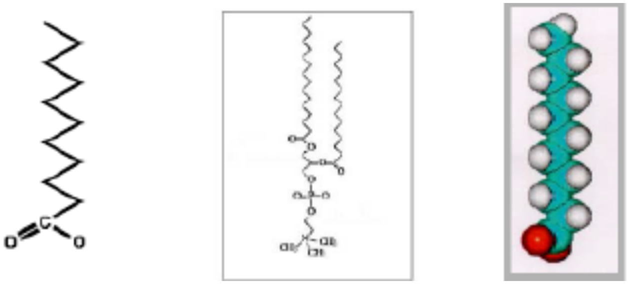
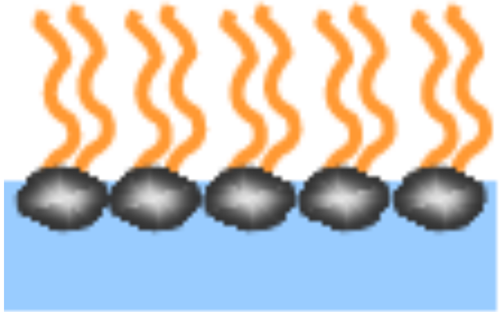
Helmuth Möhwald

lecture n°1:

Ion distribution near interfaces: their manipulation with acoustic and electric fields





Molecules with chargeable groups

Manipulation of density of chargeable groups, charge, ion binding

2014-2015

Content and Aims

- Treatment of Molecular Interfaces

  large difference interface-bulk,

  interfaces tend to be neutral

  a measured charge density without defined salt is useless

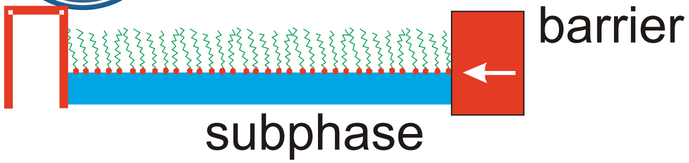
- Theoretical framework and experimental methods
- Zeta potential

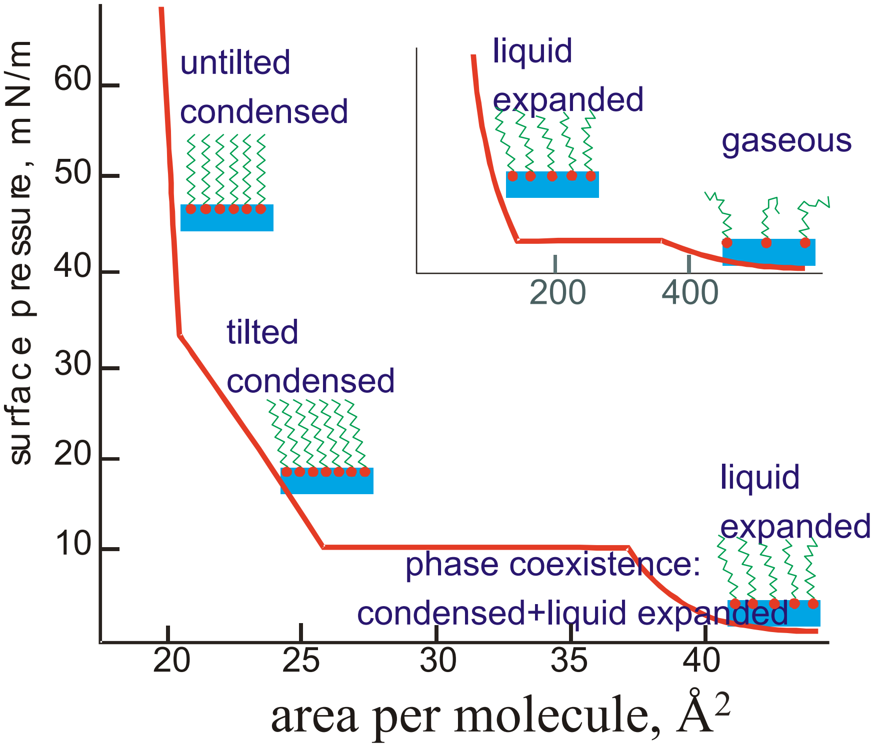
  established technique with difficult theory

- Electroacoustics

  new methods for colloidal analytics, but no solid theory

Langmuir monolayers as models





Variation of many parameters

Information on energies

π_t – transition pressure

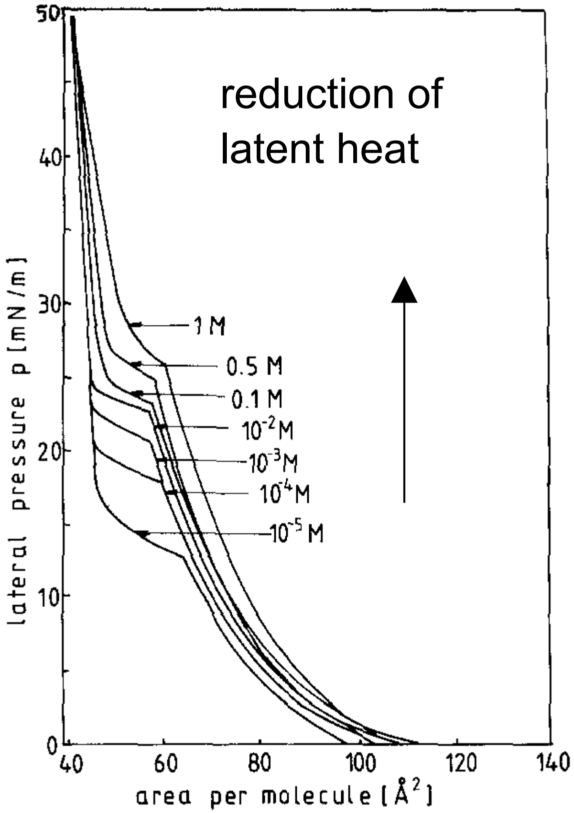
2D Clausius-Clapeyron equ.

$$d\pi_t/dT = \Delta H/(T\Delta A)$$

Theory applicable for
Air/water and
Oil/water interfaces

Experimentally Oil/water more demanding

Unusual Salt Dependence



reduction of latent heat

Fig. 5. Pressure-area diagrams of DLPA for various NaCl concentrations as indicated in the figure ($pH = 5.6$, $T = 286$ K). As the amount of lipid differed between the experiments by up to 20% the curves were normalized to yield a pressure of 50 mN/m for a molecular area of 40 Å^2. EDTA concentration in the subphase: 10^{-4} M, except for the lowest curves, where the ionic strength was established by additon of EDTA

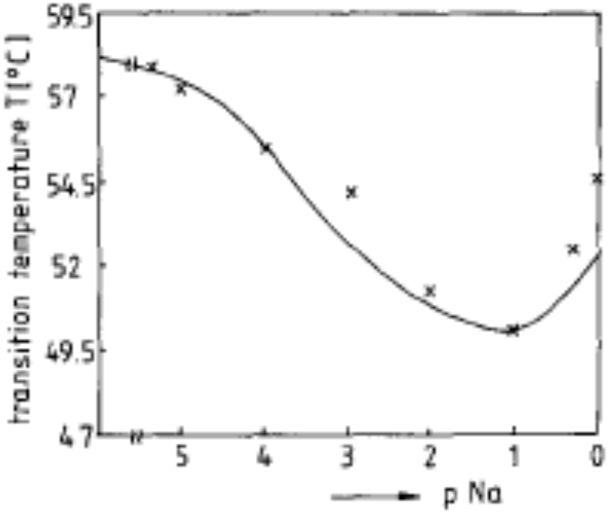


Fig. 9. Transition temperature of large unilamellar DMPA vesicles as a function of NaCl concentration determined experimentally by light scattering (+) and calculated with the following assumptions: $K = 60\ M^{-1}$, $\Delta A/\Delta S = 0.6$ Å$^2 \cdot K \cdot$ mol/J, $T = 331$ K

