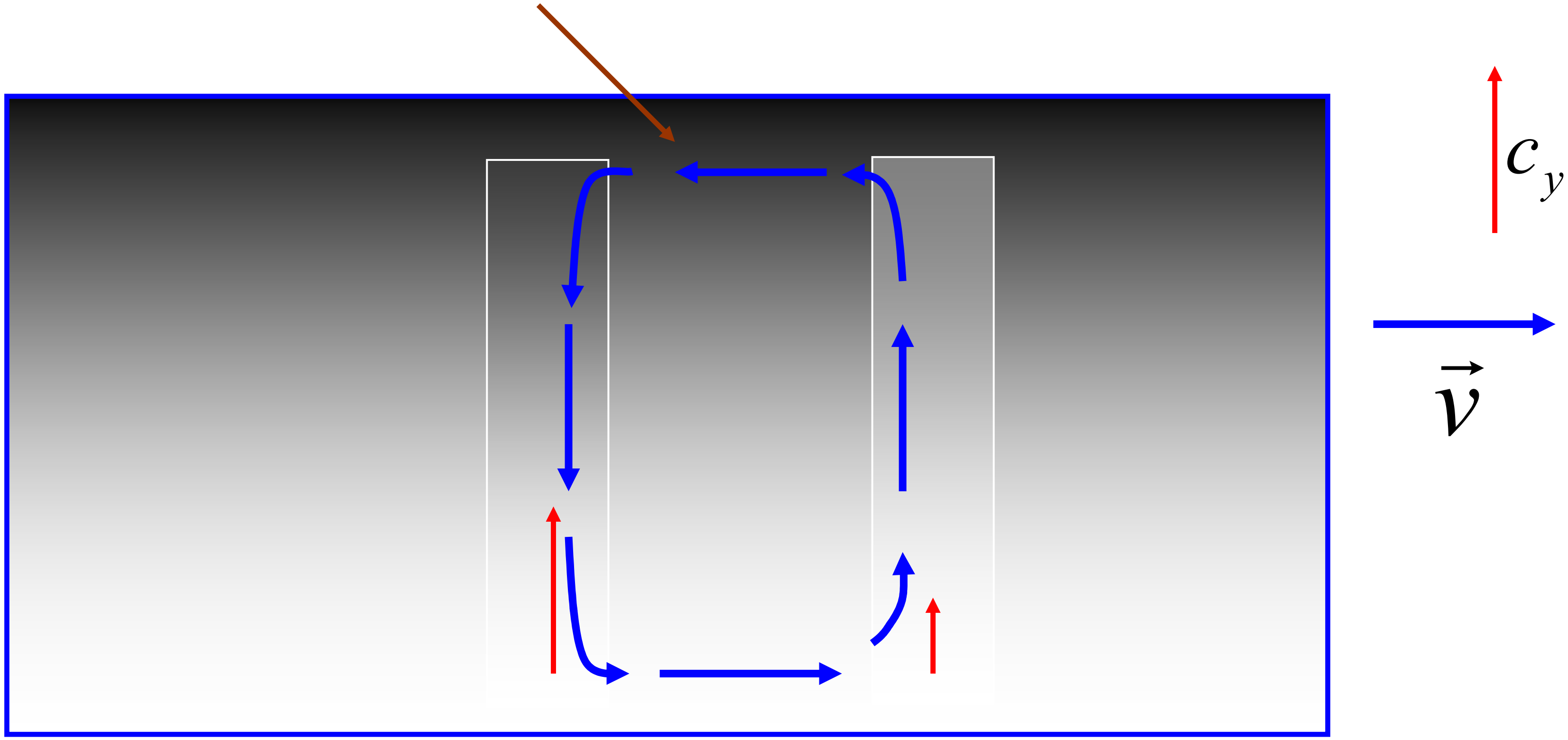
Quiescent Conduction (Concentration Polarization at the Limiting Current)

