

Lecture Note #7

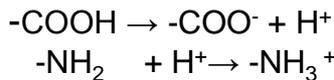
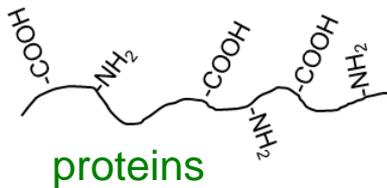
Charged Interfaces & electro- kinetic phenomena

Reading: Shaw, ch. 7

Origin of the charge at colloidal surfaces

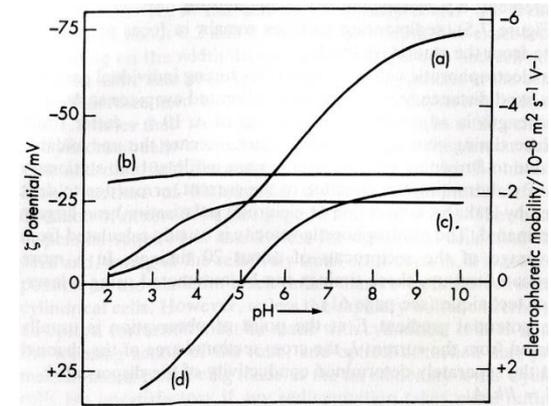
1. Ionization

- Proteins acquire their charge by ionization of $-\text{COOH}$ and NH_2 group.
- The degree of ionization, hence the charge, is pH-dependent.
- **Isoelectric point (pH)** : the pH at which the net charge is zero
- Experimentally measured **electrophoretic mobility** can provide information on the sign and magnitude of the surface charge



Isoelectric point (pH)

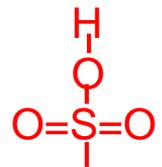
Myoglobin	7.0
Gliadin	
β -Lactoglobulin	5.2
Ovalbumin	4.55
Haemoglobin (horse)	6.9
Serum albumin (horse)	4.8
Serum globulin (horse)	
Fibrinogen (bovine)	5.2
Myosin	5.4
Bushy stunt virus	4.1



- a) HC oil droplet, b) Sulfonated PS
 c) Arabic acid (carboxylated polymer),
 d) Serum albumin adsorbed on to oil droplets

2. Ion adsorption

- Unequal adsorption of (+) and (-) ions at colloid surfaces form the bulk solution.
- Ions may be electrolytes, the ubiquitous H^+ and OH^- present in the solution.
- * (+) ions are usually small and so more hydrated than (-) ions.
- * (-) ions are less hydrated and easily polarized.
- Larger hydrated (+) ions have a smaller adsorption tendency: weaker electrostatic interaction with the surface.
- Surfaces in contact with aqueous media are more often (-)ly charged than (+)ly charged.



Sulfonic acid

- Hydrocarbon oil droplets and even air bubbles in aqueous media are (-)ly charged, which can be explained in terms of **Gibbs adsorption** at the interface:
 - The smaller (+) ions usually have a more negative adsorption at the interface than (-) ions.
 - (-) ions dislike to be at the interface than (+) ions do.
 - $\gamma \uparrow$ by addition of NaCl in water has the same origin.

ex: μ (oil droplet) = $-6 \times 10^{-8} \text{ m}^2/\text{V.s}$ vs. μ (Cl^- ion) = $-7.8 \times 10^{-8} \text{ m}^2/\text{V.s}$

Electrophoresis: $F = F_{\text{elec}} - F_{\text{fric}} = 0$ at equilibrium $\rightarrow qE = fv_d = 6\pi\eta av_d$
 mobility $\mu \equiv v_d/E = q/6\pi\eta a$

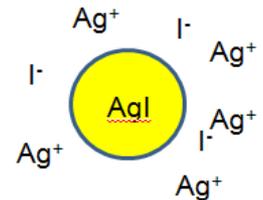
- Similar μ values mean that the oil droplet has a very large surface charge.

3. Ion dissolution

- Ionic substances can acquire a surface charge by unequal dissolution of (+) and (-) ions.

Ex: $\text{AgI}(s) \leftrightarrow \text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq})$; $K_{\text{sp}} = [\text{Ag}^+][\text{I}^-] \sim 10^{-16}$ at RT.

- Zero point of charge** is achieved at $\text{pAg} = 5.5 \rightarrow [\text{Ag}^+] = 3.16 \times 10^{-6} \text{ M}$
- The smaller Ag^+ ion is less strongly bound than I^- ion in $\text{AgI}(s)$ and so it is mobile.
- The smaller ion has a stronger tendency of solvation (hydration) than a larger ion.



$\text{Ag}^+(s) \rightarrow \text{Ag}^+(\text{aq}); \Delta G_{\text{Ag}}$ and $\text{I}^-(s) \rightarrow \text{I}^-(\text{aq}); \Delta G_{\text{I}} > \Delta G_{\text{Ag}}$ (more negative).

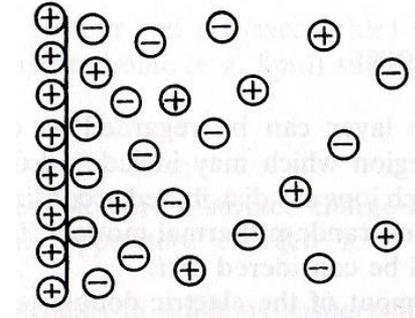
- Additionally added Ag^+ or I^- ions can modify the surface charge by via adsorption.
 - Thus, Ag^+ or I^- is called the **potential-determining ion**.

