Lecture 7

Effects at Charged Interfaces

In this lecture…

- Experimental aspects of charged interfaces: characterization of the double layer and the applications

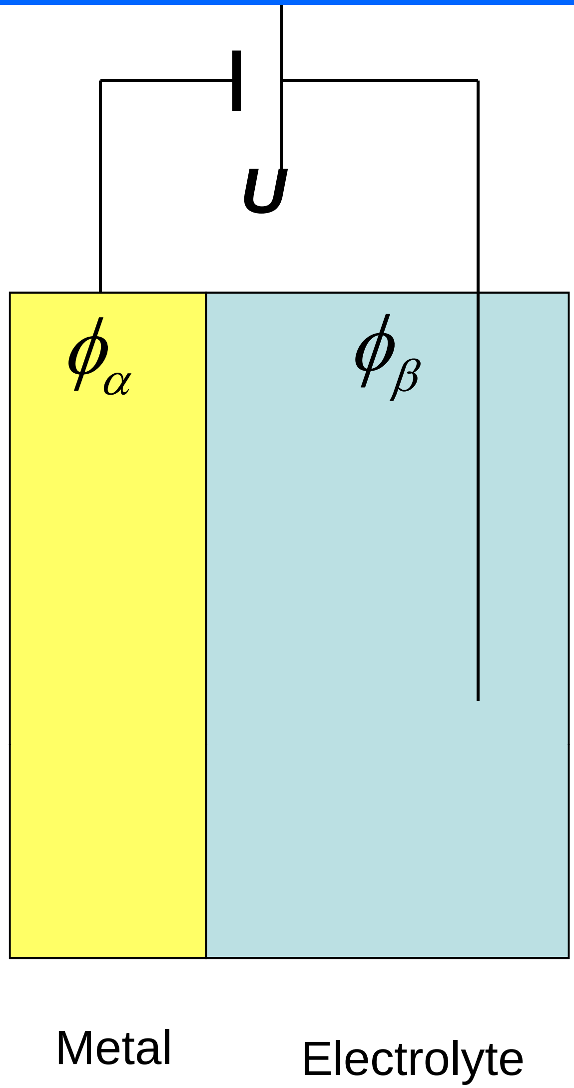
Electrocapillarity

- Gibbs-Duhem equation for the case of electrified interface:

$$d\gamma = -\sum_i \Gamma_i d\mu^*_i - \Gamma_e d\mu^*_e$$

adsorbed ions in the electrolyte

electrons in the metal attracted to the interface



Electrocapillarity

$$d\gamma = -\sum_i \Gamma_i d\mu^*_i - \Gamma_e d\mu^*_e$$

- electrochemical potential:

$$\mu^*_i = \mu_i + Z_i F d\phi^\beta$$ ions of charge Z_i.

$$\mu^*_e = \mu_e - F d\phi^\alpha$$ electrons

- electroneutrality:

$$\sum_i \Gamma_i z_i = \Gamma_e$$

$$d\gamma = -\sum_i \Gamma_i d\mu_i - \Gamma_e d\mu_e - \sigma \cdot d\left(\phi^\beta - \phi^\alpha\right)$$

⇒

Lippman equation

$$\frac{\partial \gamma}{\partial U} = -\sigma$$

Electrocapillarity

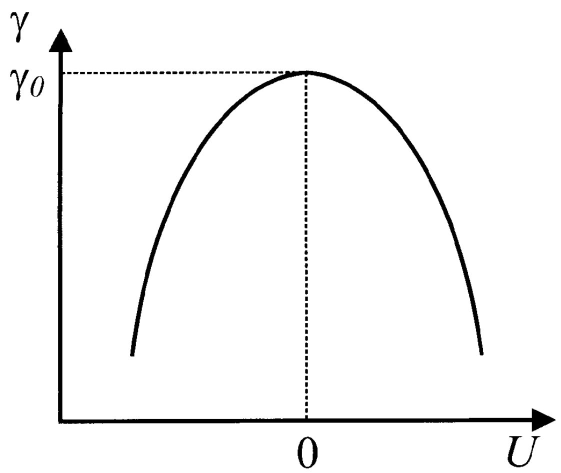
- Lippman equation

$$\frac{\partial\gamma}{\partial U} = -\sigma$$

$$-\frac{\partial^2\gamma}{\partial U^2} = \frac{\partial\sigma}{\partial U} = C$$