$$c_0 = y,\ \vec{v} = 0$$

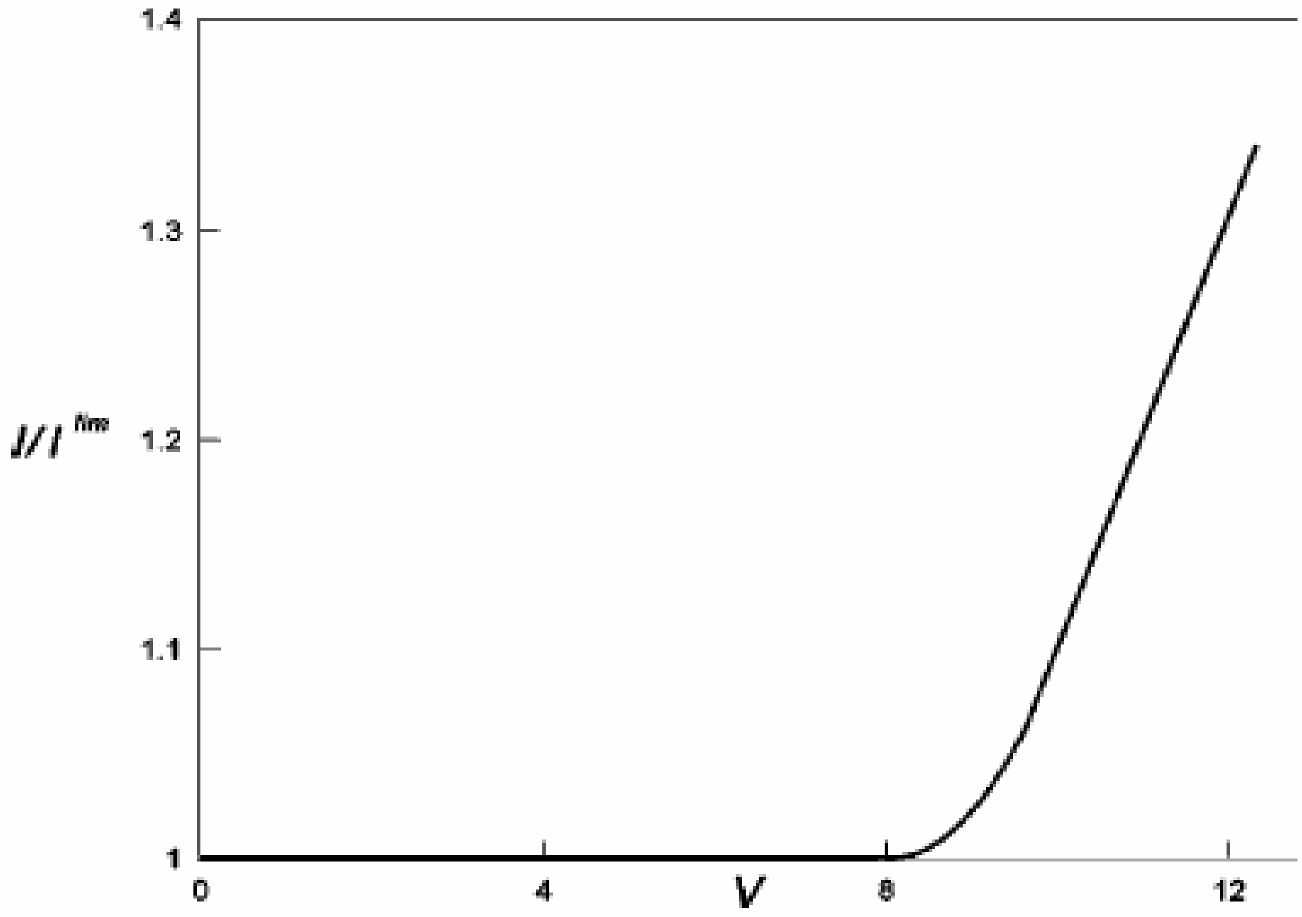
Mechanism of Non-equilibrium Electro-osmotic Instability