- H^+ and OH^- ions are the potential-determining ions for hydrous metal oxide sols.

- $-\text{M}-\text{OH} + \text{H}^+ \rightarrow -\text{M}-\text{OH}_2^+$
- $-\text{M}-\text{OH} + \text{OH}^- \rightarrow -\text{M}-\text{O}^- + \text{H}_2\text{O}$

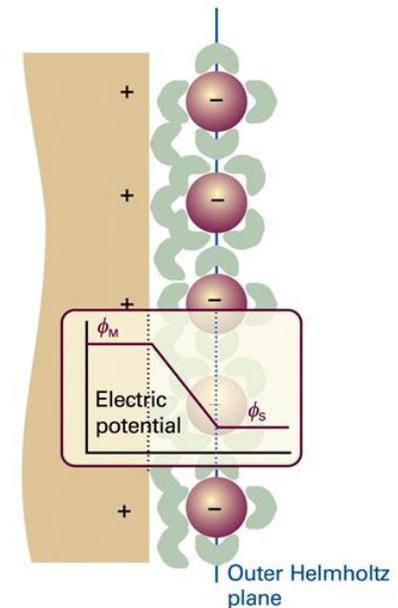
Diffuse (electrical) double layer

- Electrolytes present in the solution.
- Electrical neutrality.
- Coions and counter ions
- Coions are repelled and counter-ions are attracted by the surface charges.
- How are these ions distributed near the charged surface ?



Helmholtz model

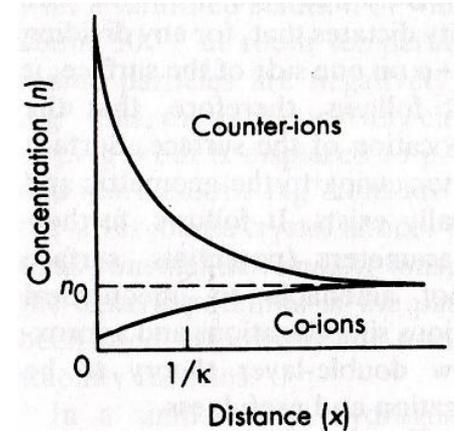
- Simplest model but it does not accurately represent the actual double layer.
- **Inner** Helmholtz plane: charged surface
- **Outer** Helmholtz plane: fixed distance from the surface equal to the **radius of a solvated counter-ion**.
- Inner region: only solvent molecules present.
- Outside OHP: random distribution of both ions.
- Electrical potential variation as show in the right figure.



Gouy-Chapman model

Assumptions

1. Uniformly charged flat surface of infinite extent.
2. Ions in the diffuse layer are **point charges**.
3. Symmetrical ions of z^+z^- type.



Boltzmann distribution law.

$$n_+ = n_0 \exp\left[\frac{-ze\psi}{kT}\right] \quad n_- = n_0 \exp\left[\frac{+ze\psi}{kT}\right]$$

$$\rho = ze(n_+ - n_-) = zen_0 \left(\exp\left[\frac{-ze\psi}{kT}\right] - \exp\left[\frac{+ze\psi}{kT}\right] \right) = -2zen_0 \sinh\frac{ze\psi}{kT}$$

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon}$$

$$\frac{d^2\psi}{dx^2} = \frac{2zen_0}{\epsilon} \sinh\frac{ze\psi}{kT}$$

Poisson-Boltzmann equation

Boundary conditions: $\psi(0) = \psi_0$ at the flat surface and $d\psi/dx = 0$ at $x = \infty$.

$$\psi = \frac{2kT}{ze} \ln\left(\frac{1 + \gamma \exp[-\kappa x]}{1 - \gamma \exp[-\kappa x]}\right) \quad \gamma = \frac{\exp[ze\psi_0 / 2kT] - 1}{\exp[ze\psi_0 / 2kT] + 1}$$

$$\kappa = \left(\frac{2e^2 n_0 z^2}{\epsilon kT}\right)^{1/2} = \left(\frac{2e^2 N_A cz^2}{\epsilon kT}\right)^{1/2} = \left(\frac{2F^2 cz^2}{\epsilon RT}\right)^{1/2}$$

$1/\kappa$ = Debye screening = avg. EDL (shielding) length thickness

Debye-Hückel approximation

If $ze\psi_0/2kT \ll 1$ ($kT/e = 25.6$ mV at 25°C)