Expectation:
electrostatic repulsion
Favors expanded phase
Salt addition hence **Increases electrostatic Forces**

(C.A. Helm, L.A. Laxhuber, M. Lösche, H. Möhwald, Coll. Polym. Sci. 264(1986)46)

Interface Electrostatics (Gouy-Chapman)
Debye Hückel in 2 D

$$\mathrm{Poisson\ Boltzmann-eq:}\ \frac{d^2}{dx^2}\Psi(x) = -\frac{1}{\varepsilon\varepsilon_o}\sum_i q_i\rho_i(\infty)\exp\left(-\frac{q_i\psi}{kT}\right)$$

Solution analytical if linearized for $e\psi/kT$ **<1,** rarely valid, but works often

Analytical solutions not difficult (see below)

Gouy-Chapman model leads to Grahame equation

$$\sigma = \{2\,\varepsilon\cdot\varepsilon_0\cdot kT\cdot\sum_i c_i(\infty)\cdot[\exp(-q_i\psi/kT)-1]\}^{1/2}$$

Charge dens concentrations potential.

Deficiencies: homogeneous charge distribution, ion correlations neglected

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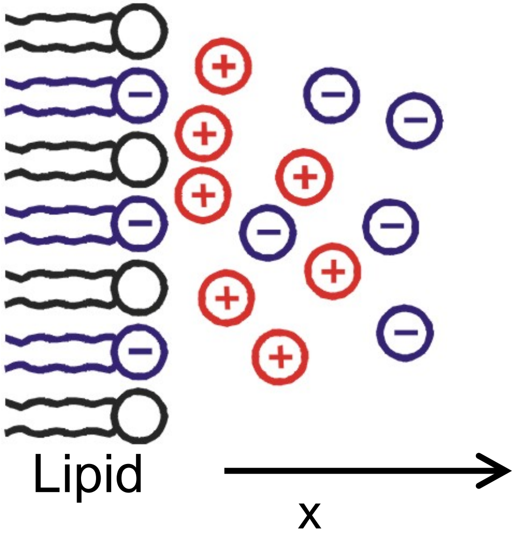
H.Träuble,M.Teubner,P.Wooley,H.J.Eibl, Biophysical Chem..4(1976)319

S.A.McLaughlin, Current Top.Membr.Transp. 9 (1977)71

C.A. Helm, L.A. Laxhuber, M. Lösche, H. Möhwald, Coll. Polym. Sci. 264(1986)46

Interface Electrostatics (thermodynamics)

(Gouy-Chapman-Stern theory applied (extended) to experiments)



Variables: molec. area A; ion conc.

pH=log$\left[H_o^+\right]$

$$K_H = \frac{[LH]_s}{[L^-]_s \cdot [H^+]_s}$$

Chemistry in
mass action law for lipid
Dissociation, metal binding

$$K_M = \frac{[LM]_s}{[L^-]_s \cdot [M^+]_s}$$

$$\alpha = \frac{[L^-]_s}{[L^-]_s + [HL]_s}$$

$$\text{Mass action law for lipid dissoc.:}\ \sigma = \frac{\mathrm{e}}{\mathrm{A}} \cdot \alpha = \frac{\mathrm{e}}{\mathrm{A}} \cdot \frac{1^{\mathrm{M}}}{1 + \mathrm{K_H} \cdot \left[\mathrm{H_0^+}\right] \cdot \exp\left(-\mathrm{e}\psi/_{\mathrm{kT}}\right)}$$

General with metal binding $\sigma = \dfrac{e/A}{1 + (K_H \cdot [H^+] + K_M \cdot [M^+]) \cdot \exp(-e\psi/kT)}$

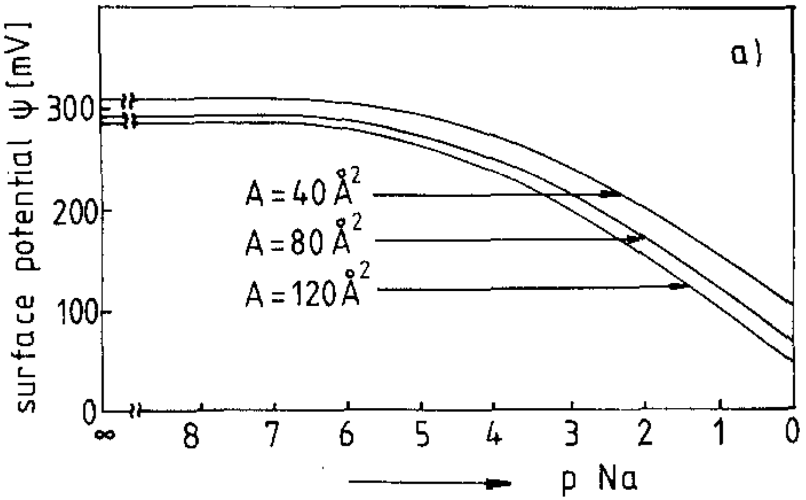
H.Träuble,M.Teubner,P.Wooley,H.J.Eibl, Biophysical Chem..4(1976)319

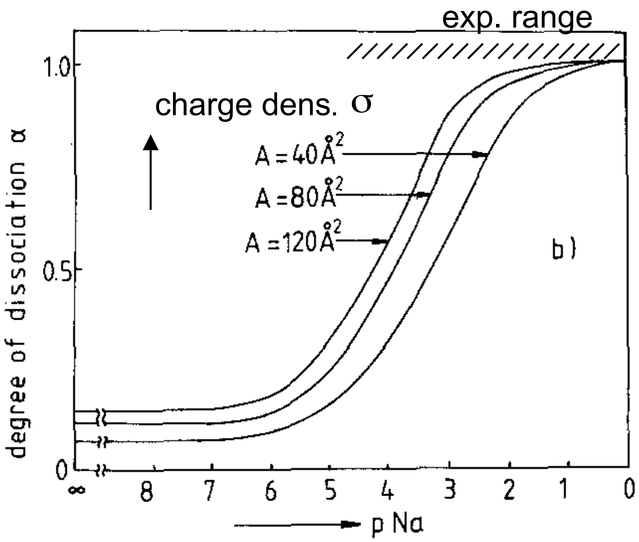
S.A.McLaughlin, Current Top.Membr.Transp. 9 (1977)71
C.A. Helm, L.A. Laxhuber, M. Lösche, H. Möhwald, Coll. Polym. Sci. 264(1986)46

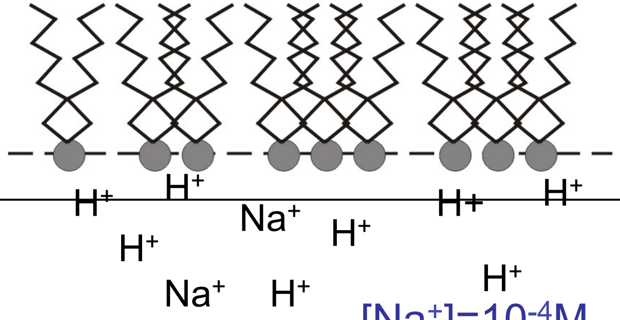
Influence of monovalent ions

- Exp. parameters: pH=6, T ≈ 300K
- Lipid param.: $pK_H=1,7$
- Variables: ionic strength, molec.area A