$$u(x,0) = -\frac{V^2}{8}\frac{c_{yx}}{c_y}\bigg|_{y=0}$$

Vortex Fluctuation



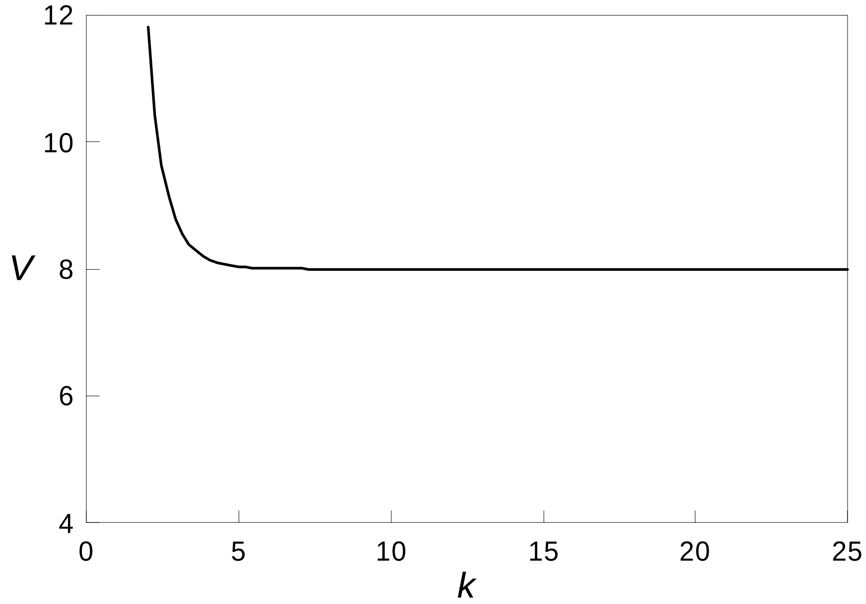
Overlimiting conductance



Neutral Stability Curve

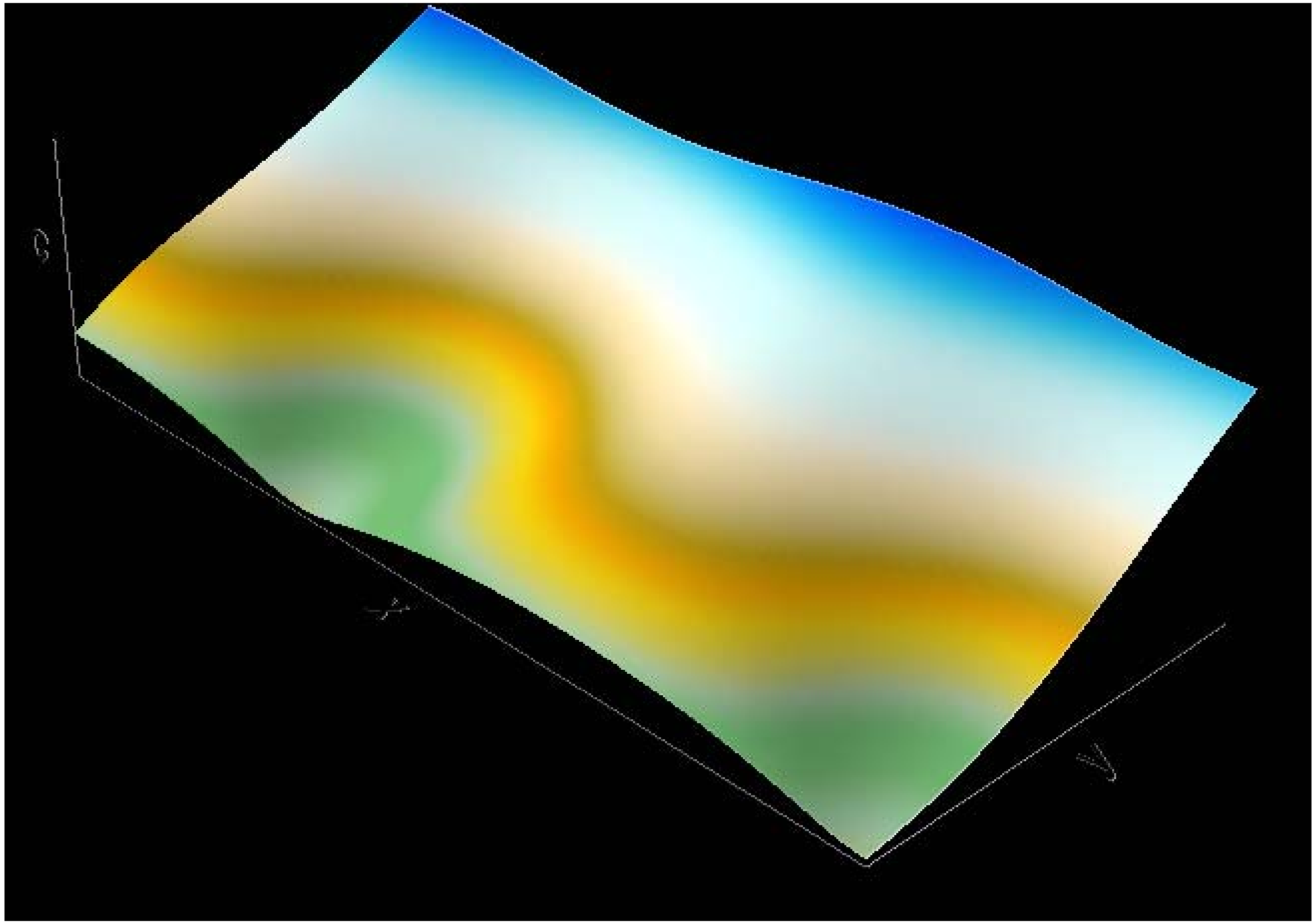
$$\frac{1}{8}\frac{\mathrm{Pe}(D+1)}{2D}V^2 = 4\frac{\sinh k\cosh k - k}{\sinh k\cosh k - 2k^2\coth k}$$