$$n_+ = n_0 \exp\left[\frac{-ze\psi}{kT}\right] = n_0(1 - ze\psi/kT)$$

$$n_- = n_0 \exp\left[\frac{+ze\psi}{kT}\right] = n_0(1 + ze\psi/kT)$$

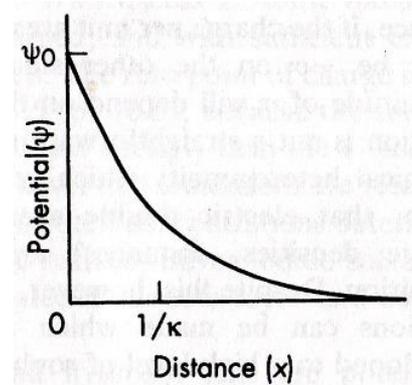
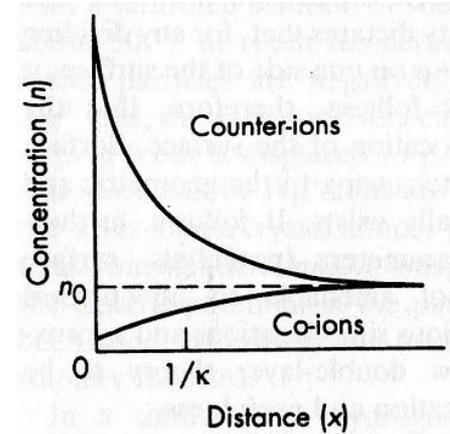
$$\rho = ze(n_+ - n_-) = -2zen_0 \frac{ze\psi}{kT}$$

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho}{\epsilon} = (2n_0 z^2 e^2 / \epsilon kT) \psi = \kappa^2 \psi$$

$$\frac{d^2 \psi}{dx^2} - \kappa^2 \psi = 0 \rightarrow \psi = \psi_0 \exp[-\kappa x]$$

- $\psi = \psi_0 \exp(\kappa x)$ was discarded because of $d\psi/dx = 0$ at $x = \infty$.

$$\sigma_0 = - \int_0^\infty \rho dx \rightarrow \sigma_0 = \epsilon \kappa \psi_0$$



Surface charge vs. surface potential

$$\sigma_0 = \epsilon \kappa \psi_0$$

- Meaning of $1/\kappa$: thick of diffuse double layer.
- ψ_0 determined by σ_0 and κ or σ_0 determined by ψ_0 and κ

Two cases

1) ψ_0 fixed and σ_0 adjusted:

- When the surface charge is due to adsorption of potential-determining ion. ex: AgI sol.
→ ψ_0 is determined by the concentration of Ag^+ (and I^-) ions in solution.
- Addition of inert electrolyte increases κ and results in more adsorption of ion to keep ψ_0 approximately constant.

2) σ_0 fixed and ψ_0 adjusted:

- The charge density at an ionogenic surface remains constant upon adding an inert electrolyte and ψ_0 decreases.
ex: protein solution

For a symmetrical electrolyte at 25 °C

$$\kappa = 0.329 \times 10^{10} \left(\frac{cz^2}{\text{mol dm}^{-3}} \right)^{\frac{1}{2}} \text{ m}^{-1}$$

$\kappa \sim 1 \text{ nm}$ for $c = 0.1 \text{ M}$ and
 $\kappa \sim 10 \text{ nm}$ for $c = 10^{-3} \text{ M}$
of 1:1 electrolyte

Gouy-Chapman model for spherical interface

$$\nabla^2 \psi = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \frac{2ze n_0}{\epsilon} \sinh \frac{ze\psi}{kT} \quad (7.11)$$

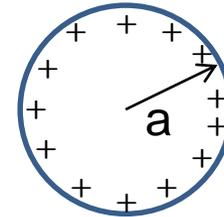
within Debye-Hückel approximation

$$\nabla^2 \psi = \kappa^2 \psi$$

Boundary conditions

$$\psi = 0, \quad d\psi/dr = 0 \quad \text{at } r = \infty,$$

$$\psi = \psi_0 \frac{a}{r} \exp[-\kappa(r - a)]$$



- Debye-Hückel approximation ($ze\psi \ll \sim 25 \text{ meV}$) is often not a good one for colloid and surface phenomena. Unapproximated, numerical solution to eq.(7.11) can be computed.

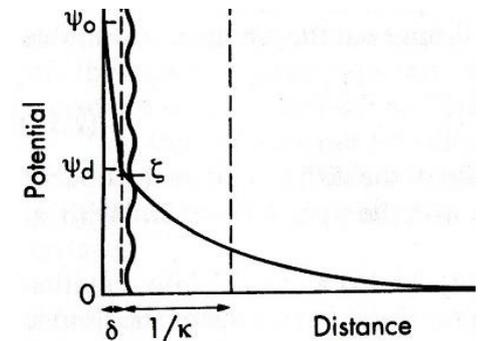
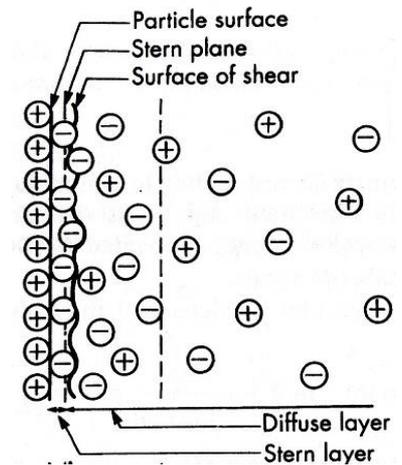
Stern model

Modification of the Gouy-Chapman model by considering

1. Finite size of ion: ions cannot approach the surface (**Stern plane**) within the radius of hydrated ion.
2. Specific ion adsorption in the Stern layer is included.
3. EDL is divided into two parts: **inner part** + **diffuse DL**, the boundary of which is the **Stern plane**.
4. **Surface of shear** is located outside of the Stern plane because of the hydrated ions
5. The potential at the shear plane is called **electrokinetic** or **zeta (ζ) potential**, which can be measured experimentally.

