Electrokinetic response of "standard particles" and more…

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System

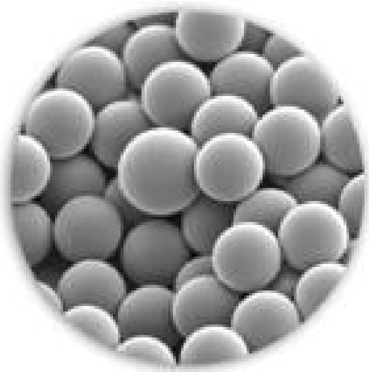
1) "standard"particles :

⇒ constant charge = 0,04 C/m^2 (sulfate latex)

⇒ radius = 265 nm (TEM)

⇒ monodisperse

⇒ Suspending medium: demi-water + salts

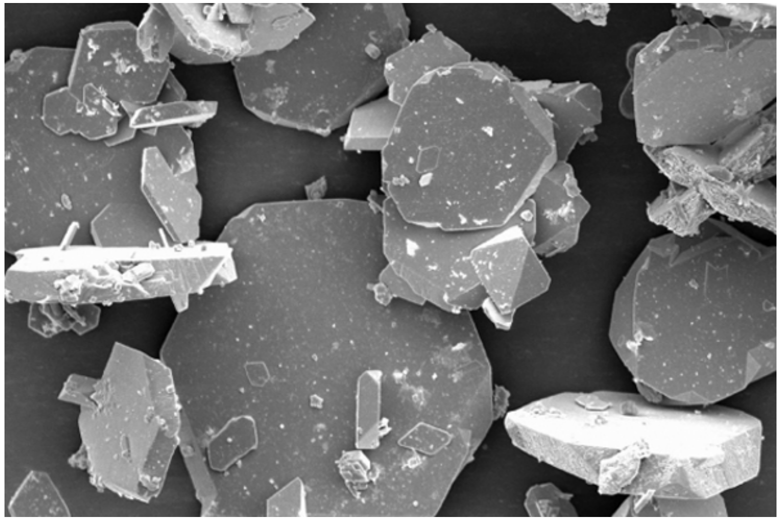


System

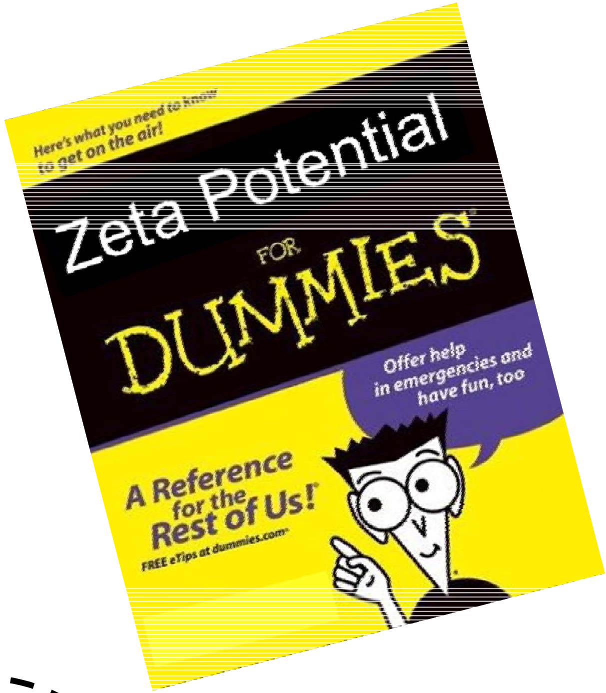
2) “more” = non-spherical particles :

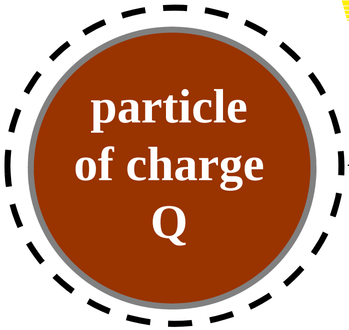
⇒ kaolinite, gibbsite, goethite (clays, oxides)

⇒ non-ideal

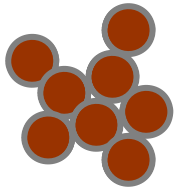


Zeta Potential

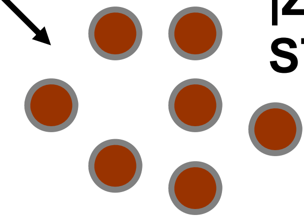




slip plane where the zeta potential ζ is defined ζ=f(Q)



|ZP| = |ζ | < 25 mV
AGGREGATE



|ZP| = | ζ | >> 25 mV
STABLE

Application

zeta pot. > interactions > rheology

Influence of anions on the theological properties of clay mineral dispersions

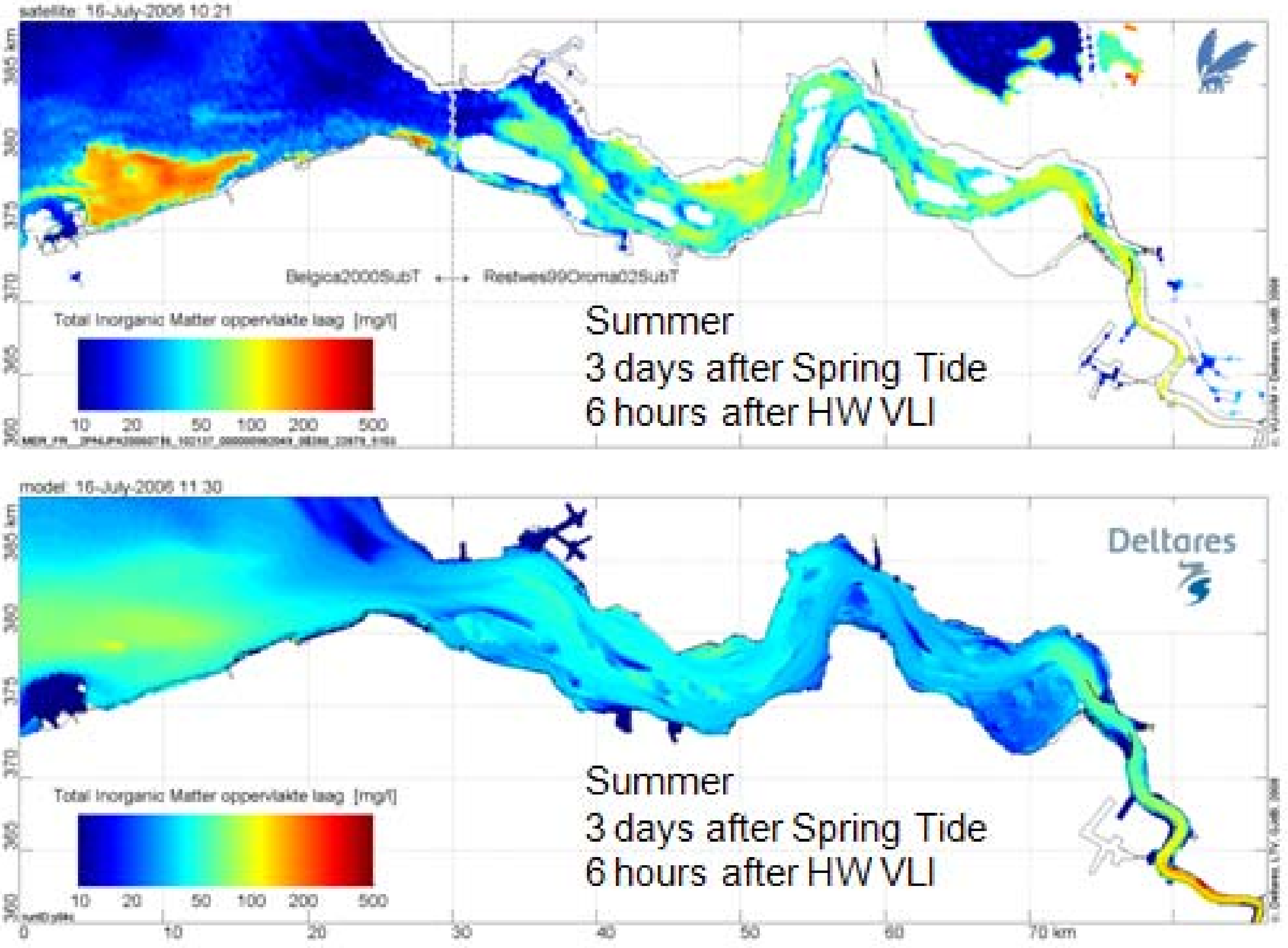
Author(s): Penner, D (Penner, D); Lagaly, G (Lagaly, G)