$$\underline{V} = 8\sqrt{\frac{D}{\mathrm{Pe}(D+1)}}$$



Short-wave singularity: $V \to \underline{V} \Rightarrow k \to \infty$

Full Nonlinear Electro-convection Numerical Solution for $\varepsilon = 0.01$



We need a universal (valid for all regimes), regular, limiting electro-osmotic formulation

Basic Singular Painleve Solution

Near the limiting current

$$F(z) = -\frac{2}{z + I^{1/3}\varepsilon^{1/3}p_1} + F_s(z - z_0) + \frac{2}{z} + O(\varepsilon^{2/3}),$$

$$F_s'' = \frac{1}{2}F_s^3 + zF_s + 1,$$

$$\left(F_s + \frac{2}{z - z_0}\right)\Big|_{z=z_0} = 0,\ \ F_s(\infty) = 0$$

$$\int_0^\infty F(z, z_0)dz = \zeta,\ \ z_0 = z_0(\zeta, \varepsilon)$$

Dukhin's Formula for $|\zeta| = O(1)$ $\qquad$ $-\zeta^2/8$ - *for* $|\zeta| >> O(1)$

$$u(x,0,t) = \left(U_\varphi + [-V - \varphi(x,0,t)]\right)\varphi_x(x,0,t) + U_I\frac{c_{xy}}{c_y}$$

$$\ln c(x,0,t) + \varphi(x,0,t) = \ln p_1 - V - \frac{\left(2\max(z_0,0)\right)^{3/2}}{3I^{1/2}}$$

$$|\varsigma| >> 1, \quad c(x,0,t) \approx \left[\varepsilon c_y(x,0,t)\right]^{2/3}$$

FLOW DRIVEN BY NON-EQUILIBRIUM ELECTROOSMOSYS

Universal Electro-Osmotic Flow Formulation

Electro-neutral bulk

$$c_t + \mathrm{Pe}\vec{v}\,\nabla c = D\nabla(\nabla c + c\nabla\varphi), \quad 0 < y < 1, -\infty < x < \infty$$

$$c_t + \mathrm{Pe}\vec{v}\,\nabla c = \nabla(\nabla c - c\nabla\varphi)$$

$$\tfrac{1}{\mathrm{Sc}}\vec{v}_t = \Delta\vec{v} + \Delta\varphi\nabla\varphi - \nabla p, \ \nabla\vec{v} = 0$$

$$\ln c(x,0,t) + \varphi(x,0,t) = \ln p_1 - V - \frac{\left(2\max(z_0,0)\right)^{3/2}}{3I^{1/2}},$$

$$u(x,0,t) = \left(U_\varphi + [-V - \varphi(x,0,t)]\right)\varphi_x(x,0,t) + U_I\frac{c_{xy}}{c_y}$$