Inner part of EDL(Stern layer)

- Thickness of $\delta \sim 5 \text{ \AA}$
- Specifically adsorbed ions may be present.
- Oriented solvent molecules in the Stern layer has a smaller $\epsilon'(\sim 5 - 10) < \epsilon (= 78.5 \text{ for H}_2\text{O})$ due to **mutual depolarization**.



Specific ion adsorption

- Counter-ion adsorption in Stern plane
- $I(\text{bulk}) + S(\text{surf}) \leftrightarrow I(\text{surf}) + S(\text{bulk})$; solvent = 1, ion = 2

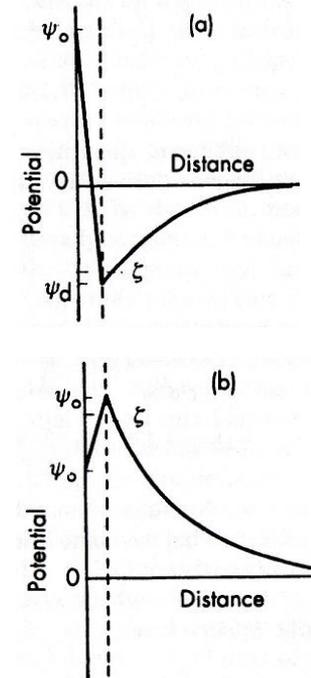
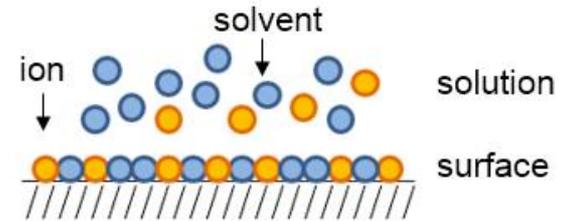
$$K' = a_2^s a_1^b / a_1^s a_2^b$$

- Assuming a 2D ideal solution for the adsorbed layer
- $a_i \sim c_i = n x_i$; n = total moles/unit surface area, x_i = mole fraction
- $a_2^s / a_1^s = x_2^s / x_1^s = x_2^s / (1 - x_2^s)$
- $K' a_2^b / a_1^b = a_1^s / a_2^s = x_2^s / (1 - x_2^s)$
- Solving for x_2^s , $x_2^s = K' (a_2^b / a_1^b) / \{1 + K' (a_2^b / a_1^b)\} = 1 / \{1 + (a_1^b / K' a_2^b)\}$
- Since $x_2^s + x_1^s = 1$, $x_2^s = \theta$ (coverage).
- Letting $K' / a_1^b = K$ (a new constant), $\theta = K a_2^b / (1 + K a_2^b)$.
- This is one form of the **Langmuir adsorption isotherm**.

cf: for gas adsorption $\theta = Kp / (1 + Kp)$

- $\Delta G^0 = -RT \ln K$
- $\Delta G^0 = \Delta H^0 - T\Delta S^0 \sim \Delta H^0 = \Delta E^0$ (no PV term involved)
 $= N_A (ze \psi_d + \Phi) \rightarrow K = \exp\{-N_A(ze \psi_d + \Phi)/RT\}$
 (Φ = van der Waals term)
- The electrical interaction is the dominant term at RT.
- Let σ_1 is the surface charge density due to specifically adsorbed ions.
- $x_2^s = \sigma_1 / \sigma_m = 1 / \{1 + (a_1^b / K a_2^b)\} \sim 1 / \{1 + (c_1^b / K c_2^b)\}$
- $c_1^b / c_2^b = (1/V_m) / (n_0/N_A)$, where V_m is the molar volume of solvent.

$$\sigma_0 = \sigma_m / [1 + (N_A/V_m n_0) \exp\{(ze\psi_d + \Phi)/kT\}]$$



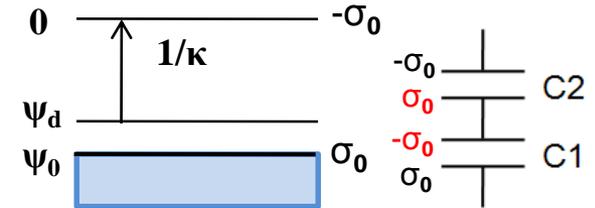
- Reversal of charge due to the adsorption of surface-active or polyvalent counter-ions.
- Adsorption of surface-active co-ions.

Capacitance of EDL

- Usually counter-ion adsorption is dominant.
- Adsorption of polyvalent ions can result in charge reversal.