Source: APPLIED CLAY SCIENCE **Volume:** 19 **Issue:** 1-6 **Special Issue:** SI **Pages:** 131-142 **DOI:** 10.1016/S0169-1317(01)00052-7 **Published:** JUL 2001

Conference: European Clay Conference on Surface Modification of Clay Minerals (EUROCLAY '99) **Location:** KRAKOW, POLAND **Date:** SEP 05-09, 1999

Abstract: The flow behavior of sodium montmorillonite dispersions and kaolin slurries can have different responses to anionic dispersants. Viscosity, pH, and dynamic mobility measurements using a variety of salts help elucidate this important observation. The flow behavior is determined not only by the counterions but also by the colons (anions) surrounding the clay mineral particles. The viscosity of sodium montmorillonite dispersions with increasing salt or acid concentration decreased to a minimum, then increased sharply. The concentration at this point was identified as the critical coagulation concentration, c(K). Salts with multivalent anions such as sulphates and phosphates increased the critical coagulation concentration. Na4P2O7 actually impeded coagulation. The liquefying effect of these anions was counterbalanced by the protons of acidic salts such as NaHSO4, Na2HPO4, and NaH2PO4 and by acids. The critical coagulation concentration for sodium montmorillonite was a function of the montmorillonite concentration and the type of ion. In 2% sodium montmorillonite dispersions, c(K) for sodium chloride and sulphate was higher than c(K) in dilute dispersions (0.025%). For the strongly liquefying agents Na2HPO4, NaH2PO4, and H3PO4, the opposite was true. The c(K) values for the dilute dispersion were 1100, 460, and 32 mmol/l respectively, and for the 2% dispersion 80, 40, and 10 mmol/l. Kaolinite dispersions in contrast to sodium montmorillonite showed the pronounced liquefying effect of multivalent anions up to high salt concentrations. The data underscored the complexity of dispersed systems. For example, the dynamic mobility of the particles and the viscosity of the system were not always directly related. An interesting aspect concerns the dynamic mobility of the montmorillonite and kaolinite particles which in different ways changed with concentration of salts and acids.

Application



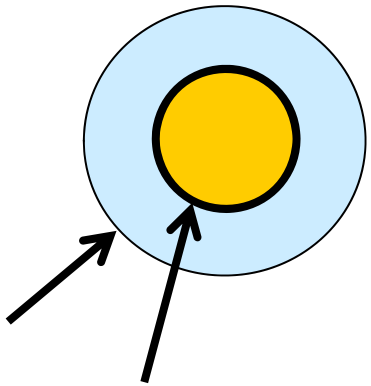
Assumptions

T = constant (no "thermo-dynamic")

E = applied electric field (but "electro-dynamic")

E (V/cm) << zeta potential (mV)/ double layer (nm)

$\Rightarrow$ X = Xeq + dX



double layer (ion cloud)

ζ (zeta potential)

Shear plane = surface particle : $\zeta = \Psi_0$

Relation charge / potential at eq.

$$\left(\frac{d\Psi_{eq}}{dx}\right)_{x=0} = \frac{-\sigma}{\varepsilon}$$

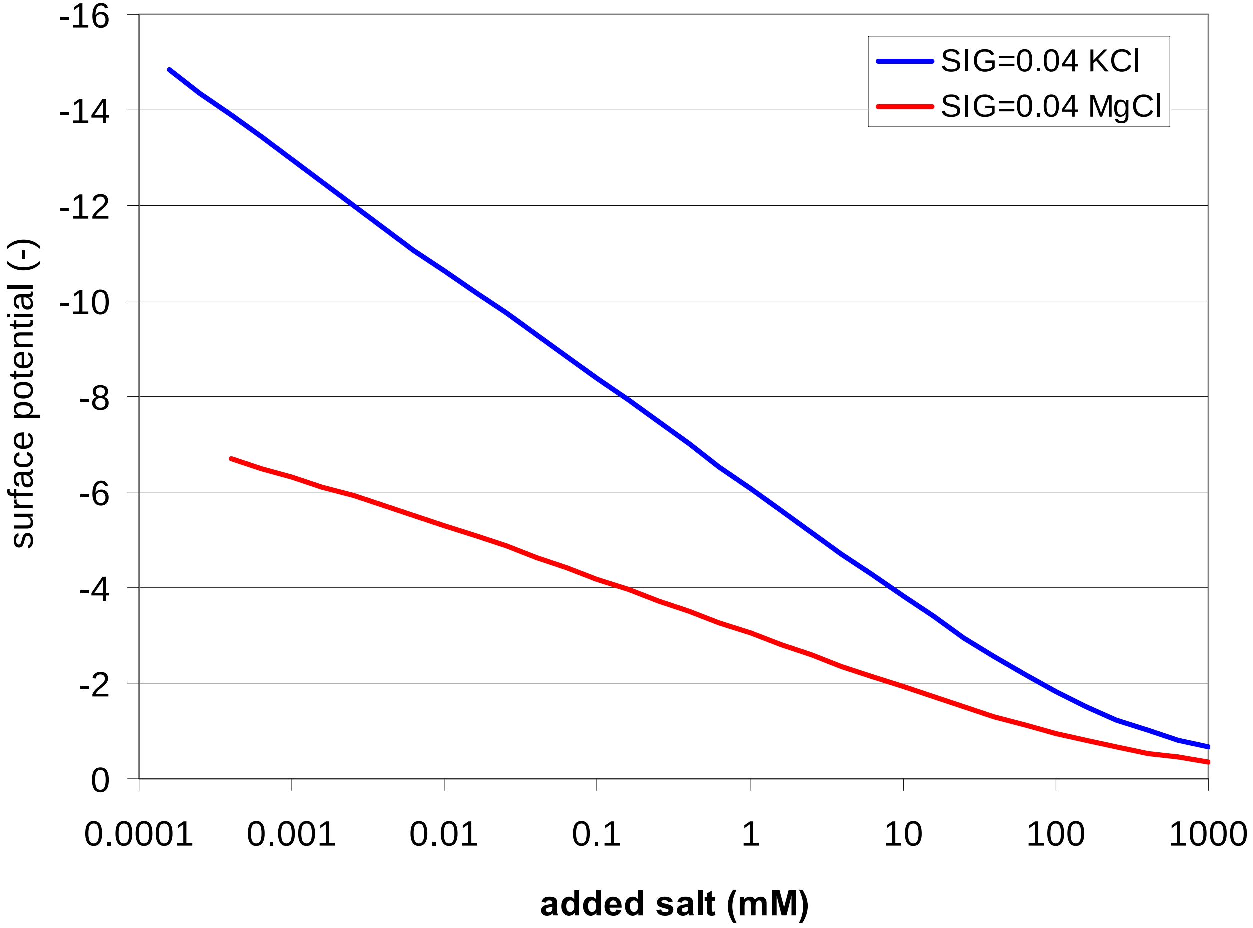
We will assume a **constant surface charge** :