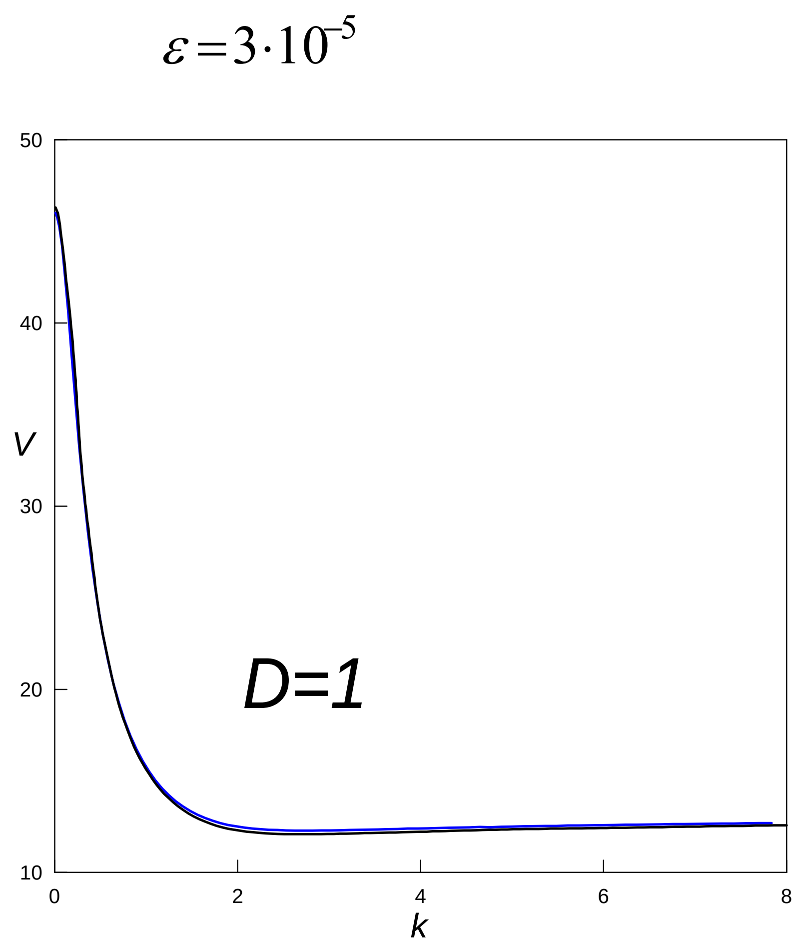
$$z_0 = z_0(\zeta,\varepsilon), \quad \zeta = -V - \varphi(x,0,t), \quad \int_0^\infty F(z,z_0,\varepsilon)dz = \zeta$$

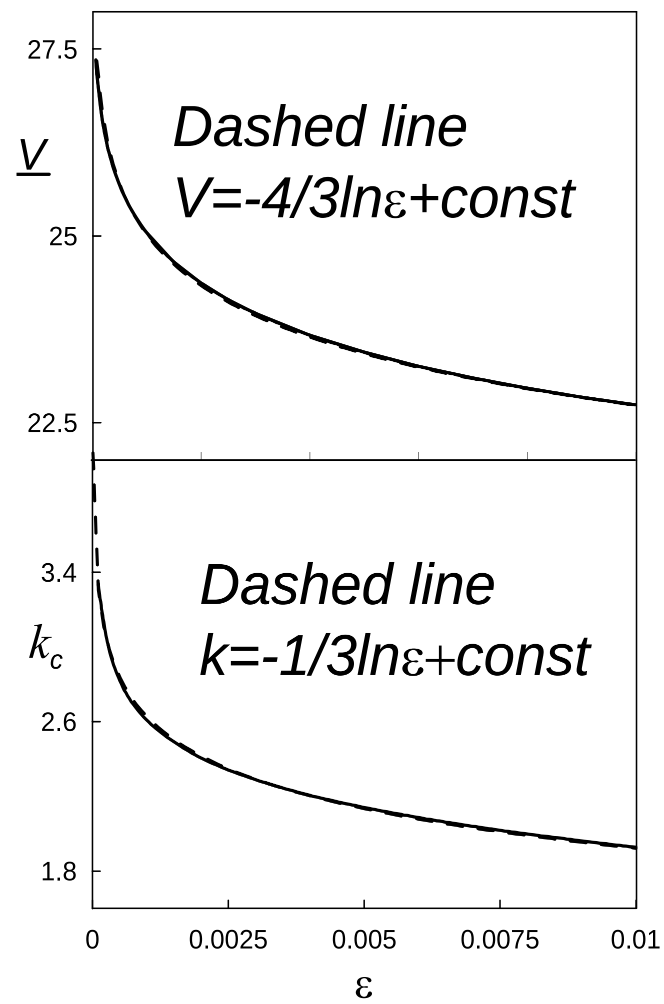
$$\ln c(x,1,t) + \varphi(x,1,t) = \ln p_1, c_y(x,1,t) - c(x,1,t)\varphi_y(x,1,t) = 0,$$

$$w(x,1,t) = 0, \ u(x,1,t) = -4\ln 2\varphi(x,1,t),.$$

$$c_y(x,0,t) - c(x,1,t)\varphi_y(x,0,t) = 0, w(x,0,t) = 0.$$

Comparison of Neutral-Stability Curves in Full and Limiting Formulations





Full Nonlinear Electro-Osmotic Convection Numerical Solution for $\varepsilon = 10^{-4}$