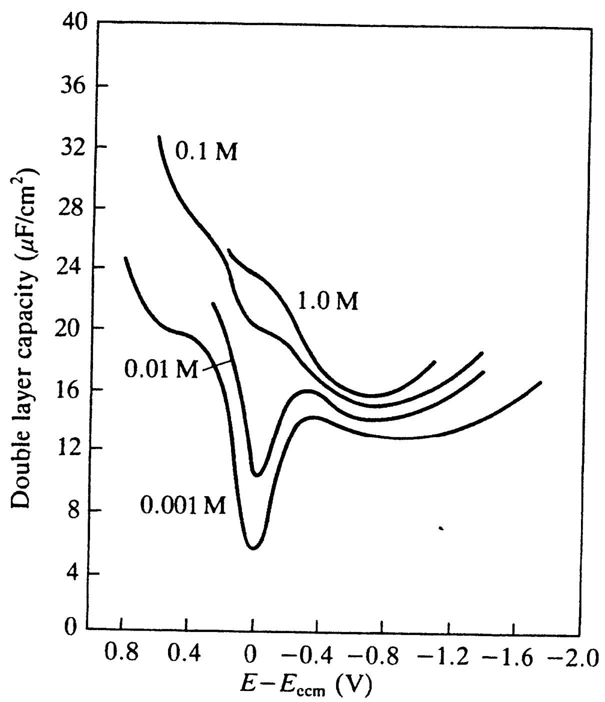
- Assuming capacity constant:

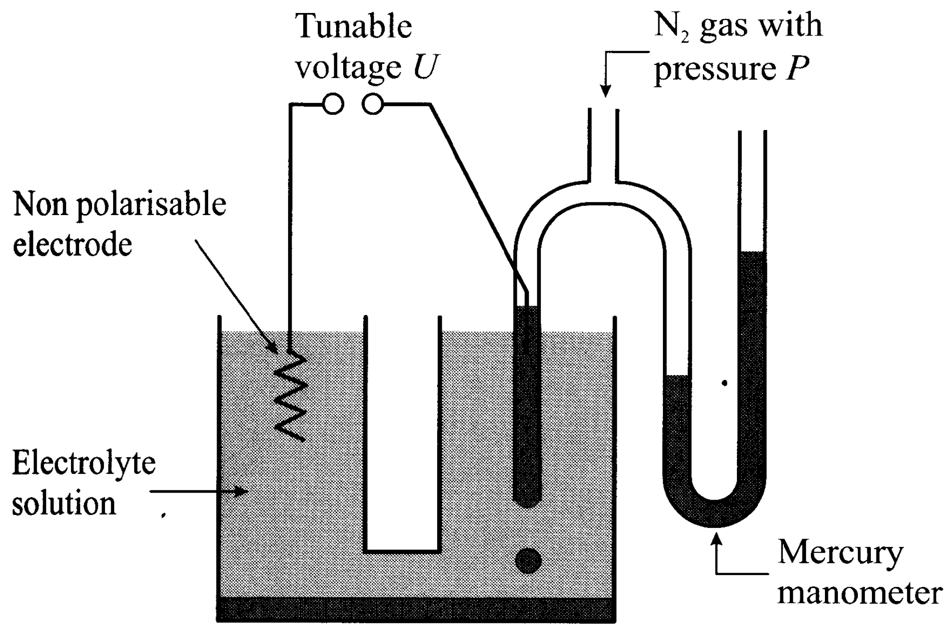
$$\gamma = \gamma_0 - \frac{1}{2}CU^2$$



Electrocapillarity

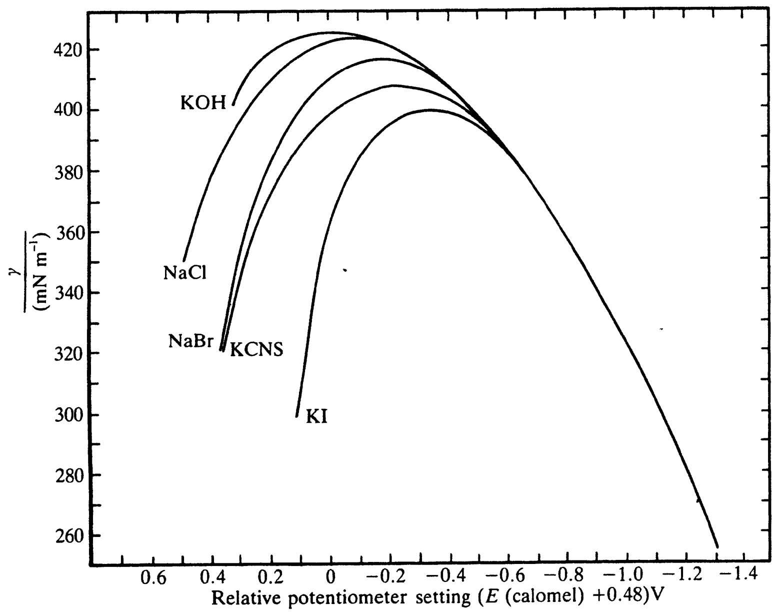
- Measurements on Dropping mercury electrode (DME)
  - surface tension can be determined using maximal bubble pressure method
  - best arrangement in terms of interpretation