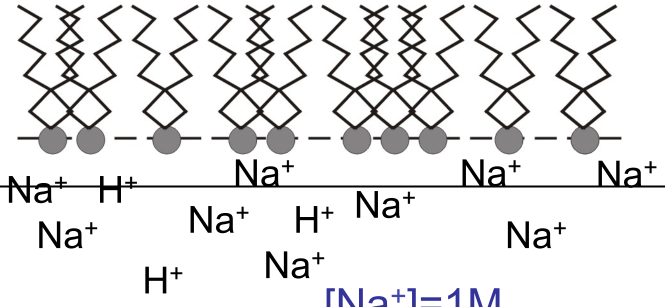
Even at pH 6 and 1mM salt major fraction of L not dissociated







$[Na^+]=10^{-4}M$



$[Na^+]=1M$

Energetics

$$G_c = A \cdot \int_0^{\sigma} \psi(\sigma')\, d\sigma'$$

Electric energy to charge a capacitor

$$G_d = kT \int_0^{\alpha} \ln\left\{[H^+] \cdot K_H \cdot \frac{\alpha'}{1-\alpha'}\right\} d\alpha'$$

Chemical contribution
from dissoc., ion binding

$$G_{el} = G_d + G_c = kT \cdot \ln(1-\alpha)$$
$$-\left(\frac{kT}{e}\right)^2 \cdot \varkappa \cdot \varepsilon \cdot \varepsilon_0 \cdot A \cdot \left[\cosh\left(-\frac{e\psi}{2kT}\right) - 1\right.$$

$$\varkappa = \left[\frac{2e^2}{\varepsilon \cdot \varepsilon_0 \cdot kT} \cdot ([H^+] + [M^+])\right]^{1/2}$$

1/Debye length

$$p_{el} = -\frac{\partial G_{el}}{\partial A}$$

Pressure contrib.

$$p_{el} = \varepsilon \cdot \varepsilon_0 \cdot \left(\frac{kT}{e}\right)^2 \cdot \varkappa \cdot \left[\cosh\left(-\frac{e\psi}{2kT}\right) - 1\right]$$

$$\Delta p_{el} = \frac{G_{el}(A_s) - G_{el}(A_l)}{A_l - A_s}$$

Change of transition pressure
best meaurable

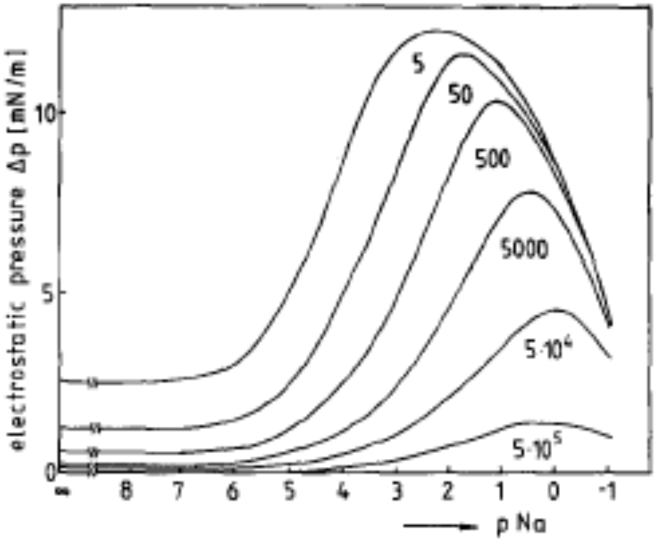
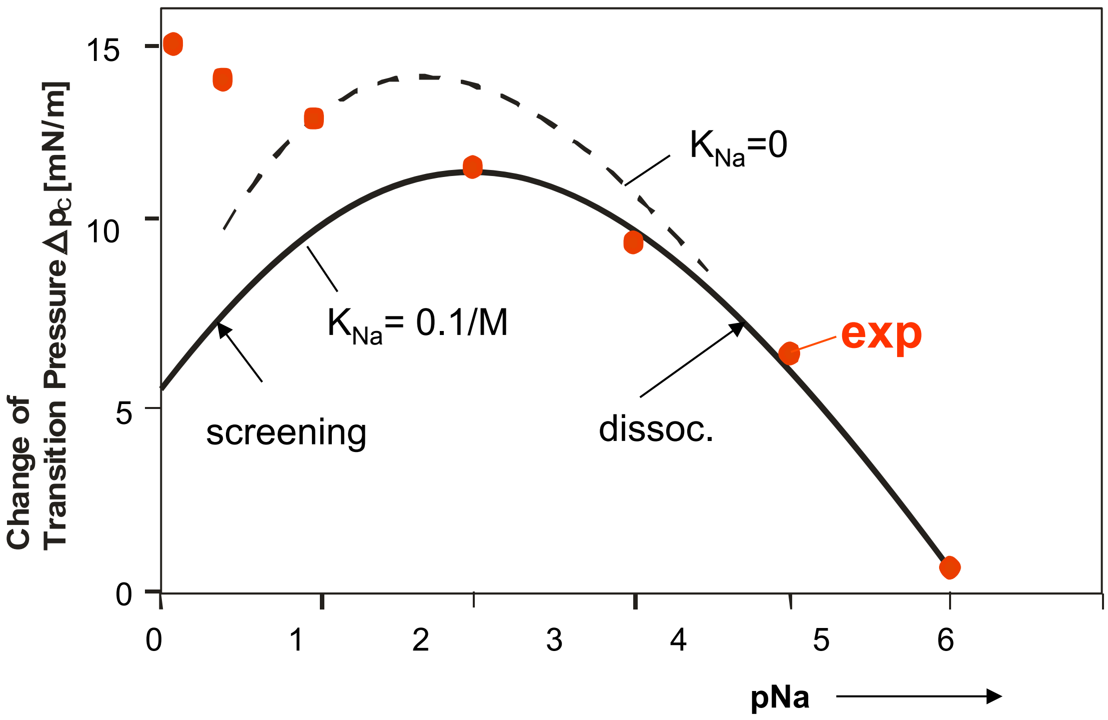


Fig. 3. Electrostatic contribution (Δp) to the surface pressure for various values of K_H as indicated as a function of ionic strength. Assumptions: pH = 6, molecular area $A = 60\,\text{Å}^2$