I. If there is no specifically adsorbed ions

$$C_1 = \frac{\sigma_0}{\psi_0 - \psi_d} \quad \text{and} \quad C_2 = \frac{\sigma_0}{\psi_d} \quad \rightarrow \quad \psi_d = \frac{C_1 \psi_0}{C_1 + C_2}$$



II. If specifically adsorbed ions are present

$\sigma_0 + \sigma_1 + \sigma_2 = 0$; electrical neutrality

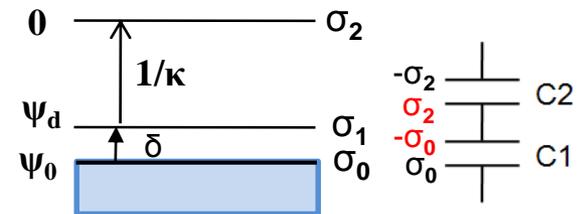
$$\sigma_0 = \frac{\epsilon'}{\delta} (\psi_0 - \psi_d), \quad \sigma_1 = \frac{\sigma_m}{1 + \frac{N_A}{n_0 V_m} \exp\left[\frac{ze\psi_d + \phi}{kT}\right]}$$

$$\sigma_0 + \sigma_1 + \sigma_2 =$$

$$\frac{\epsilon'}{\delta} (\psi_0 - \psi_d) + \frac{\sigma_m}{1 + \frac{N_A}{n_0 V_m} \exp\left[\frac{ze\psi_d + \phi}{kT}\right]} - (8n_0\epsilon kT)^{1/2} \sinh\frac{ze\psi_d}{2kT} = 0$$

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2},$$

$$C_2 = \frac{\sigma_2}{\psi_d} = \epsilon\kappa = 2.28 \left(\frac{cz^2}{\text{mol dm}^{-3}} \right)^{1/2} \text{ F m}^{-2} \quad \text{for aqueous electrolyte at } 25^\circ\text{C} \quad (1)$$

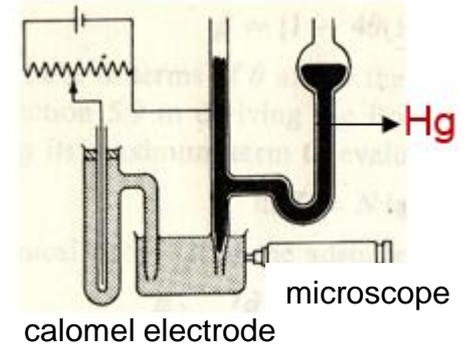


- For Hg- aqueous electrolyte interfaces C can be measured from electrocapillary measurements and for AgI- aqueous electrolyte interfaces from potentiometric measurements.
- C_2 can be calculated from the eq.(1) above.
- Then, from $C_1 = \epsilon'/\delta$ (Stern layer capacitance) can be obtained.
- For the AgI- aqueous electrolyte interface $C_1 \approx 0.1 - 0.2 \text{ F m}^{-2}$.
- Taking $\delta = 5 \text{ \AA}$, one gets $\epsilon' = 5 - 10$ ($\ll \epsilon = 78.5$ for H_2O at RT) \rightarrow ordering of H_2O in the Stern layer.

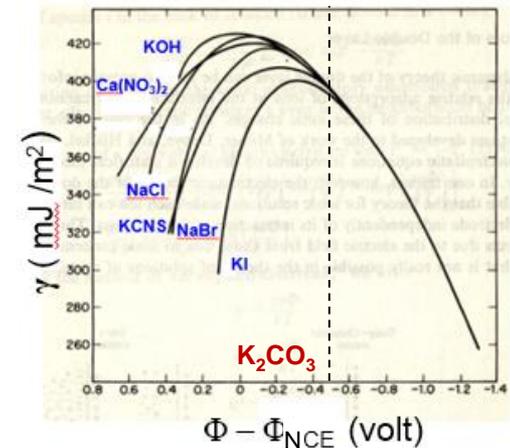
Electrocapilarity

Lippmann apparatus

- **Ideally non-polarizable** normal calomel electrode (reference)
- Hg electrode in contact with nonreactive salt solution (ideally polarizable electrode).
- When a potential Φ is to the Hg electrode, charge accumulates at its surface.
- Simultaneously, the γ of Hg changes to cause a shift of the meniscus, which is observed with a microscope.
- $dG = \gamma dA + \Phi dQ$ at fixed T,P, and μ .
- Similarly to the Gibbs-Duhem equation,
 $A d\gamma + Q d\Phi = 0 \rightarrow (\partial\gamma / \partial\Phi)_{T,P,\mu} = - Q/A = \sigma$
- The capacitance of the EDL is
 $C = (\partial Q / \partial\Phi) / A = - (\partial^2\gamma / \partial\Phi^2)$; constant \rightarrow parabolic $\gamma - \Phi$ curve.
- γ is maximum when the surface is not charged.
- For an inert electrolyte such as K_2CO_3 , γ_{\max} occurs at $\Phi - \Phi_{NCE} = - 0.48$ V.
- For other electrolytes the maximum shifts due to specific ion adsorption.
Ex: - ion adsorption (OH^- , Cl^- , Br^- , CNS^- etc.) as shown in the Figure.