Examples of charged surfaces: Mercury

- Surface tension of mercury can be easily measured
- Typically a parabola is observed,
  - width of the parabola decreases with salt concentration,
  - minimum position stays the same
- In the solutions of KI, KOH, KCNS a shift of the minimum is observed due to preferential binding of anions for mercury



Examples of charged surfaces: AgI

- as AgI is slightly soluble:

$$AgI \rightleftarrows Ag^{+} + I^{-} \qquad K = a_{Ag^{+}} \cdot a_{I^{-}} = 10^{-16}$$

- due to preferential adsorption of I^- ions to the surface it acquires negative charge. Small change in the concentration of one of the "potential determining ions" is sufficient to change the point of zero charge.

- In equilibrium:

$$\mu_L^0\left(Ag^+\right) + RT\ln a_L\left(Ag^+\right) + F\phi_L = \mu_C^0\left(Ag^+\right) + RT\ln a_C\left(Ag^+\right) + F\phi_C$$

- at the point of zero charge:

$$=$$

$$\mu_L^0\left(Ag^+\right) + RT\ln a_L{}^{pzc}\left(Ag^+\right) = \mu_C^0\left(Ag^+\right) + RT\ln a_C{}^{pzc}\left(Ag^+\right) + F\Delta\chi^{pzc}$$

- substracting:

$$\psi = \frac{RT}{F}\ln\frac{a_L\left(Ag^+\right)}{a_C{}^{pzc}\left(Ag^+\right)}$$

increase of the concentration by x10 changes surface potential by 59mV

Examples of charged surfaces: Oxides

- If protonation can occur at the interface (potential determining ions are H^+ and OH^-)

$$K_A = \frac{\left[A^-\right]\left[H^+\right]_{local}}{\left[AH\right]}$$

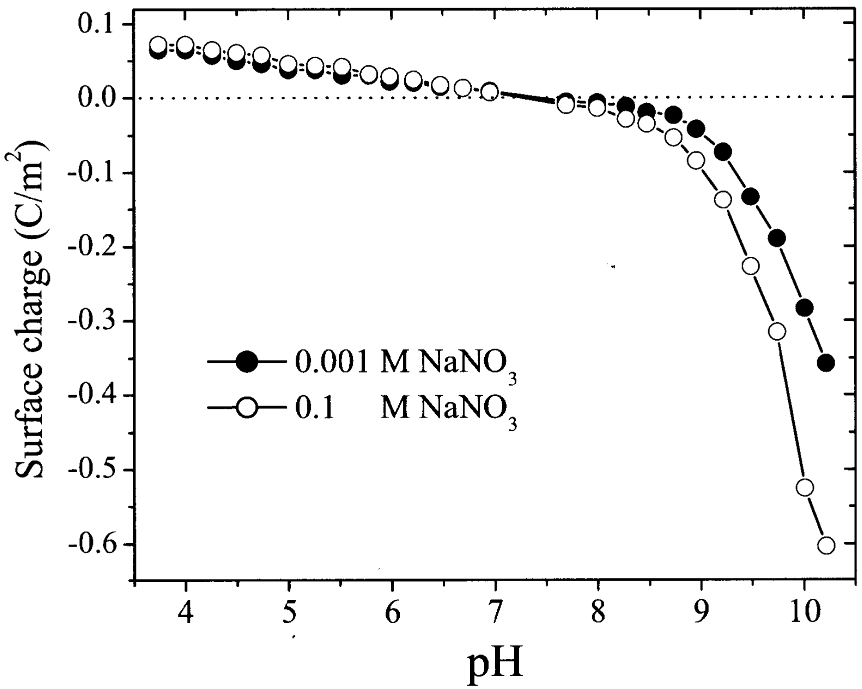
$$\left[H^+\right]_{local} = \left[H^+\right]\exp\left(-\frac{e\psi_0}{kT}\right)$$

- at 25ºC, the charge at the interface will depend on pH

$$\psi_0 = 59mV \cdot \left(\left(pK_A - pH\right) + \log\frac{\left[A^-\right]}{\left[AH\right]}\right)$$