fixe charge => find the zeta potential for each ionic strength using (PB) + bisection method

$$\boxed{\nabla^2 \Psi_{eq} = \kappa^2 \sinh\left(\Psi_{eq}\right)} \qquad \kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_1 kT}{2e^2 \mathrm{N}_A \mathrm{Cs}}}$$

Surface potential / added salt

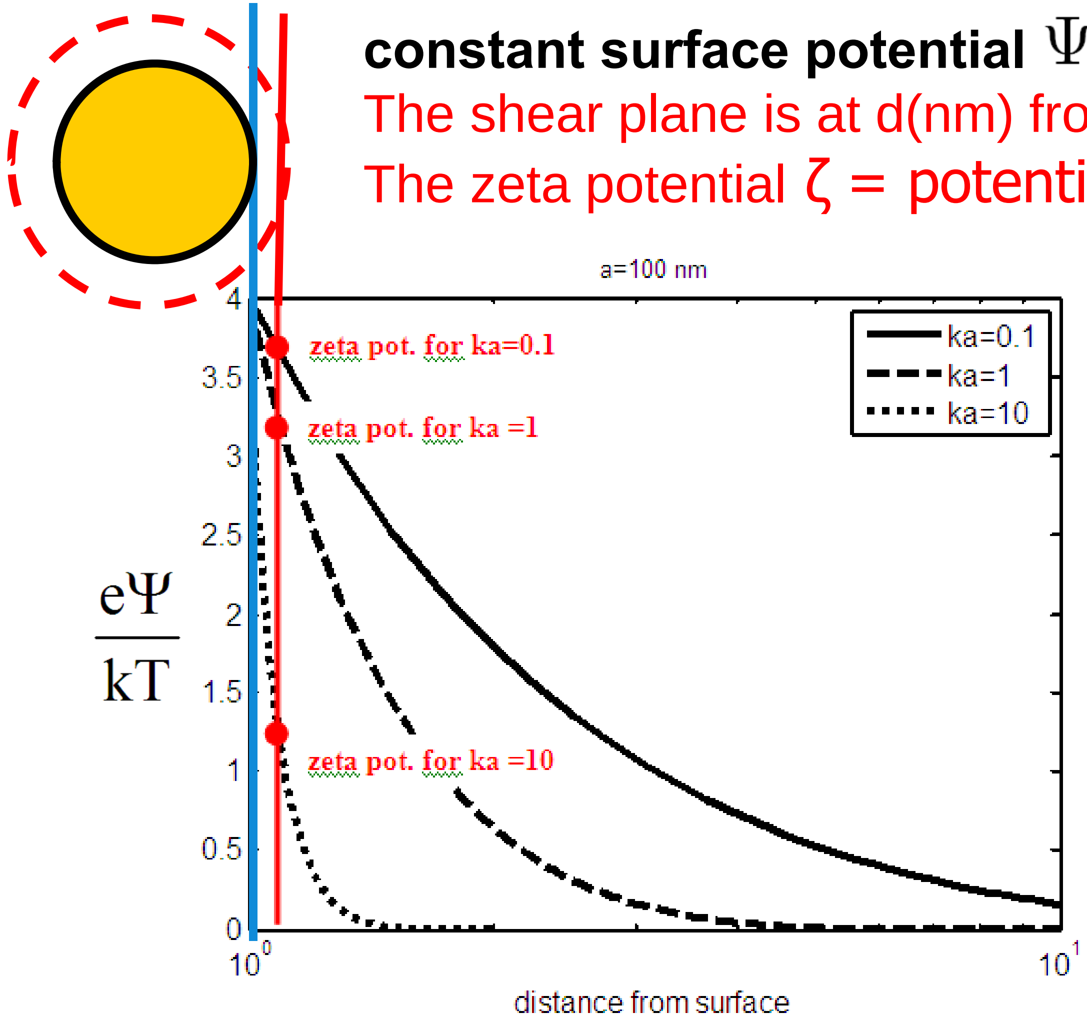
in case of a constant charge



constant surface potential Ψ_0

The shear plane is at d(nm) from the surface

The zeta potential ζ = potential at shear plane



Constant surface potential but zeta potential decreases with ionic strength when d ≠ 0

Standard electrokinetic equations

Poisson :

$$\nabla^2 \delta\Psi = \frac{-1}{\varepsilon_0 \varepsilon_1} \sum e z_i \delta n_i$$

Conservation of mass:

$$\mathbf{J}_i = n_{i,\mathrm{eq}} \mathbf{u} - n_{i,\mathrm{eq}} D \nabla \left[\frac{z_i e}{kT} \delta\Psi + \frac{\delta n_i}{n_{i,\mathrm{eq}}} \right]$$

$$\frac{\partial \delta n_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0.$$

Note:

$$\mathbf{u}_{\mathrm{tot}} = \mathbf{u}_{\mathrm{eq}} + \delta\mathbf{u} = \delta\mathbf{u} \equiv \mathbf{u}.$$

Standard electrokinetic equations

Boundary conditions

Potential :

$$\varepsilon_0\varepsilon_2\left(\frac{\partial(\delta\Psi_2)}{\partial r}\right)_{r=a} = \varepsilon_0\varepsilon_1\left(\frac{\partial(\delta\Psi)}{\partial r}\right)_{r=a}$$

$$\delta\Psi_2(a) = \delta\Psi(a), \quad (\Delta\delta\Psi_2 = 0)$$

No flux:

$$(\mathbf{J}_i \cdot \mathbf{e}_r)_{r=a} = 0$$

No slip:

$$\mathbf{u}(r = a) = \mathbf{0}$$

$$\mathbf{u}(\infty) = -\mathbf{U}$$

Electrophoresis
standard electrokinetic equations

relation electrophoretic mobility / zeta potential:

$$U = f\frac{\varepsilon\zeta}{\eta}$$

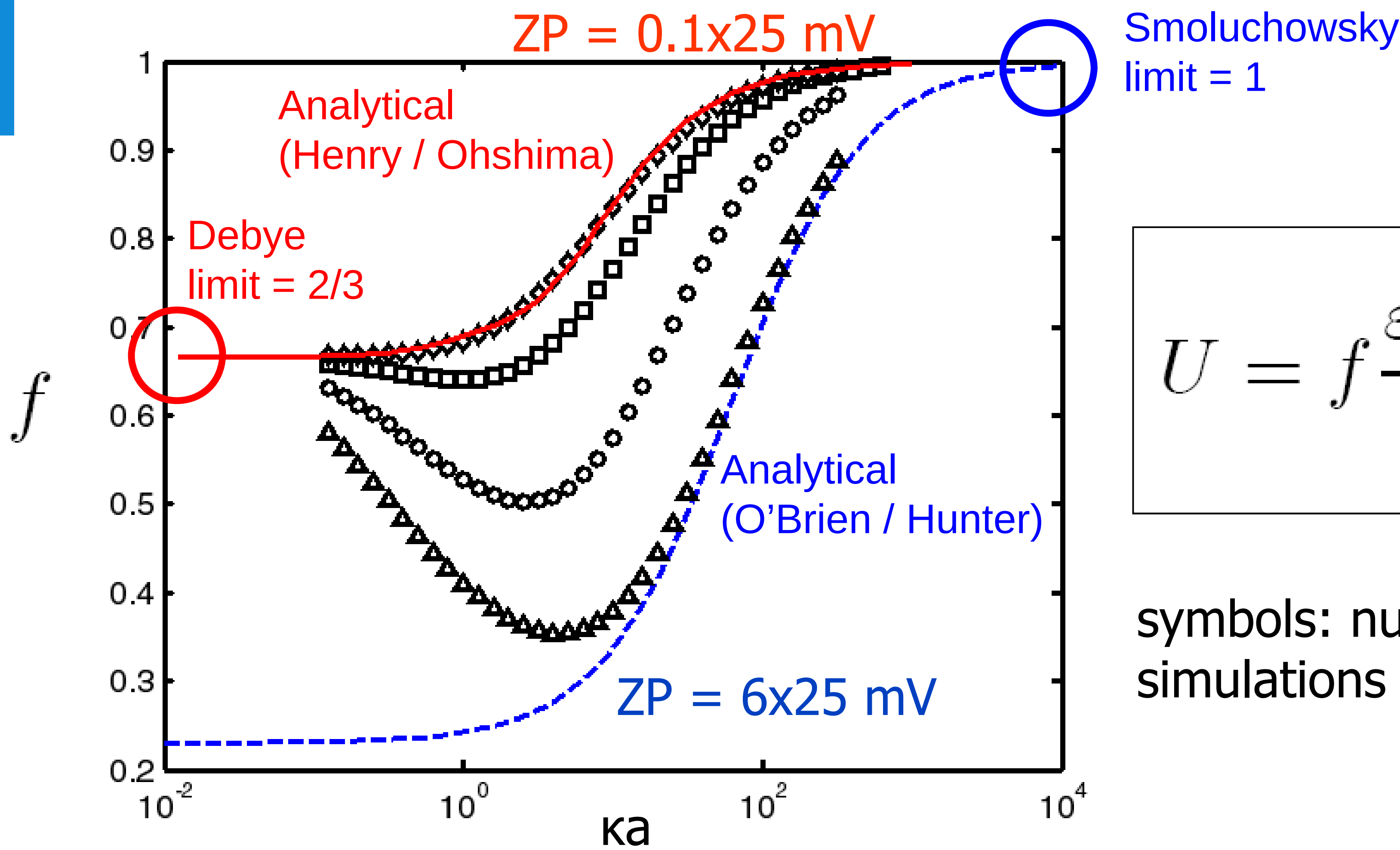
found with no adjustable parameter

found from solving numerically the set of standard electrokinetic equations

found from (PB) assuming (given) constant charge

Electrophoresis

constant zeta potential



$$U = f\frac{\varepsilon\zeta}{\eta}$$

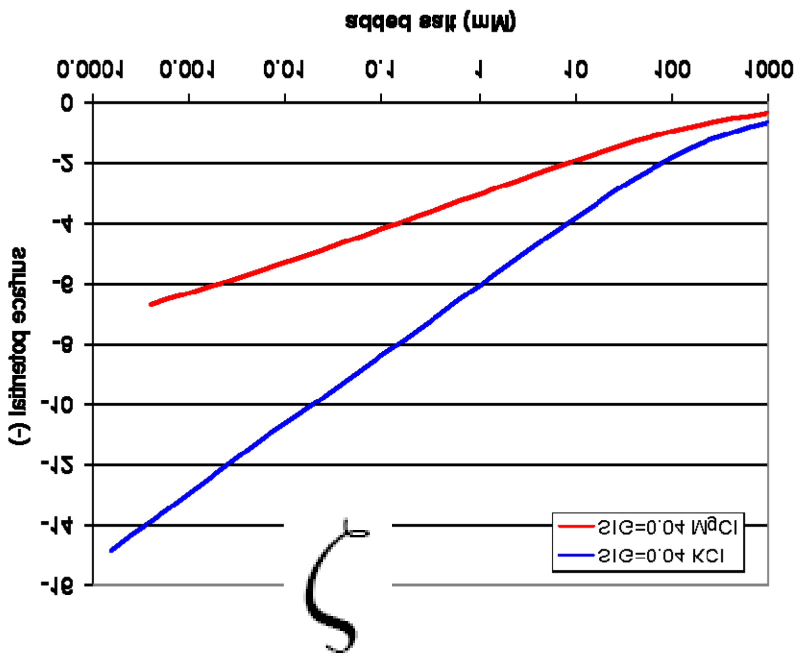