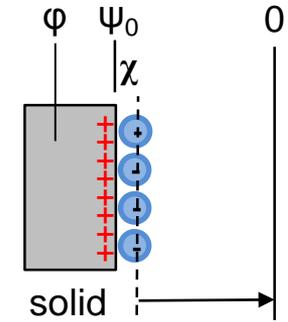
Lippmann apparatus



electrocapillary curve

Surface potentials

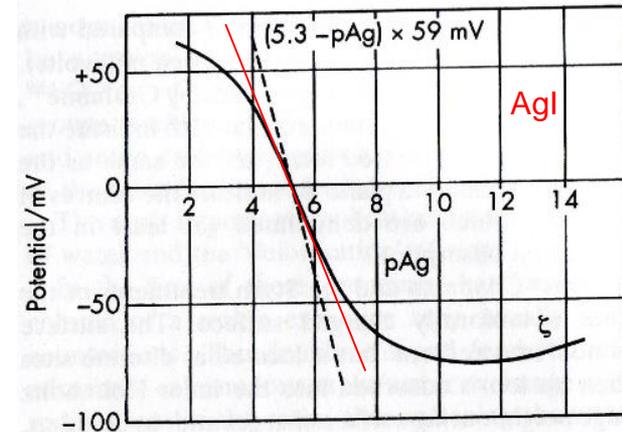
- The **measurable** electric potential difference ϕ between the solid interior and the bulk solution varies according to the Nernst equation; $E = E^\circ - RT \ln Q / \nu F$
 Ex: For a AgI-aqueous electrolyte interface
 $d\phi / d(pAg) = - 2.303 RT/F$ ($= - 59 \text{ mV at } 25 \text{ C}$)
- $\phi = \psi + \chi$, where χ is due to adsorbed ions and orientation dipolar solvent.



- Experimentally, $\left(\frac{d\zeta}{d(pAg)} \right)_{\zeta \rightarrow 0} = - 40 \text{ mV}$ at RT was found.

$$\left(\frac{d\zeta}{d(pAg)} \right)_{\zeta \rightarrow 0} = \left(\frac{d\psi_0}{d(pAg)} \right) \left(\frac{d\psi_d}{d\psi_0} \right)_{\zeta \rightarrow 0} = -59 \frac{C_1}{C_1 + C_2} \text{ mV} \quad (1)$$

- The measures C_1 and C_2 values are qualitatively consistent with the above eq.(1)
- The **Stern layer model** and the **assumptions** made are **qualitatively correct**.



Electrokinetic Phenomena

Relative motion between charged surface and diffuse double layer

1. Electrophoresis: $\mathcal{E} \rightarrow$ charge particle movement.
2. Electro-osmosis: $\mathcal{E} \rightarrow$ DL layer movement against fixed surface charge.
3. Streaming potential: DL layer movement $\rightarrow \mathcal{E}$ generation.
4. Sedimentation potential: charge particle movement $\rightarrow \mathcal{E}$ generation.

- All arising from the relative movement of particle with respect to the liquid.
- \mathcal{E} field \rightarrow relative motion: Electrophoresis, electro-osmosis
- relative motion $\rightarrow \mathcal{E}$ field: Streaming potential, sedimentation potential

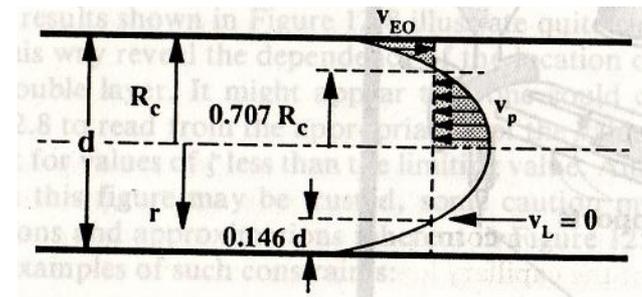
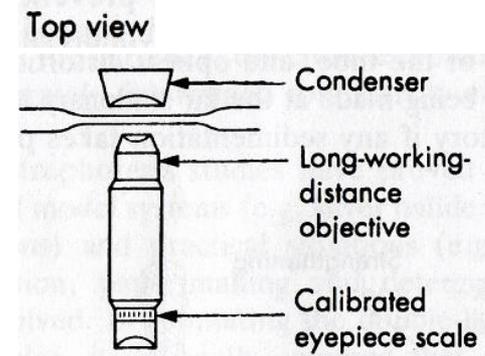
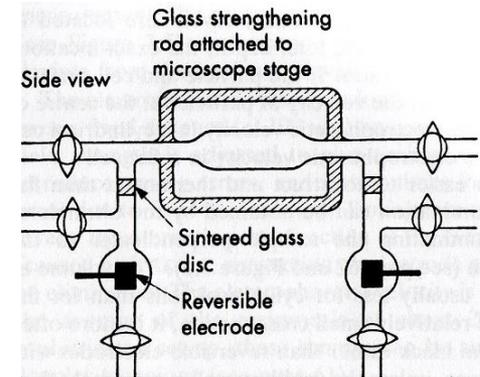
Electrophoresis

1. Particle (microscope) electrophoresis

- Microscopically visible particles or droplets.
- Adequate selection of electrode material to avoid gas evolution due to electrochemical red-ox reactions.
Ex: **reversible electrodes**: Cu/CuSO₄, Ag/AgCl
- Simultaneous electro-osmotic and return flow of liquid.
- Laminar flow: **parabolic velocity distribution**
- Observation has to be made at the stationary levels located at $r = 0.707 r_0$ for a cylindrical cell and $x = 0.3 t$ for a flat cell.

$$\frac{dV}{dt} = \frac{(p_1^2 - p_2^2)\pi r^4}{16l\eta p_0}$$

Poisellie's formula



2. Tiselius moving boundary electrophoresis

- Movement of a boundary formed between a colloidal solution and a pure dispersion medium is observed by an optical method (Schlieren technique).
- Electrophoretic mobility is measured.
- Widely applied for separating, identifying, and estimating dissolved macromolecules, particularly proteins.