Examples of charged surfaces: Oxides

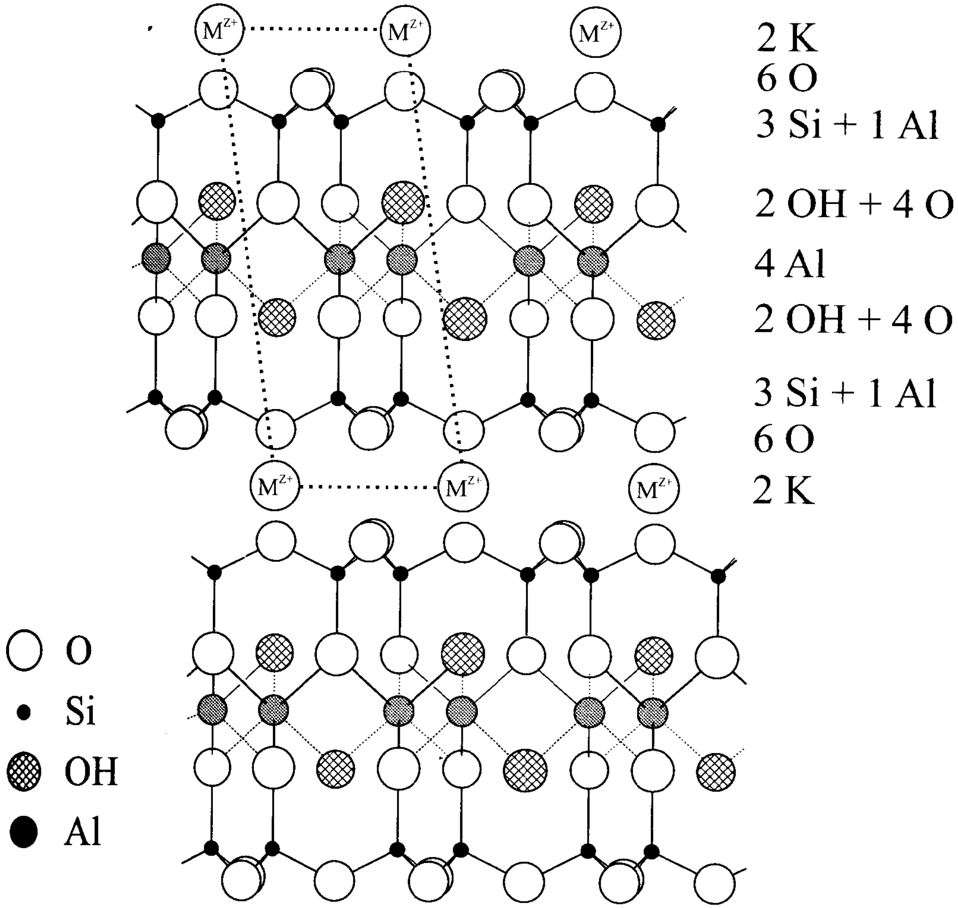
- Most of the oxides are negatively charged at neutral pH



Substance	pzc
SiO_2	1.8–3.4
TiO_2	2.9–6.4
Al_2O_3	8.1–9.7
MnO_2	1.8–7.3
Fe_3O_4	6.0–6.9
α-Fe_2O_3	7.2–9.5

Examples of charged surfaces: Mica

- Negative charge on mica surface is related to cations (K^+, Si^{4+}, Al^{3+} and Mg^{2+}) leaving the surface and relatively insensitive to pH



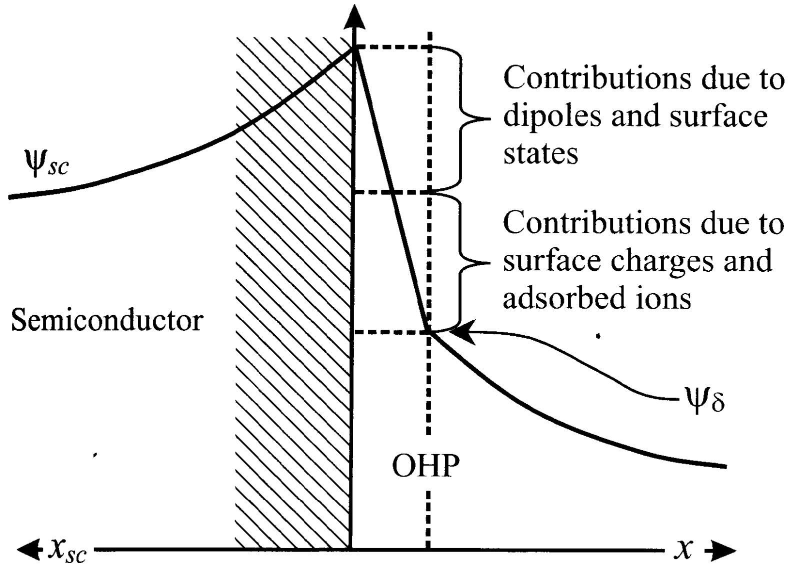
Examples of charged surfaces: Semiconductors