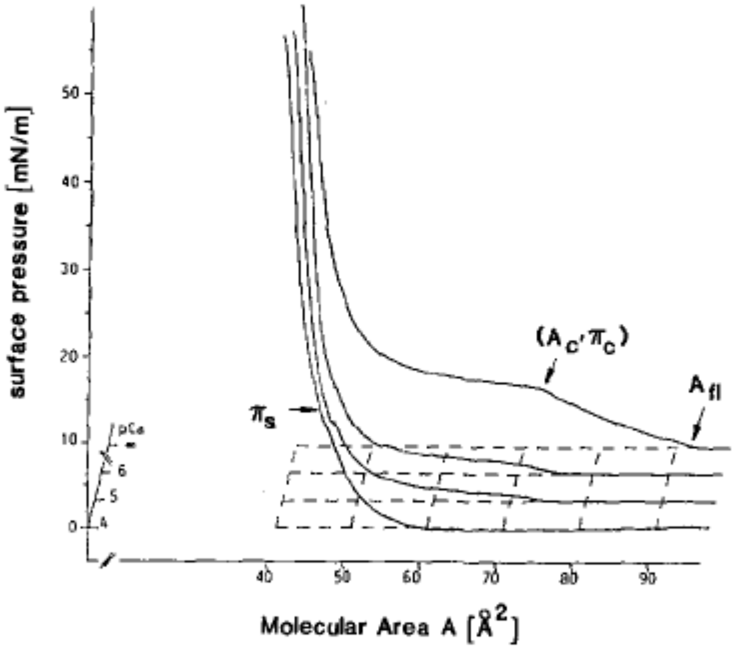
Energetics and Phase Transition

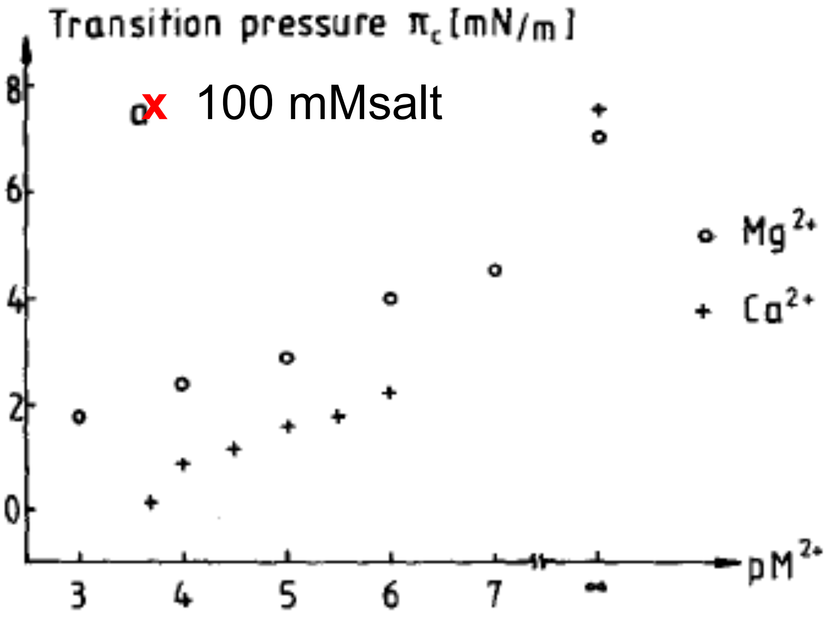


Conclusions:
dissociation
and ion binding
at interface drastically
different from bulk

- Electrostatic energy $G_{el} = \int \sigma d\psi + E_{diss}(\text{head})$
- Contribution to surface pressure $\pi_{el} = \frac{-dG_{el}}{dA}$
- Transition pressure change $\Delta_{Pc} = \frac{G_{el}(\text{solid}) - G_{el}(\text{fluid})}{A_{solid} - A_{fluid}}$

Divalent ions



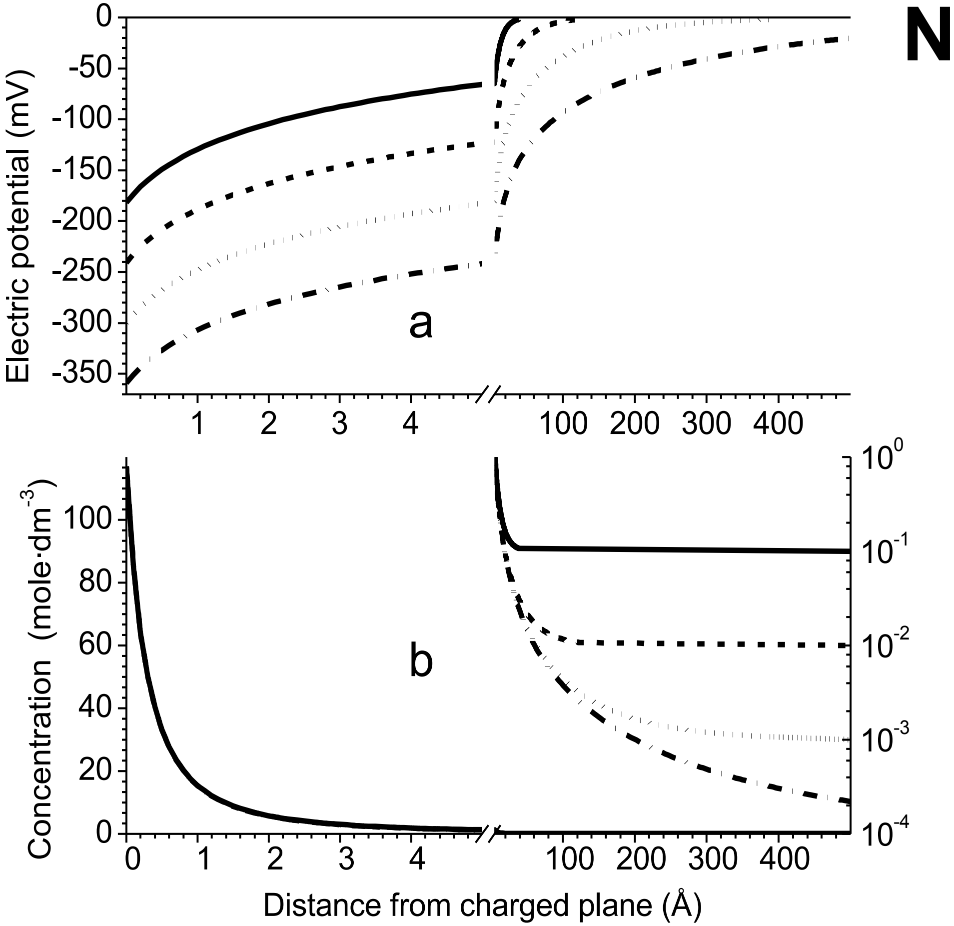


Influence remarkable for nM ionconcentration

Balance achievable with 100nM conc.of monovalent ions

M.Lösche, H.M. JCIS 131 (1989) 56

Potential and counterion distribution



Numerical simulation

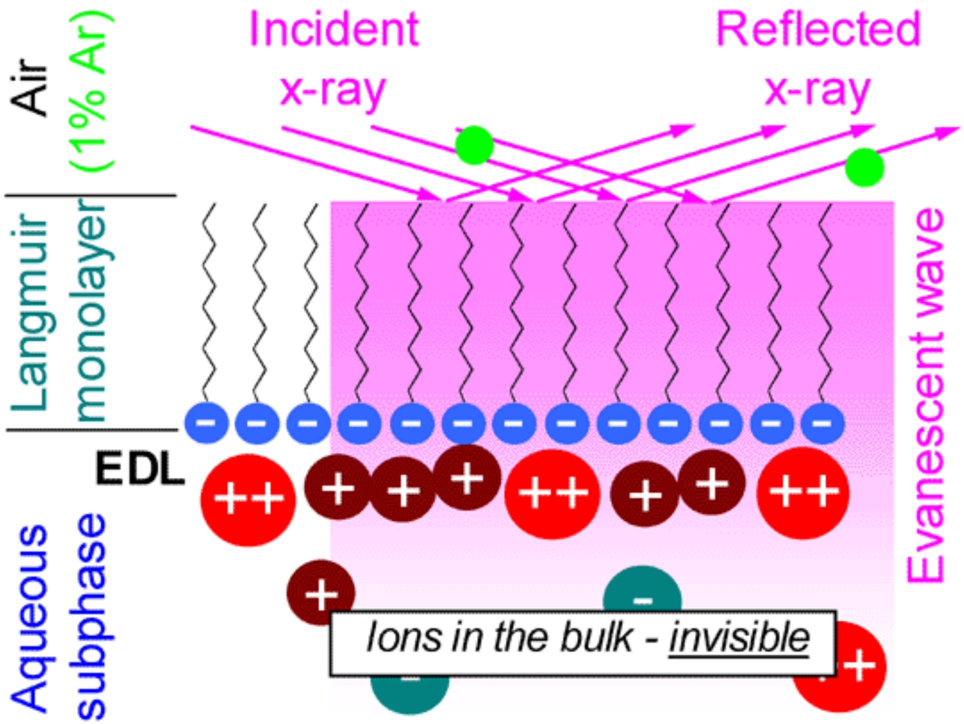
Most ions within 0.2nm near interf. hence difficult to resolve