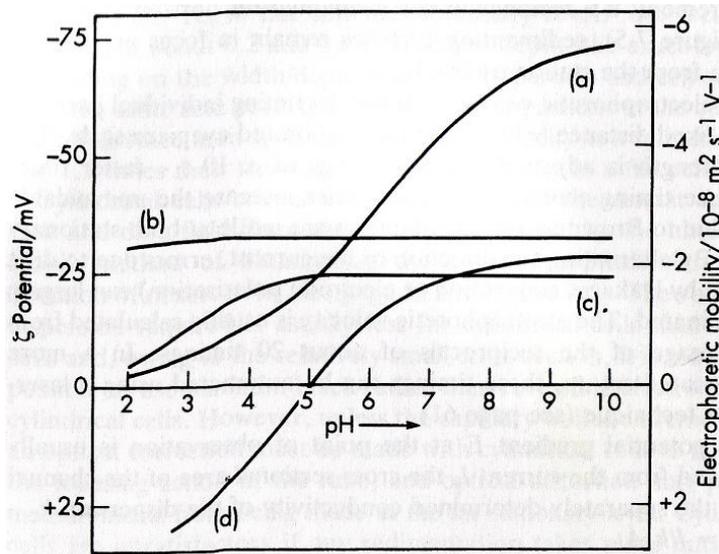
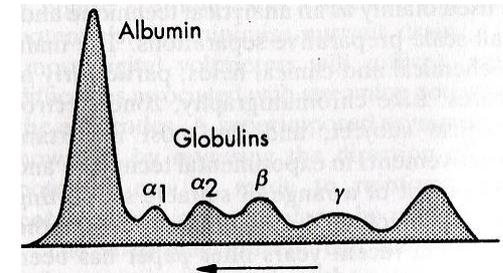
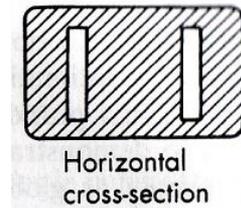
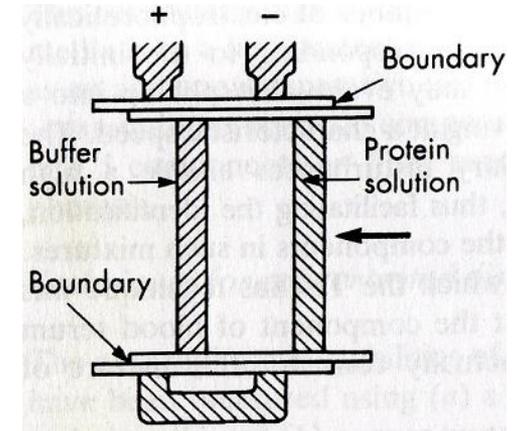


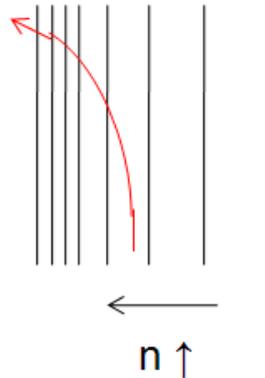
Figure 7.7 Zeta potentials (calculated from electrophoretic mobility data) relating to particles of different ionogenic character plotted as a function of pH in acetate-veronal buffer at constant ionic strength of 0.05 mol dm^{-3} . (a) Hydrocarbon oil droplets. (b) Sulphonated polystyrene latex particles. (c) Arabic acid (carboxylated polymer) adsorbed on to oil droplets. (d) Serum albumin adsorbed on to oil droplets



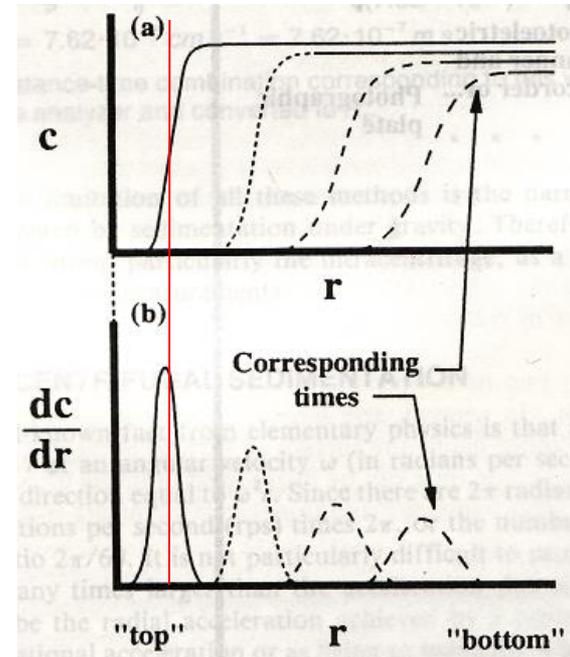
Electrophoretic diagram (ascending) for human blood serum