symbols: num. simulations

Electrophoresis / added salt

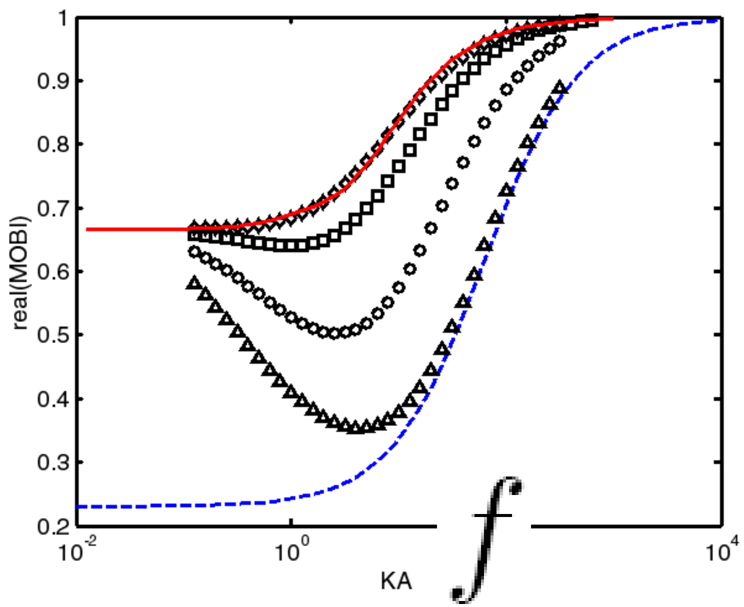
constant charge

$$f\,\zeta \quad =$$

$$U = f\,\frac{\varepsilon\zeta}{\eta}$$

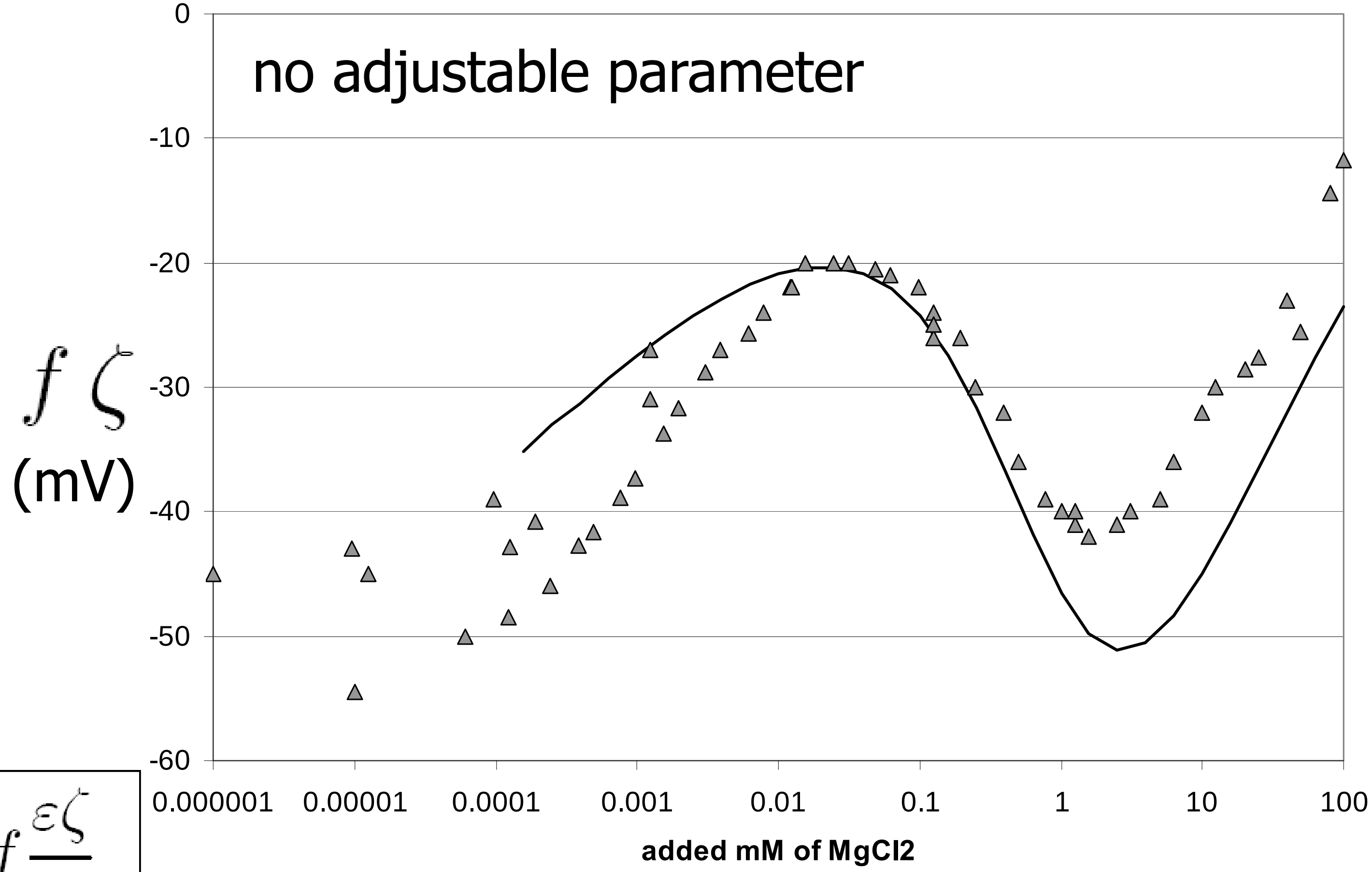


x



Electrophoresis / added salt

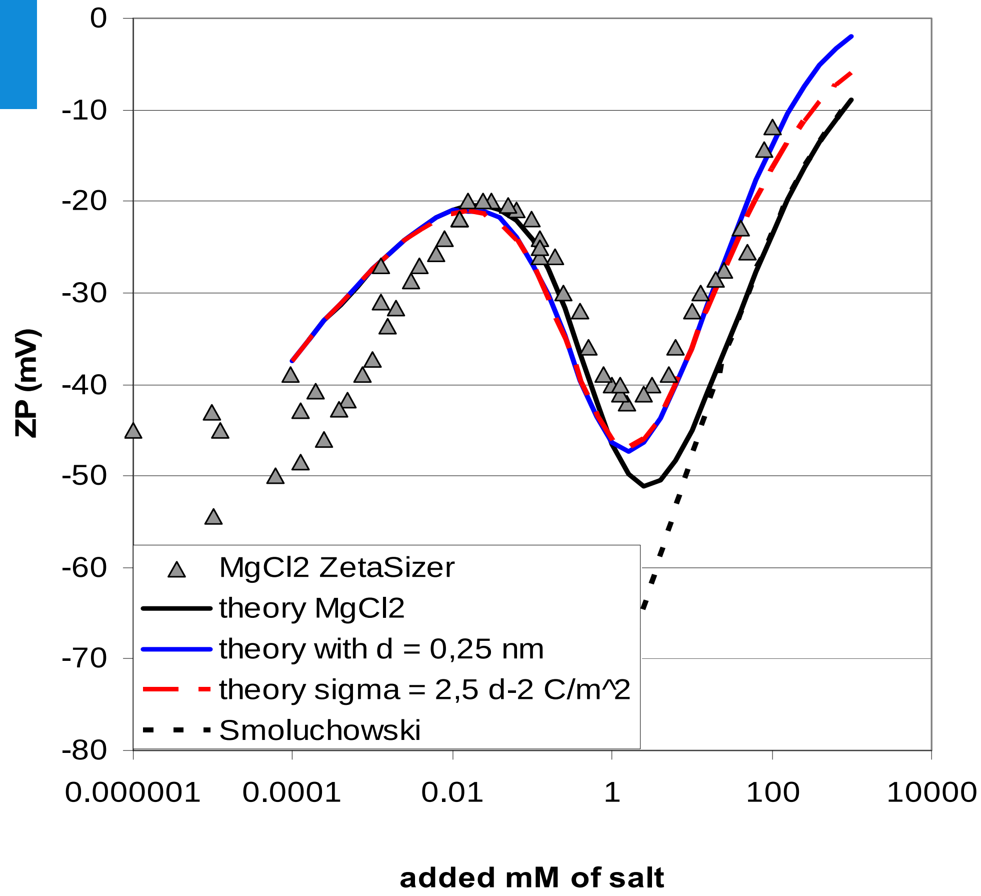
constant charge

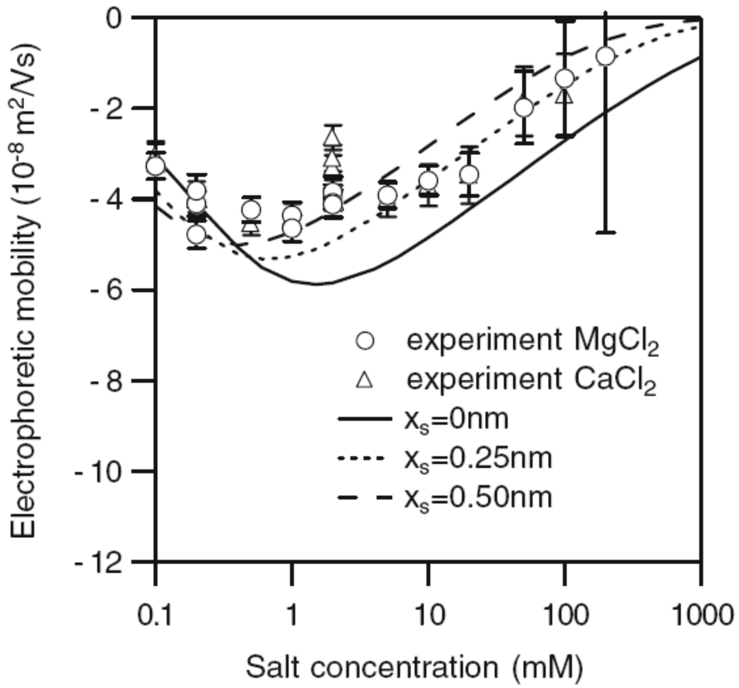