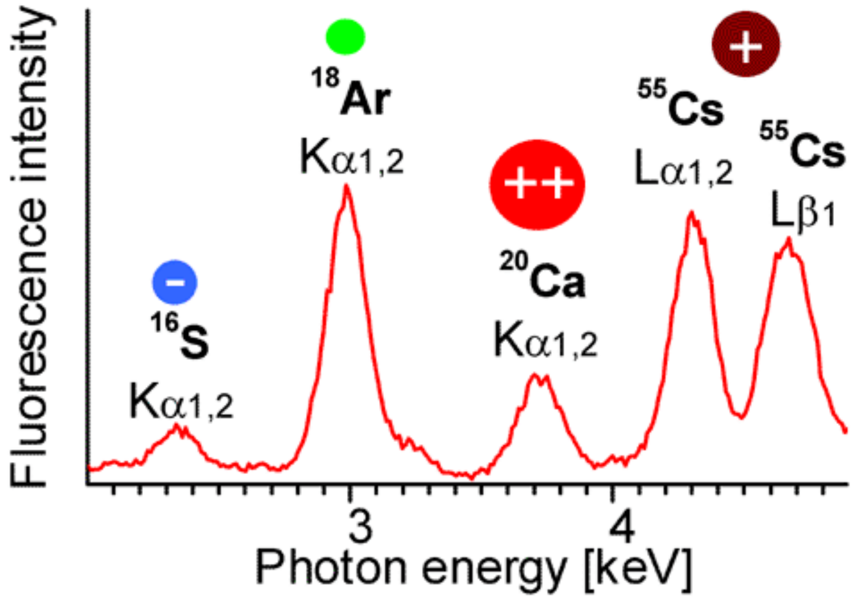
Give up high depth resolution,measure Ion concentration with 10 nm sublayer

Electric potential (**a**) and counterion concentration (**b**) for the GC model of the EDL. Parameters taken for simulation are: surface charge density: -1 ē/25 Å^2; dielectric constant: 80; 1-1-electrolyte (mmole·dm^{-3}): 100 (solid lines), 10 (dashed), 1 (dotted), 0.1 (dashed-dotted).

Shapovalov et al. J.Phys.Chem.111(2007)

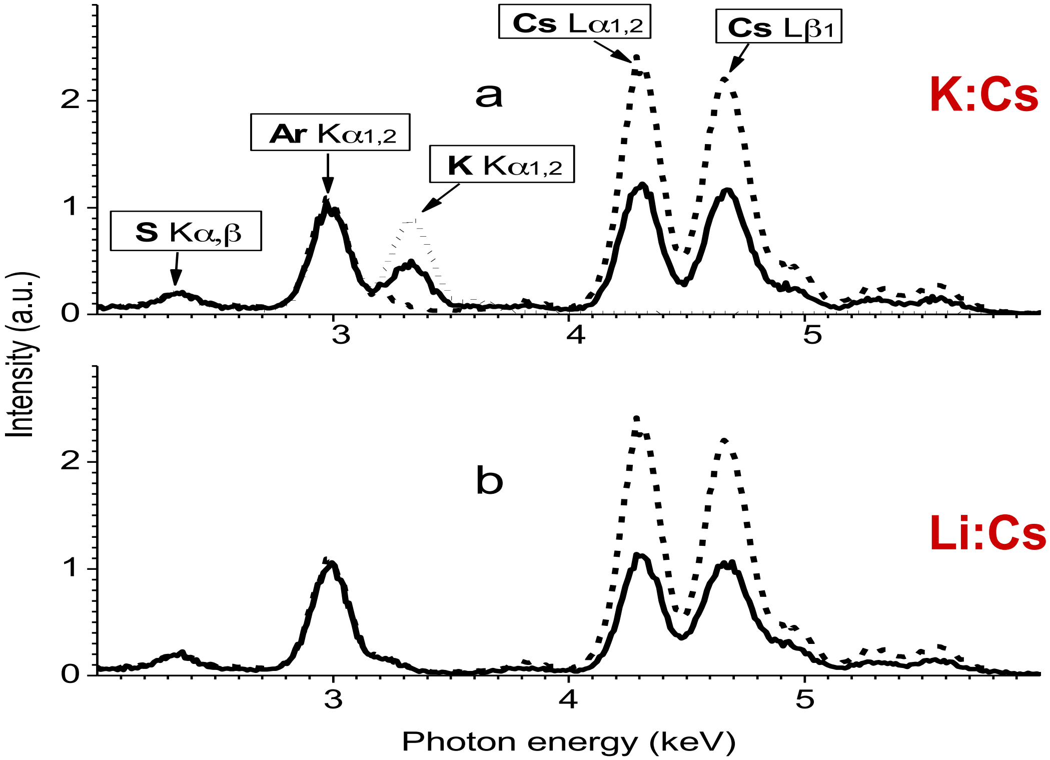
X-Ray Fluorescence at grazing incidence





Measure ion concentration within 4-5 nm from interface
difficult for oil/water interface

Competitive Adsorption (monovalent)