- In semiconductors a smaller density of electrons leads to non-negligible distribution of electrons inside the semiconductor. Debye screening length approach can be applied to the electrons in the semiconductors

$$\lambda_D = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{2c_e e^2}}$$

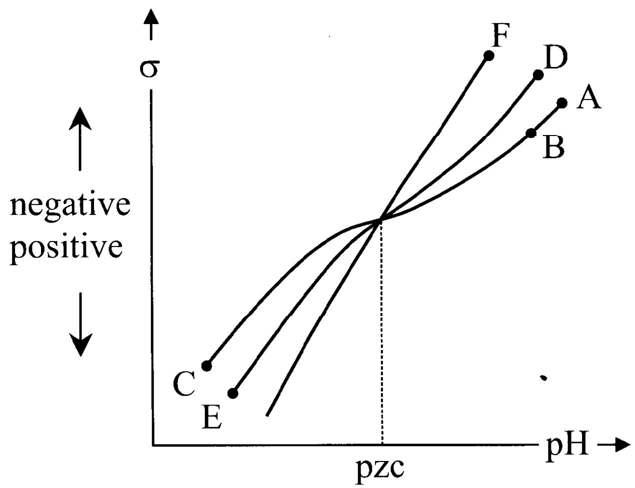
- e.g. in Ge, at 25ºC

$$\lambda_D \approx 615nm \ \ (at\, \varepsilon = 16)$$

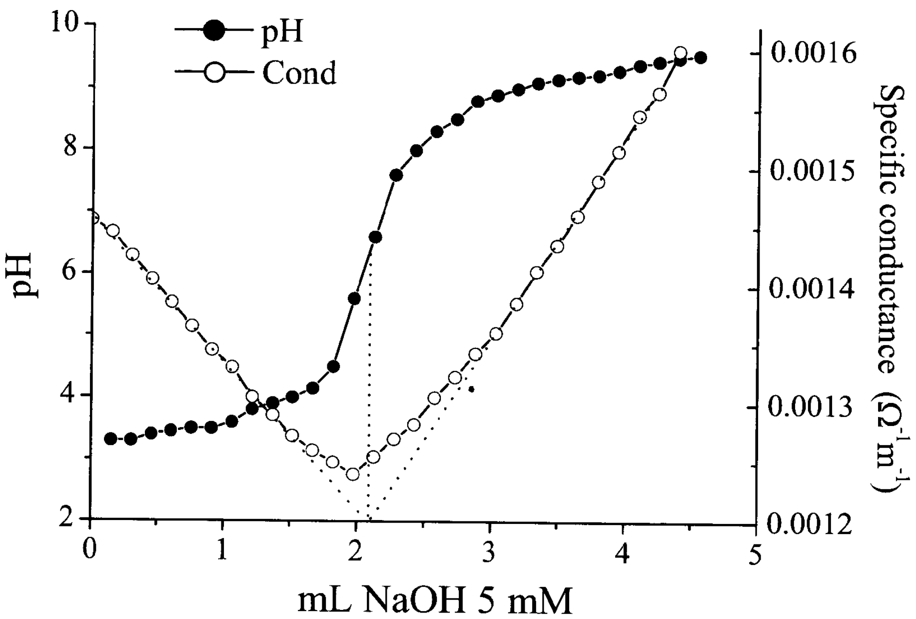


Measuring surface charge density

- potentiometric titration

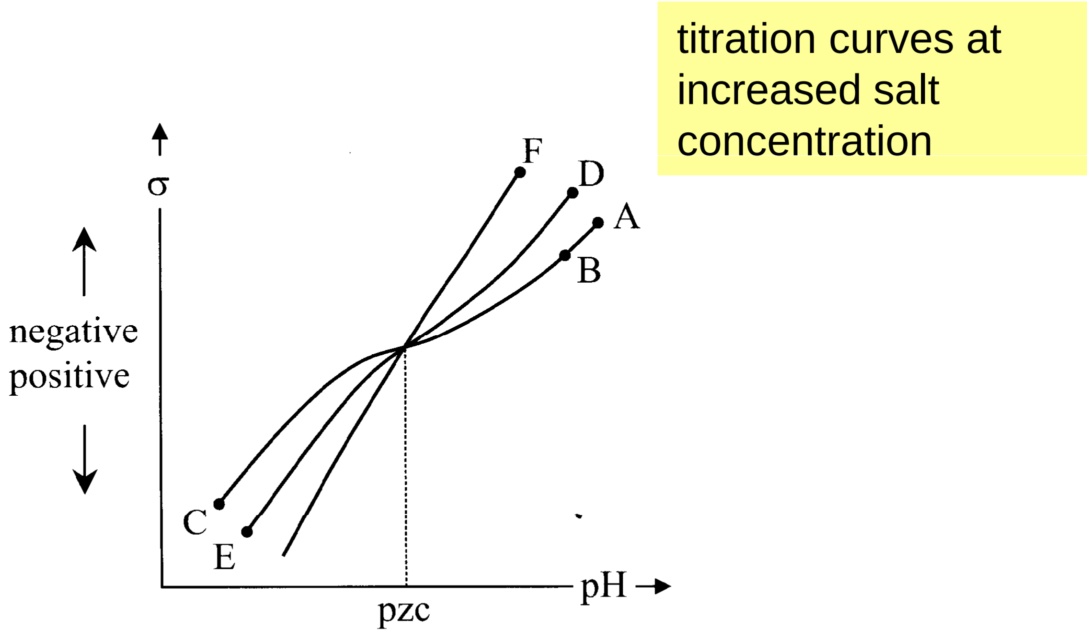


- conductimetric titration

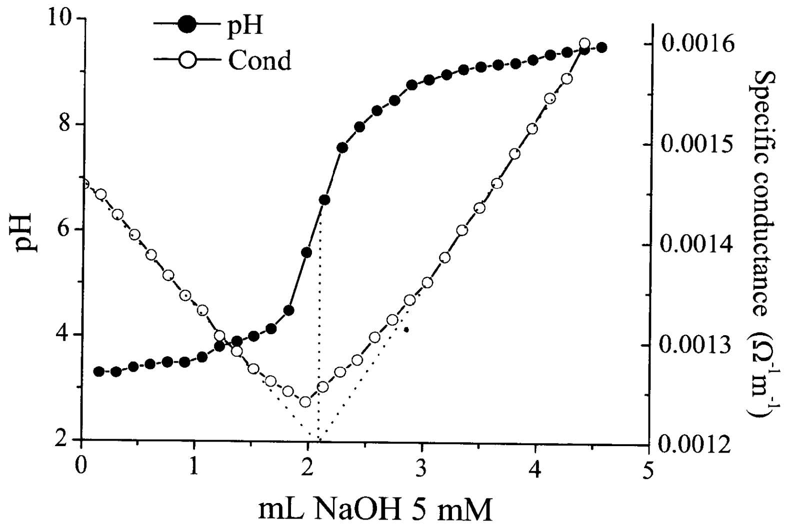


Measuring surface charge density

- potentiometric titration: indifferent salt (that doesn't absorb at the surface) is used for titration of a solution of dispersed phase, e.g. KOH and HNO_3.



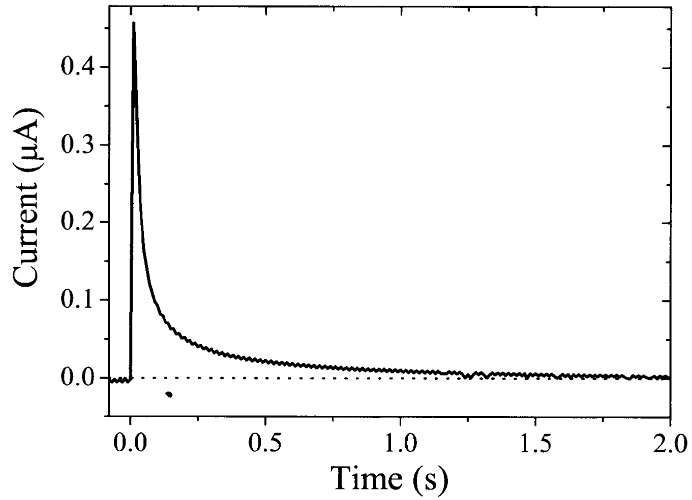
- conductometric titration: electrical conductivity vs. amount of potential determining ions



Capacitance measurements

- chronoamperometric measurements

- cyclic voltammetry



- impedance spectroscopy

Electrokinetic effects

- Navier-Stokes equations with the electric force

$$\rho(\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}+w\frac{\partial u}{\partial z})=-\frac{\partial p}{\partial x}+\rho_e E_x+\mu(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2})$$

$$\rho(\frac{\partial v}{\partial t}+u\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial y}+w\frac{\partial v}{\partial z})=-\frac{\partial p}{\partial y}+\rho_e E_y+\mu(\frac{\partial^2 v}{\partial x^2}+\frac{\partial^2 v}{\partial y^2}+\frac{\partial^2 v}{\partial z^2})$$

$$\rho(\frac{\partial w}{\partial t}+u\frac{\partial w}{\partial x}+v\frac{\partial w}{\partial y}+w\frac{\partial w}{\partial z})=-\frac{\partial p}{\partial z}+\rho_e E_z+\mu(\frac{\partial^2 w}{\partial x^2}+\frac{\partial^2 w}{\partial y^2}+\frac{\partial^2 w}{\partial z^2})$$