$$U = f\,\frac{\varepsilon\zeta}{\eta}$$

Electrophoresis / added salt

constant charge



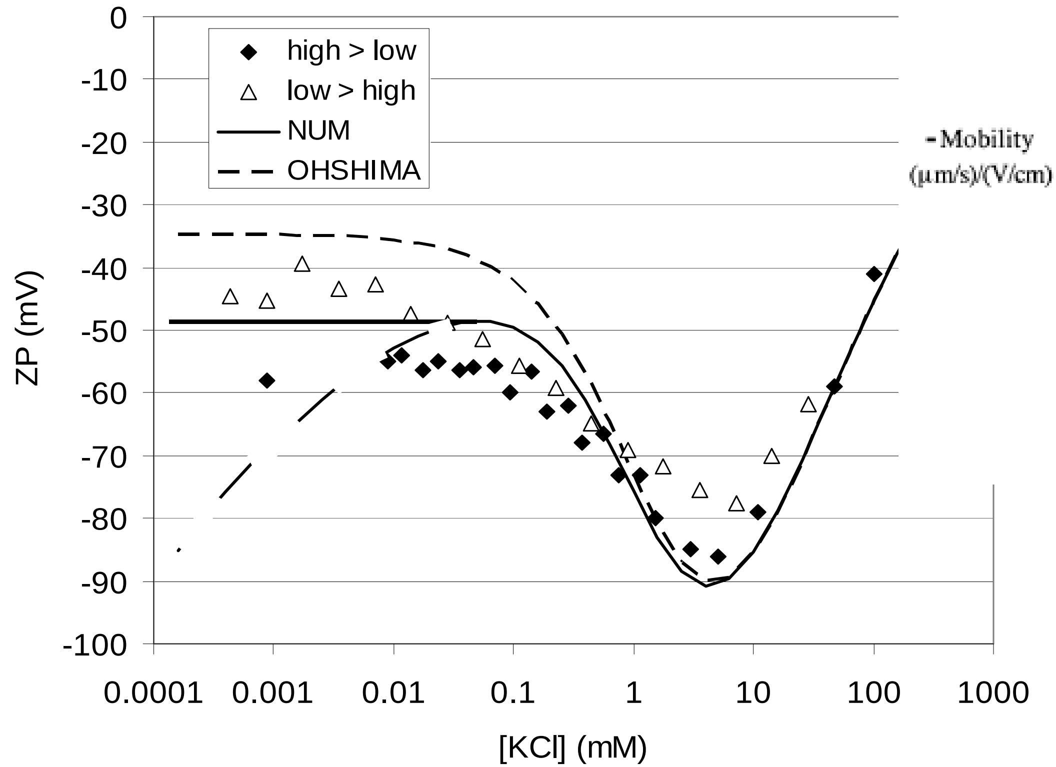


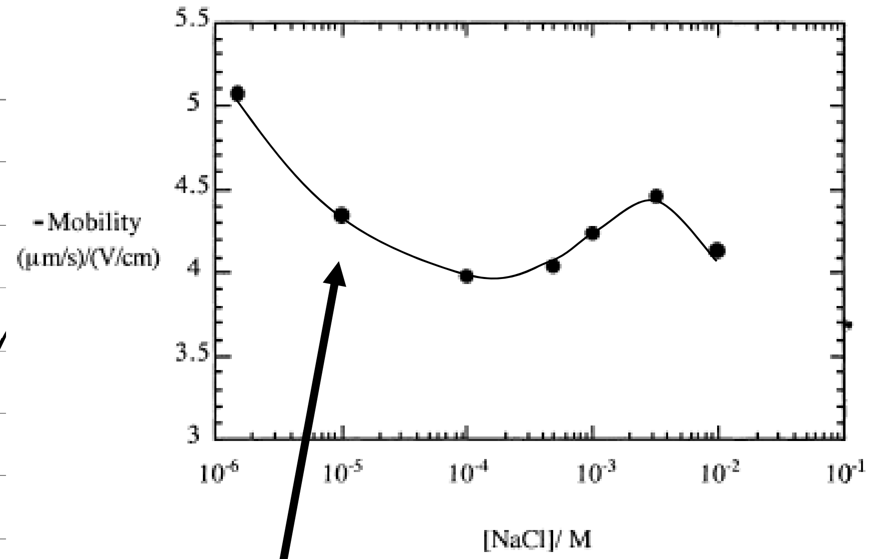
same behavior for 2800 nm spheres (Kobayashi, Colloid Polym Sci (2008) 286:935–940)

Electrophoresis / added salt

constant charge

Gittings and Saville, Colloids and Surfaces A (1998)