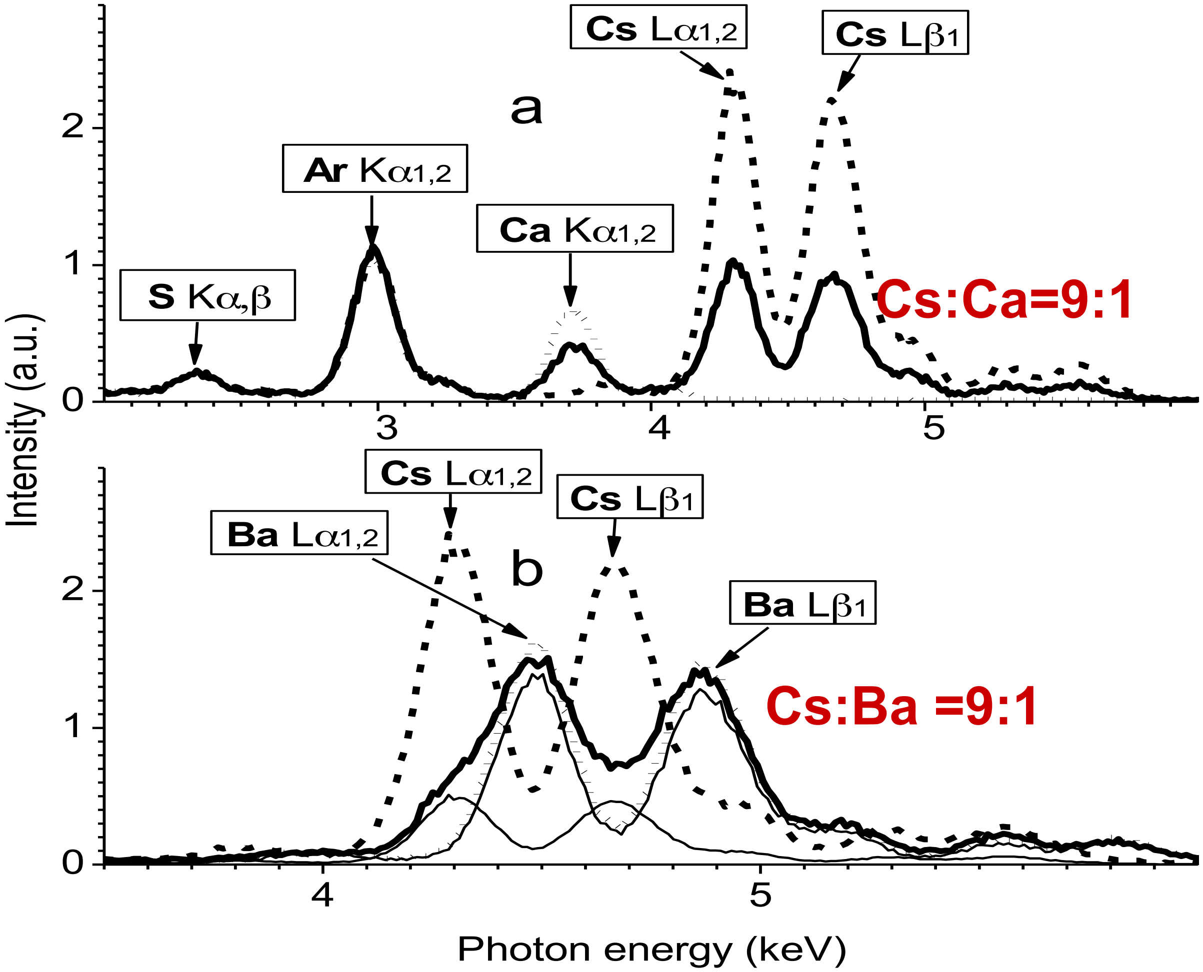
K:Cs =1:1

Li:Cs=9:1

Very high
Ion specifity

TRXF spectra of BS monolayer on subphases containing individual alkali metal chlorides ("calibration samples") and their mixtures (systems under investigation). Subphase compositions are: KCl/CsCl 1:1 (**a**, solid line); LiCl/CsCl 9:1 (**b**, solid); CsCl (**a** and **b**, dashed) and KCl (**a**, dotted). The total salt concentration is 10 mM in all cases.

Competitive adsorption (monovalent-divalent)



Cs competitive with Ca, not with Ba

TRXF spectra of BS monolayer on subphases containing individual alkali and alkali earth metal chlorides and their mixtures. Subphase compositions are: CsCl/CaCl2 9:1 (**a**, solid line); CsCl/BaCl2 9:1 (**b**, solid); CsCl (**a** and **b**, dashed); CaCl2 (**a**, dotted) and BaCl2 (**b**, dotted). Total salt concentration is 10 mM in all cases.

Important numbers

Numbers

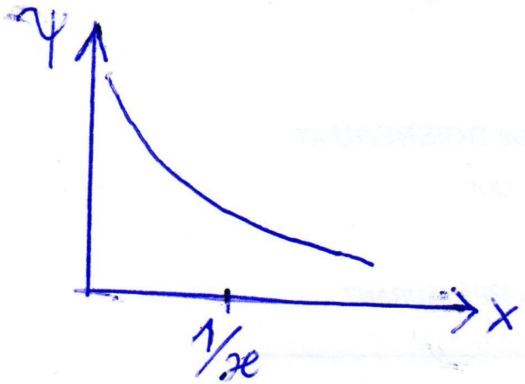
1) Time τ to establish Debye layer with thickness $\varkappa^{-1}$

$\varkappa^{-1} = 10\,nm$ ($10^{-3}M$ salt, 300K, water)

$\varkappa^{-1} \sim \frac{1}{\sqrt{conc.}} \rightsquigarrow \varkappa = 1\,nm$ fo $10^{-1}M$ salt

$\tau = \frac{\varkappa^{-2}}{2D}$ with diffusion coefficient(Na^+) $\sim 2 \cdot 10^{-5} \frac{cm^2}{sec}$

$\tau = \frac{1}{4} \cdot 10^{-9} sec$ (for $10^{-3}M$) $\rightsquigarrow$ <u>nsec scale</u>



2.) Charge density on a spherical particle

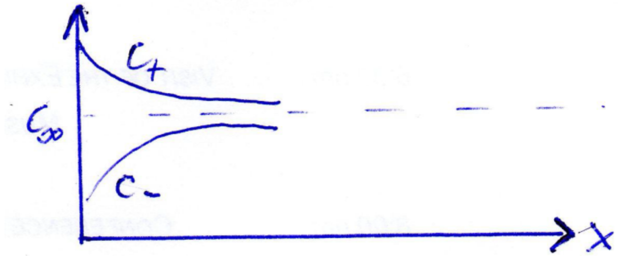
Ass: zeta potential $100\,mV = \Psi$

radius $R = 100\,nm$, e = elementary charge

Charge $Q = 4\pi \cdot \varepsilon \varepsilon_0 R \cdot \Psi \approx 500\,e$

Density $\frac{Q}{4\pi R^2} = 4 \cdot 10^{11}/cm^2 \triangleq 4 \cdot 10^{-3}/nm^2$

$\rightsquigarrow$ very small fraction of chargeable groups

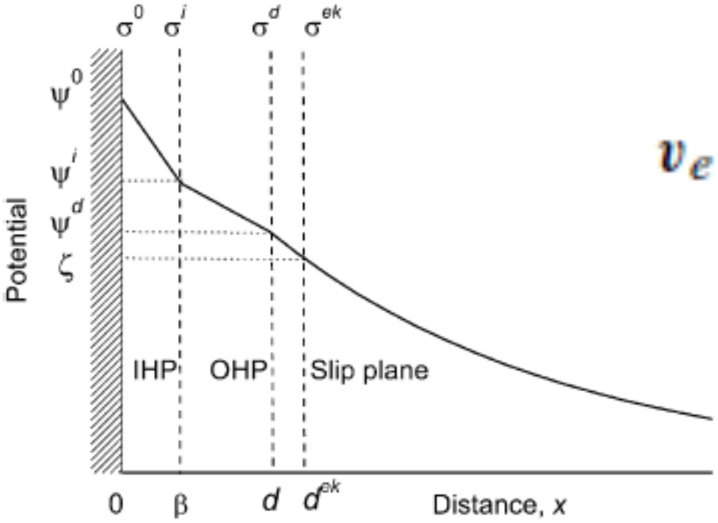


3.) Jon distribution

potential $\Psi = \Psi_0 \cdot exp(-\varkappa x)$

concentration $(c - c_\infty) = (c_0 - c_\infty)\, exp\left(+\frac{e\Psi}{kT}\right) = (c_0 - c_\infty)\, exp\left(+\frac{e}{kT} exp(-\varkappa x)\right)$

Zeta-potential



$$v_e = \frac{\varepsilon_{\mathrm{rs}}\varepsilon_0\zeta}{\eta}E$$

$$u_e = \frac{\varepsilon_{\mathrm{rs}}\varepsilon_0\zeta}{\eta}$$

Fig. 1. Schematic representation of the charges and potentials at a positively charged interface. The region between the surface (electric potential ψ^0; charge density σ^0) and the *inner Helmholtz plane* (distance β from the surface) is free of charge. The IHP (electric potential ψ^{i}; charge density σ^{i}) is the locus of specifically adsorbed ions. The diffuse layer starts at $x = d$ (*outer Helmholtz plane*), with potential ψ^{d} and charge density σ^{d}. The *slip plane* or *shear plane* is located at $x = d^{\mathrm{ek}}$. The potential at the slip plane is the *electrokinetic* or *zeta*-potential, ζ; the *electrokinetic charge density* is σ^{ek}.