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}=0$$

$$\rho\frac{D\vec{V}}{Dt}=-\nabla p+\rho\vec{E}+\mu\nabla^2\vec{V}$$

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

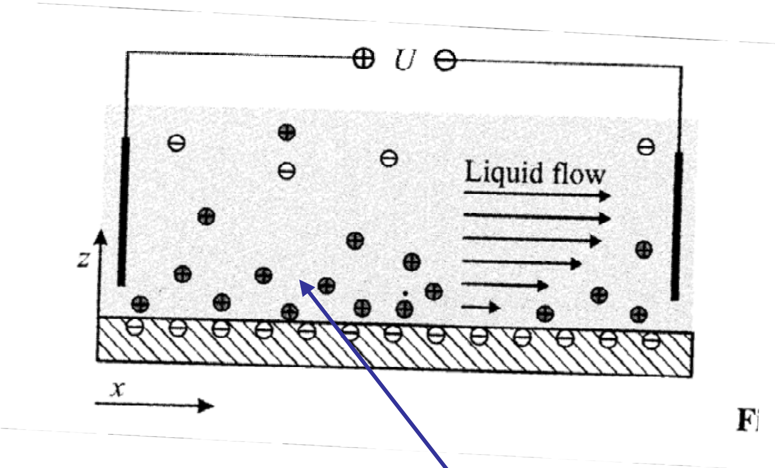
Electrokinetic effects

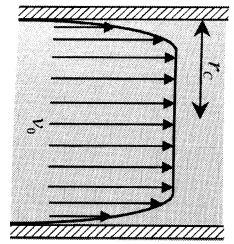
- Let's consider a capillary with a voltage applied along it:

$$0 = -\frac{\partial p}{\partial x} + \rho_e E_x + \mu \frac{\partial^2 w}{\partial z^2}$$

$$0 = -\frac{\partial p}{\partial z} + \rho_e E_z + 0$$

$$\frac{\partial u}{\partial x} = 0$$





Higher concentration of counterions next to the surface

- From the Poisson equation

$$\frac{\partial^2 \psi}{\partial z^2} = -\rho_e / \varepsilon\varepsilon_0$$

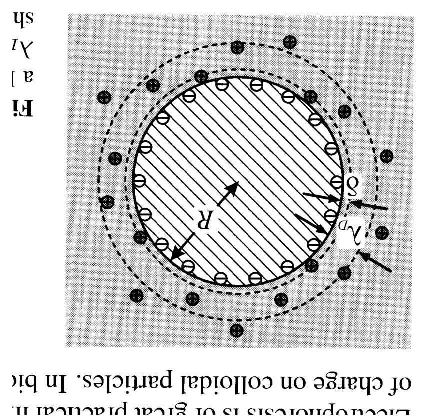
- Combining

integrating for inf to d

$$\varepsilon\varepsilon_0 \frac{\partial^2 \psi}{\partial z^2} E_x = \mu \frac{\partial^2 w}{\partial z^2}$$

$$\varepsilon\varepsilon_0 \zeta E_x = -\mu u_0$$

Electrokinetic effects



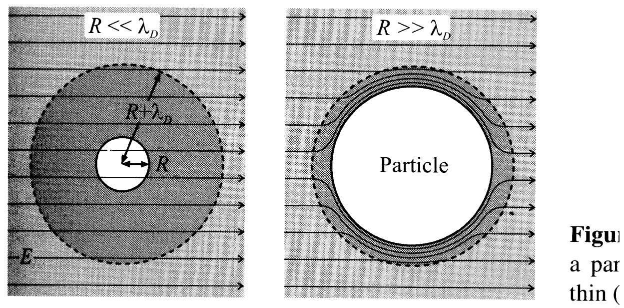
- Electrophoresis:
  - charged particles will move in electric field
  - the movement will be determined by the charge and the radius

$$v = v_i + v_o = \frac{QE}{6\pi\eta R}\left(1 + \lambda_D / R\right)^{-1}$$

- R>>l_D:

$$v = \frac{2\sigma E \lambda_D}{3\eta} = \frac{2\varepsilon\varepsilon_0 \zeta E}{3\eta}$$