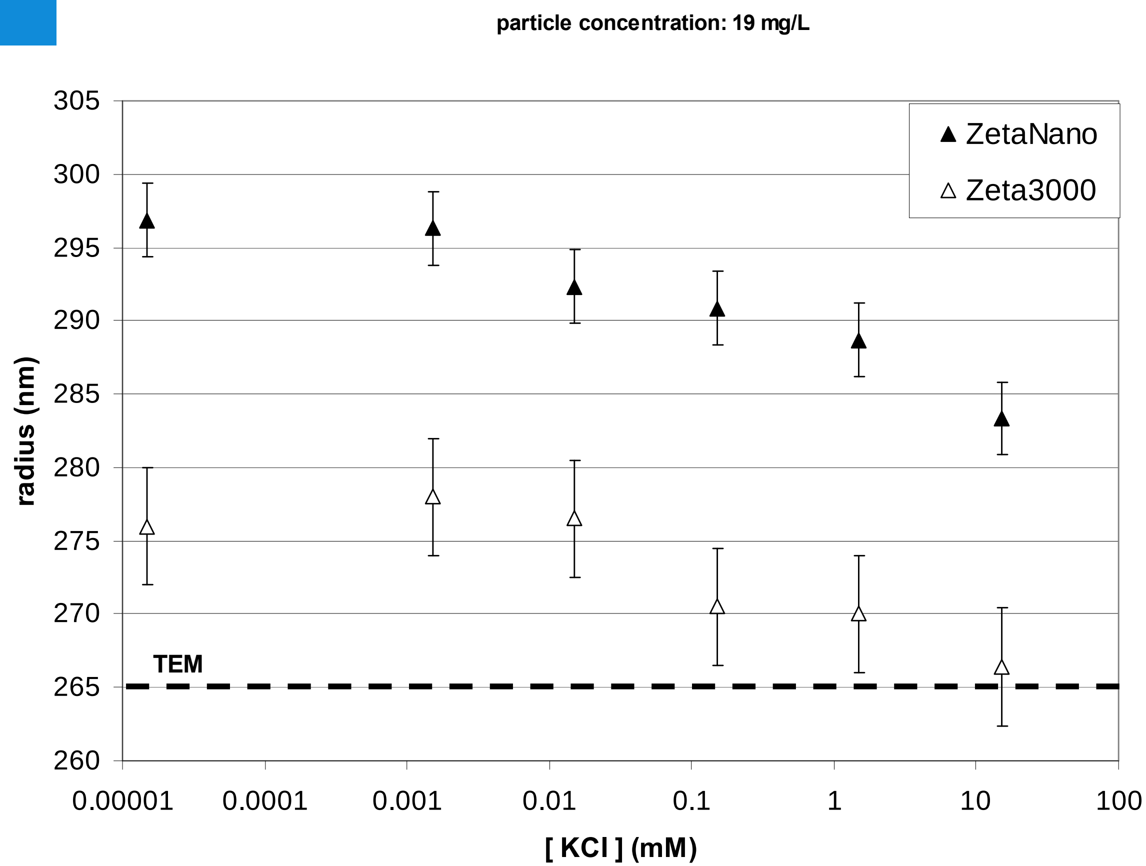


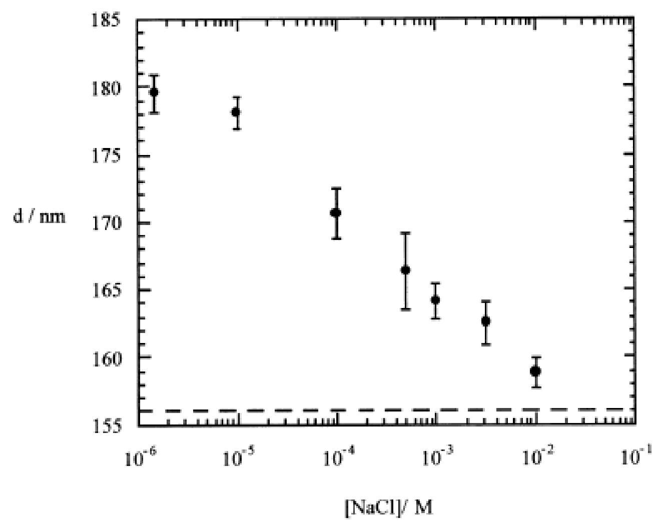
curvature!

Hairy layer : Particle size / added salt

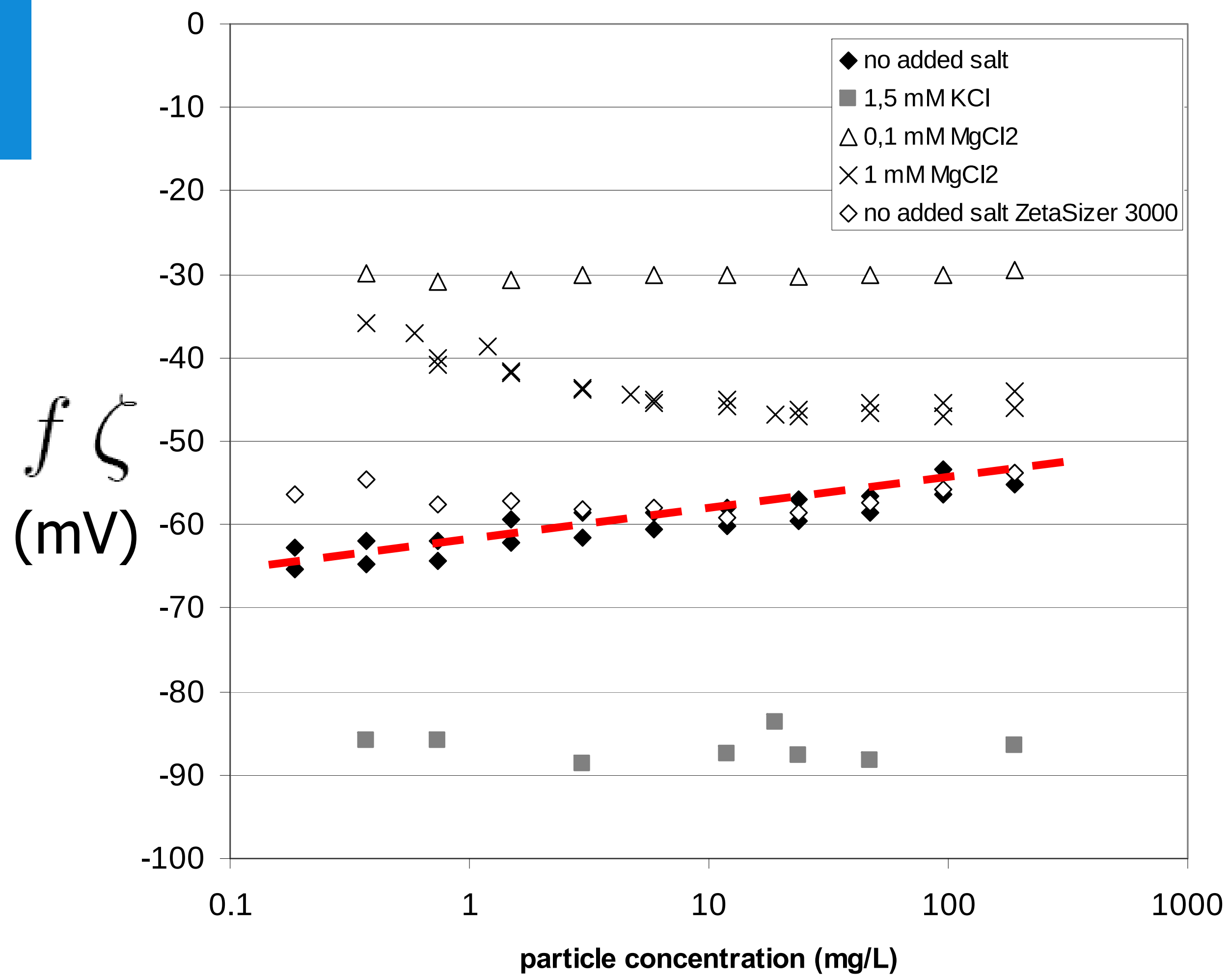
DLS and TEM

Gittings and Saville, Colloids and Surfaces A (1998)





Electrophoresis / particle concentration



"salt-free"

ZP ≈ - log (1/Φ)

Ohshima, Journal of Colloid and Interface Science **247,** 18–23 (2002)

Summary for spheres

- Standard theory describes reasonably well the electrokinetic behavior of the latex particles, with no adjustable parameter (electrophoresis, dielec. spectro., conductivity)

- adding a Stern layer conductance does not improve the fit

=> hairy layer ("soft particles") could be explanation for shifting the shear plane approx. 0.25 nm from the particle surface

- behavior as function of particle volume fraction follows prediction for nearly no salt

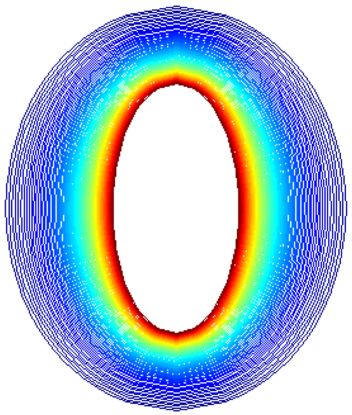
Outlook

electrokinetic response of spheroidal particles

2008 : => analytical solution (reproduce O'Brien + Loewenberg)