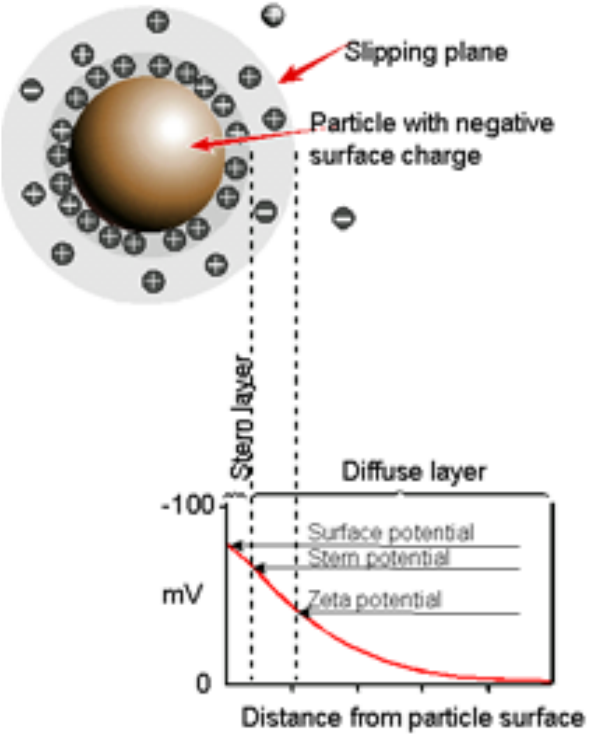
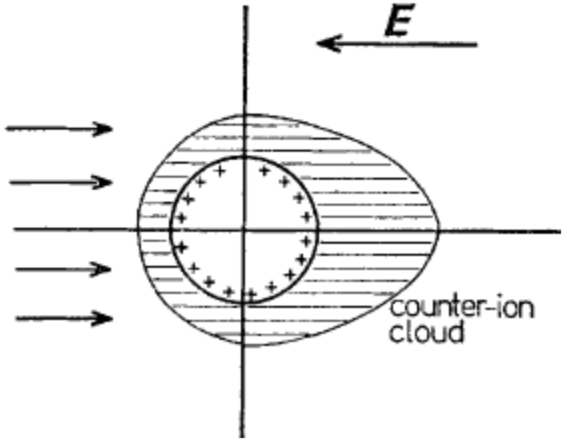


Image from Malvern

Mobility U = 2 ε z f(κa)/3η in the general case and f has to be calculated

A.V. Delgado et al. / Journal of Colloid and Interface Science 309 (2007) 194–224

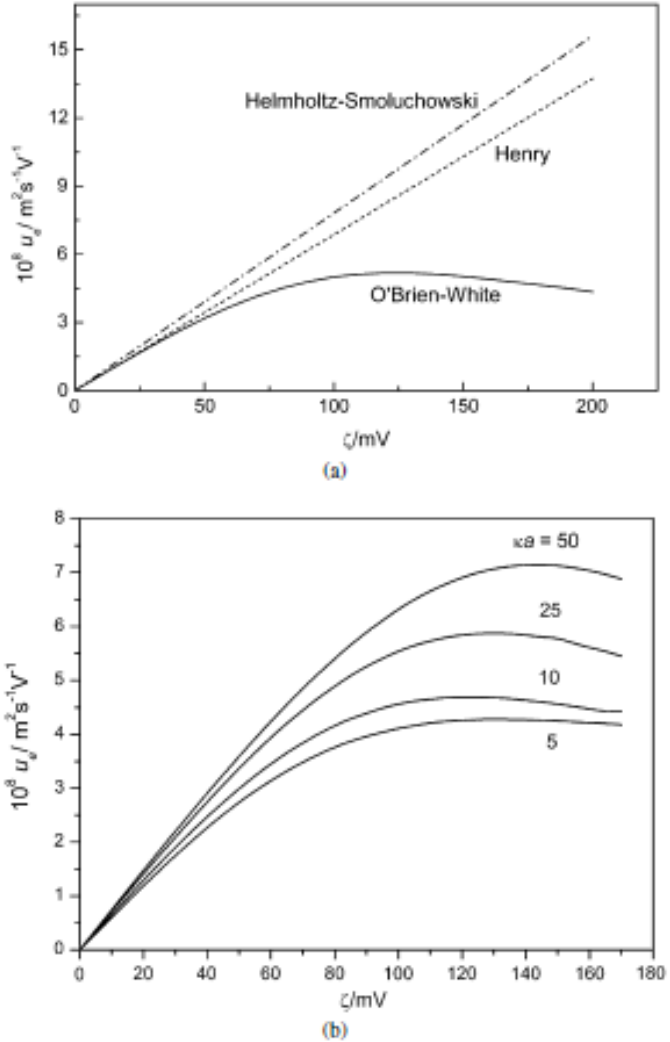
Refined theory on zeta potential



$$-\lambda_i(\boldsymbol{v}_i-\boldsymbol{u})-z_i e\nabla\Psi-kT\nabla\log n_i=0$$

Viscous electrostatic chemical

$$\lambda_i=\frac{Ne^2|z_i|}{\Lambda_i^0}$$



Refinement needed for small particles

R.W.O`Brien, L.R.White, J.Chem.Soc.Farady Trans.II 74(1978)1607

Examples of refinements

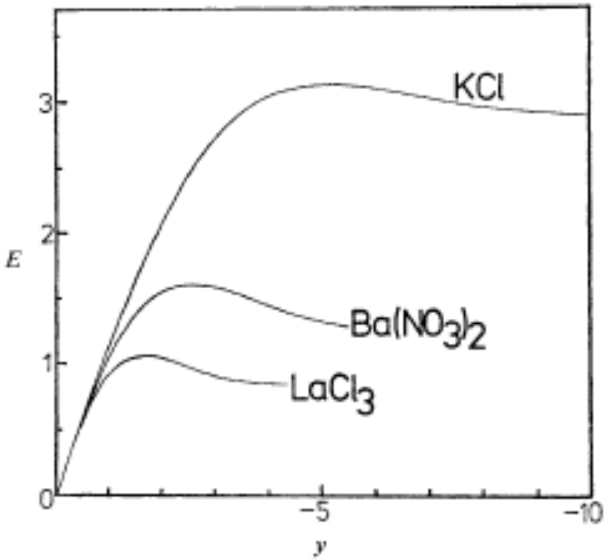


FIG. 6.—Effect of counterion valency on the form of the mobility against
for $\kappa a = 5$.