$$\sigma = \varepsilon\varepsilon_0 \zeta / \lambda_D$$

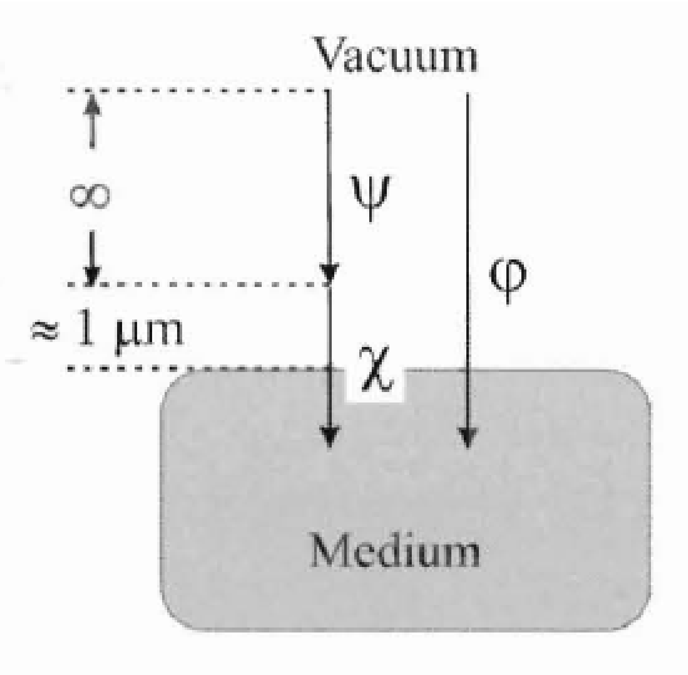


- R<<l_D:

$$v = \frac{\varepsilon\varepsilon_0 \zeta E}{\eta}$$

Types of Potentials

- Galvani potential φ: work required to bring a charge from infinity into bulk
- External potential ψ: work –" – from infinity to the close proximity of the interface
- Surface potential (jump) χ.

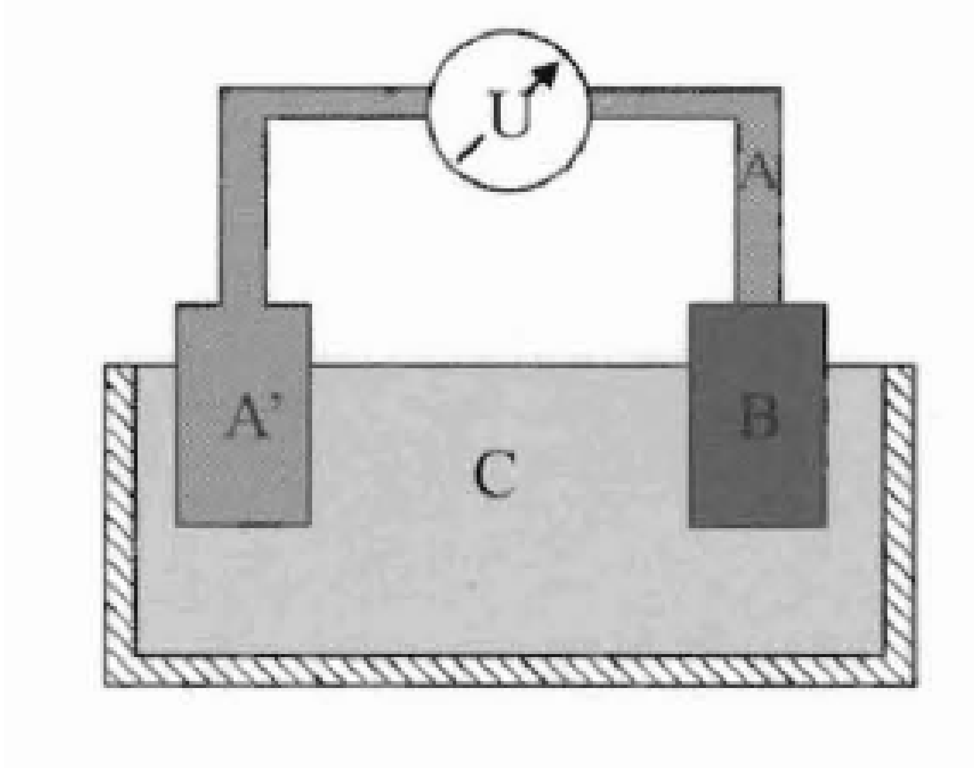


$$\varphi = \psi + \chi$$

- Work function Φ: work required to move an electrone from a Fermi level to vacuum far away from the surface

Types of Potentials

- Potentials in an electrochemical cell



$$U = \frac{\mu_e^{A'} - \mu_e^{A}}{e} = \frac{\mu_e^{A'} - \mu_e^{B}}{e}$$

$$U = {}^{A'}\Delta^{A}\Phi = {}^{A}\Delta^{B}\varphi + {}^{B}\Delta^{C}\varphi + {}^{C}\Delta^{A'}\varphi$$

Problems (Ch.5)

1. For a microfluidic application, a capillary of 10µm radius and 5 cm length was fabricated in glass. The zeta potential of this glass in 0.01 M KCl aqueous solution at neutral pH is -30 mV. A potential of 5 V is applied along the capillary. How fast and in which direction does the liquid flow?
2. To observe the flow, small spherical polystyrene particles of 50 nm radius which are fluorescently labeled, are added. To keep them dispersed they have sulfate groups on their surface. This leads to a zeta potential of -20 mV. How fast and in which direction do these particles move? A good marker should move with the same speed as the liquid flow. Was it a good idea to use these particles as markers?