C. Chassagne, D. Bedeaux / Journal of Colloid and Interface Science 326 (2008) 240–253

2012 : => numerical solution (=> improve analytical solution)



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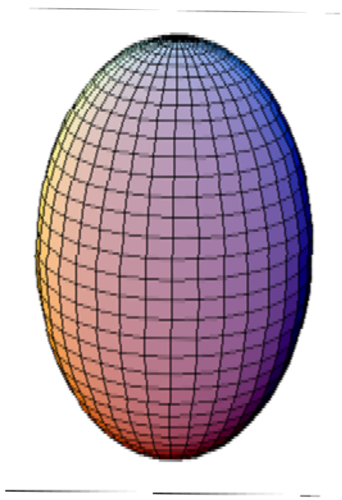
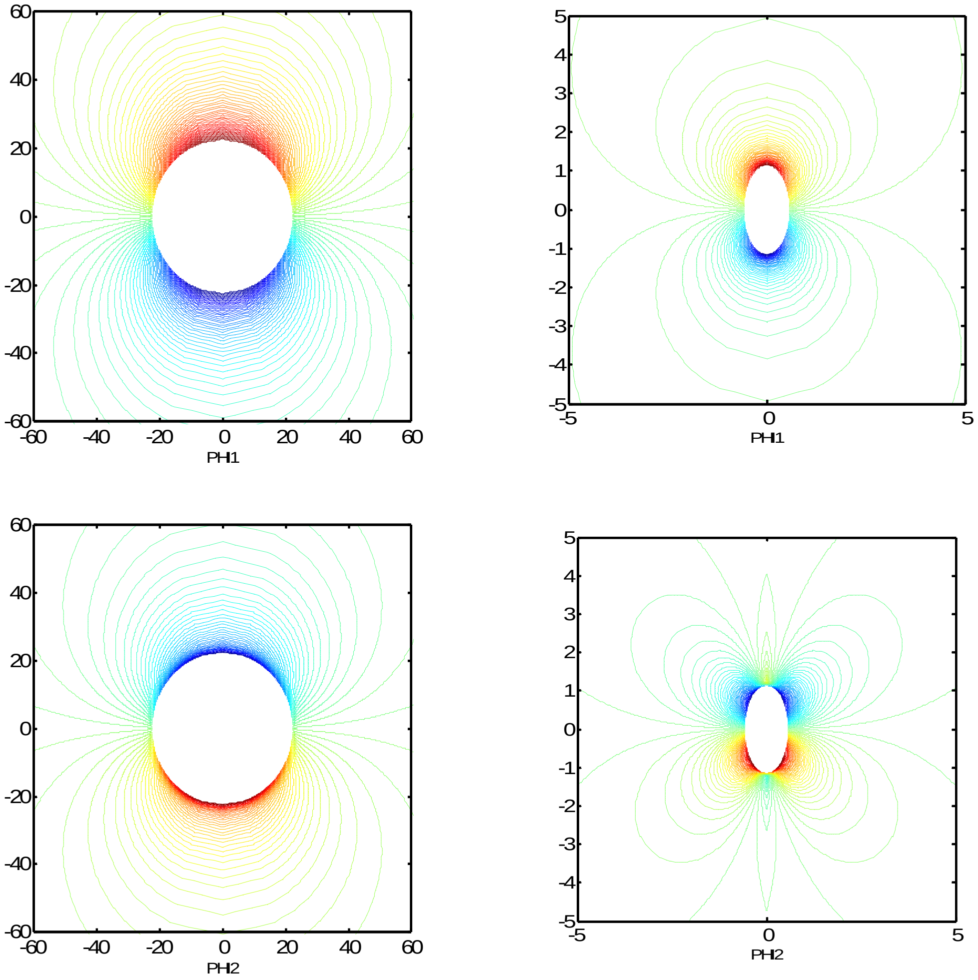
Prolate spheroids (cigars)



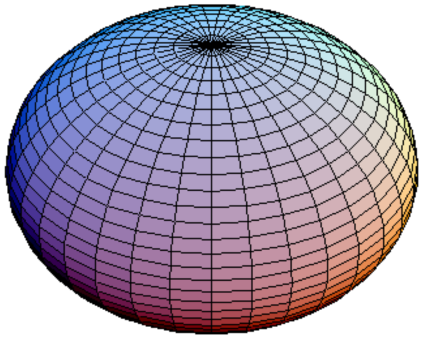
Prolate spheroids (cigars)

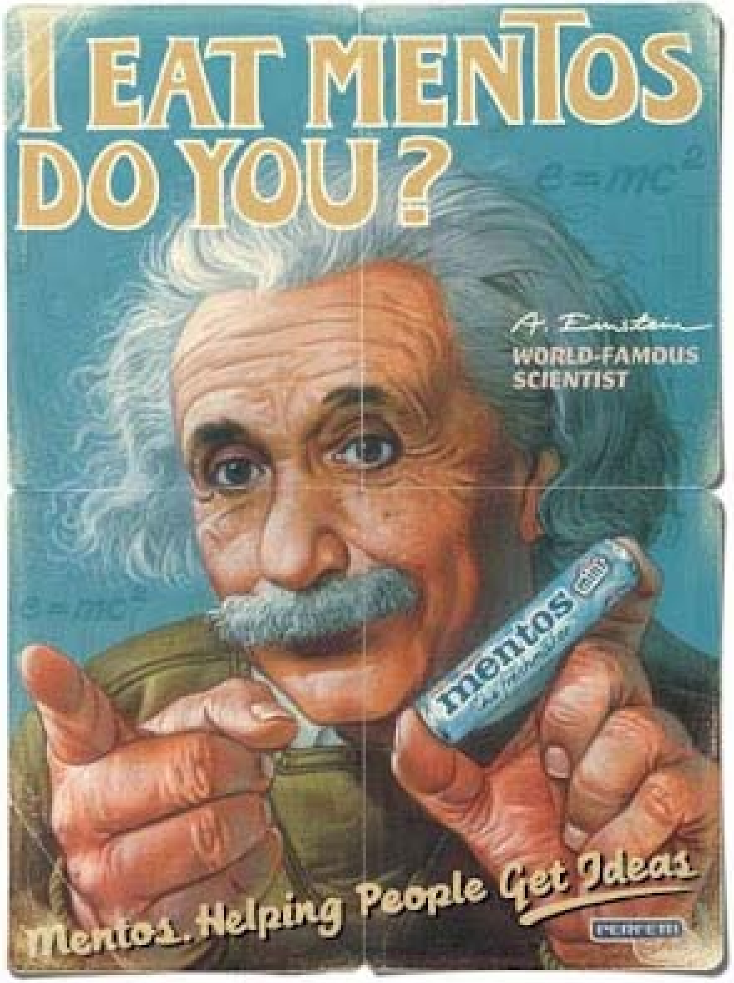


electrochemical potential counterions

electrochemical potential co-ions

Oblate spheroids (mentos)





Doppler electrophoresis at **low** volume fraction
(original vol. frac. = 0.6%)