Ion specifics

Concentration dependence

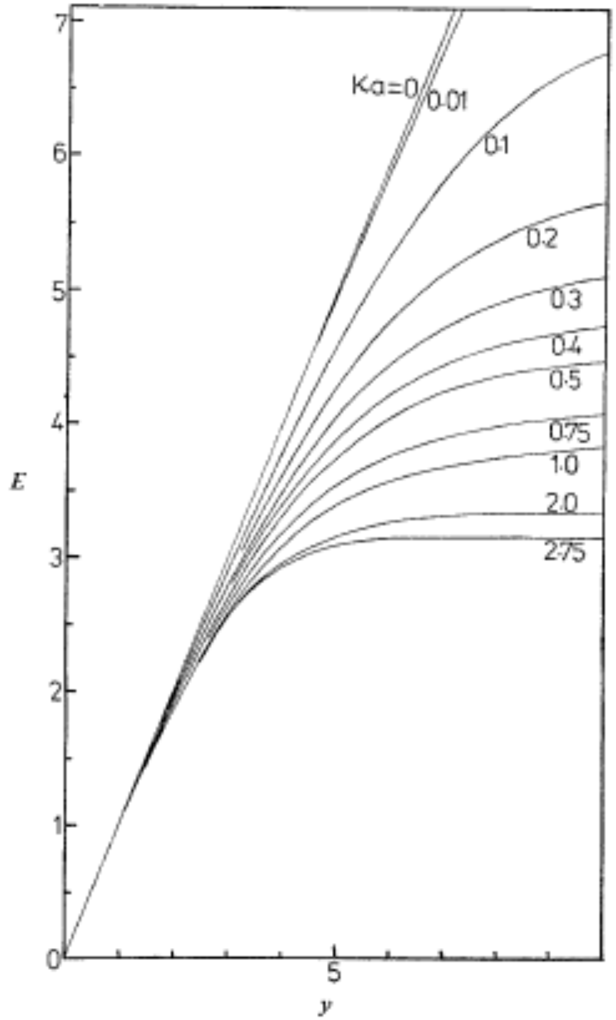
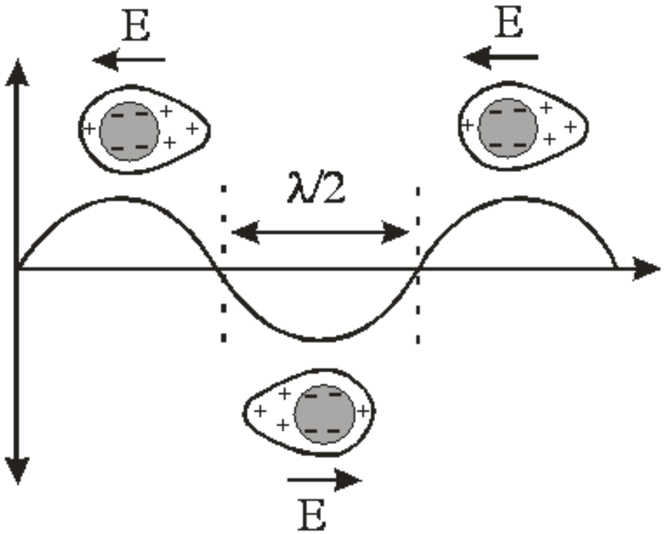


FIG. 3.—Reduced mobility E of a spherical colloidal particle in a KCl solution as a function of reduced zeta potential y, for $\kappa a < 2.75$. In this regime the mobility appears to increase monotonically with zeta potential.

Electroacoustics

Alternating E-Field compresses and expands and thus creates sound wave
(Electrokinetic sonic amplitude(ESA),loud speaker)

Sound wave creates alternating E-field
(Colloidal Vibration Current, CV potential)



Wavelength=Velocity x frequency=
1000m/sec x 1 MHZ = 1 mm >> debye length

Density **mobility**

$$\frac{U_{CV}}{\Delta p} \propto \phi \frac{\Delta\rho}{\rho} \frac{u_d^*}{K^*},$$

$$\frac{I_{CV}}{\Delta p} \propto \phi \frac{\Delta\rho}{\rho} u_d^*,$$

$$\frac{A_{ESA}}{E} \propto \phi \frac{\Delta\rho}{\rho} u_d^*.$$

ESA of Dispersions

Informative for frequencies
1-100 MHz
At high frequencies surface conduction on particles becomes relevant

Hence Colloidal Dispersions can be studied

Dynamic particle mobility

Theoretical and experimental
a separate topic

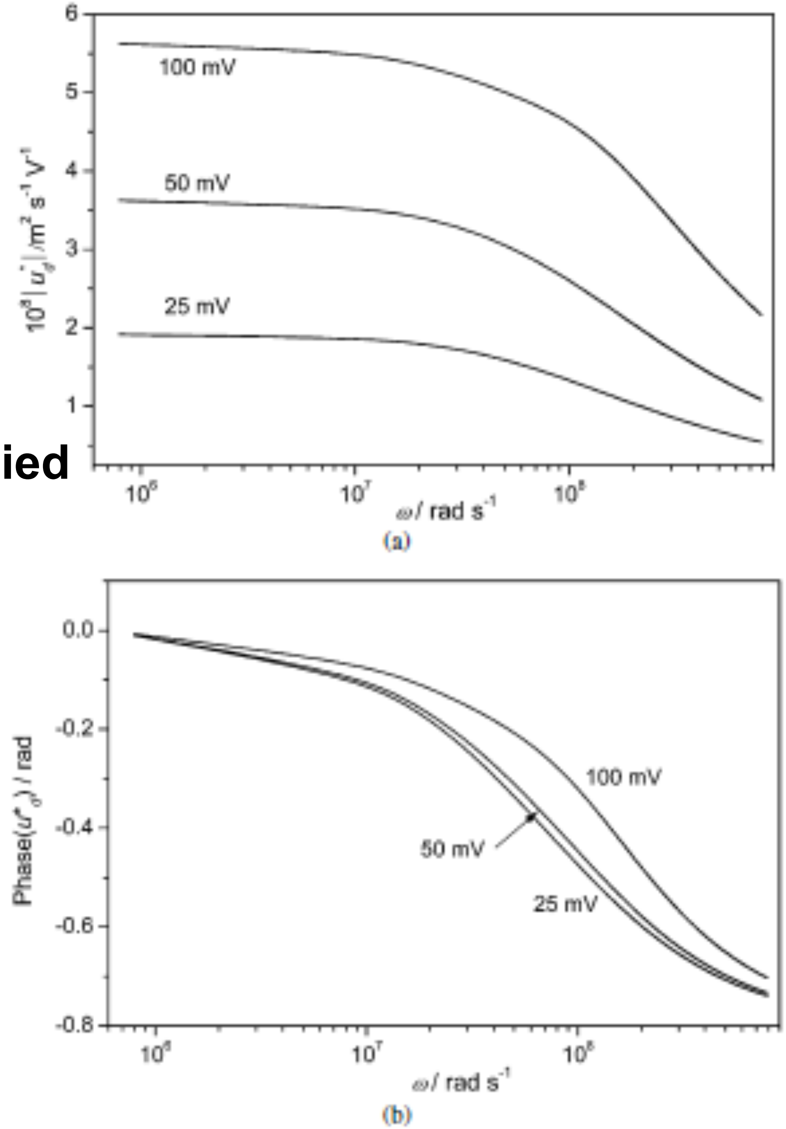


Fig. 8. Modulus (a) and phase angle (b) of the dynamic mobility of spherical particles in a KCl solution with $\kappa a = 20$ as a function of frequency for different ζ-potentials; cf. Eqs. (80)–(82). Parameters: particle radius 100 nm; dielectric constant of the particles (dispersion medium): 2 (78.54); density of the particles (dispersion medium): 5×10^3 (1×10^3) kg m^{-3}.

Litterature

- **Ion distribution** : standard text books like J. Lyklema, Fundamentals of Interfaces and Colloid Science, vol. II, Academic Press, New York, 1995, Chaps. 3, 4

  specifics in citations on slides

- **X-Ray-fluorescence and simulation.**

  V.L.Shapovalov et al., J.Phys.Chem. 111 (2007)3927-3934

- **Zeta potential**: J.Lyklema, above , andJ.R.Hunter

  Foundations of Colloid Science, Oxford Univ. Press, Oxford,2001, Chap. 8.

- **Electroacoustics**:Best review, including experimental details

  A.V.Delgado et al. J. Coll.Interf.Sci. 309 (2007) 194-224