Schlieren technique

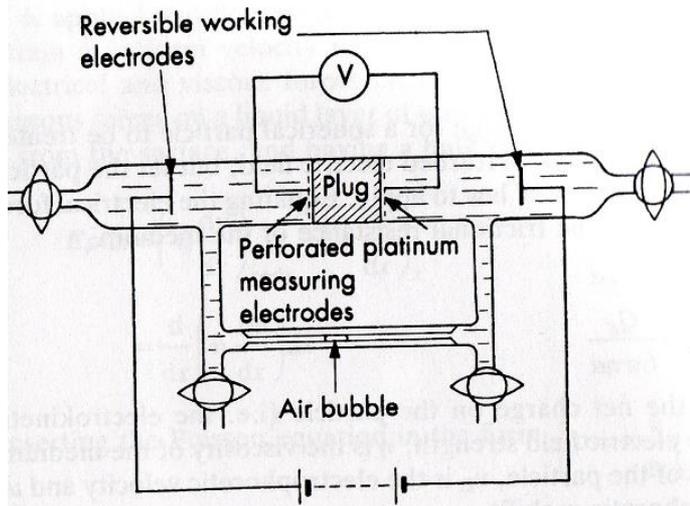
- Used for ultracentrifuge and moving boundary electrophoresis
- $n \sim n_0 + a[c]$: refractive index.
- light bends (refracts) when propagating in a medium of non-uniform concentration.
- Light deviate most where dn/dr is maximum.
- Boundary appears as a peak.



3. Zone electrophoresis



Electro-osmosis and Streaming potential measurements



An electro-osmosis apparatus⁹³

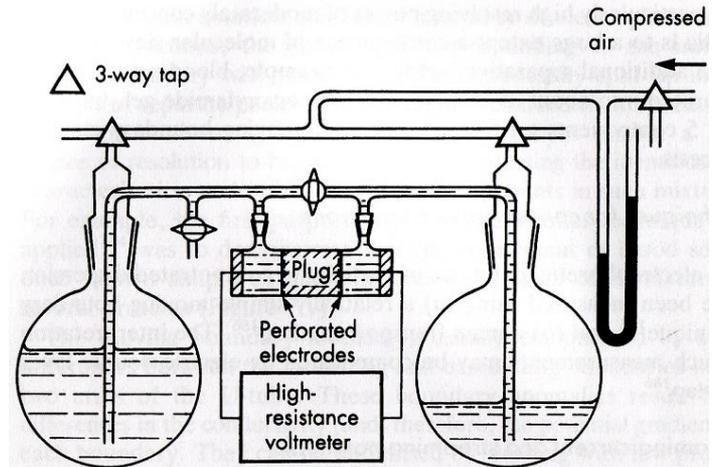


Figure 7.10 A streaming potential apparatus⁹³ (By courtesy of Academic Press)

Theory of Electrokinetic Phenomena

1. The Hückel equation (small κa)

$$\kappa a \ll 1$$

$$Q_E E = 6\pi\eta v_E a$$

Electrophoretic mobility u_E : $u_E = \frac{v_E}{E} = \frac{Q_E}{6\pi\eta a}$

$$\zeta = \frac{Q_E}{4\pi\epsilon a} - \frac{Q_E}{4\pi\epsilon\left(a + \frac{1}{\kappa}\right)} = \frac{Q_E}{4\pi\epsilon a(1 + \kappa a)} \sim \frac{Q_E}{4\pi\epsilon a}$$

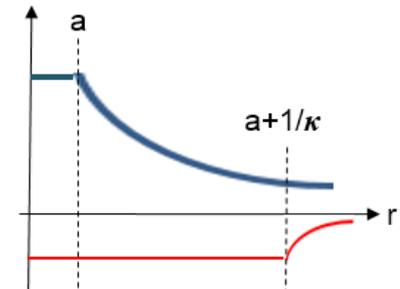
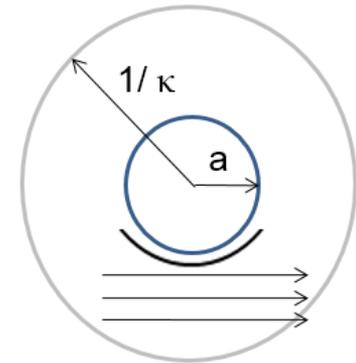
$$u_E = \frac{\zeta\epsilon}{1.5\eta}$$

- The ζ potential can be estimated from the measured u_E .
- If a is measured by other method, Q can be obtained.

For a symmetrical electrolyte at 25 °C

$$\kappa = 0.329 \times 10^{10} \left(\frac{cz^2}{\text{mol dm}^{-3}} \right)^{\frac{1}{2}} \text{ m}^{-1}$$

$\kappa \sim 1 \text{ nm}$ for $c = 0.1 \text{ M}$ and
 $\kappa \sim 10 \text{ nm}$ for $c = 10^{-3} \text{ M}$
of 1:1 electrolyte



2. The Smoluchowski equation (large κa)

$\kappa a \ll 1$ usually corresponds to a nearly flat surface.

$\mathbf{F}_{\text{elec}} = -\mathbf{F}_{\text{vis}}$: steady flow

- Consider the force acting on a slab of thickness dx at x

$$E\rho dx = \left(\eta \frac{dv}{dx} \right)_{x+dx} - \left(\eta \frac{dv}{dx} \right)_x = \frac{d}{dx} \left(\eta \frac{dv}{dx} \right) dx$$

Inserting the Poisson equation $\rho = -\frac{d}{dx} \left(\epsilon \frac{d\psi}{dx} \right)$

$-E\epsilon\psi'' dx = \eta v'' dx$. Integrating, this eq.

Since E is the externally applied electric field, which is constant.

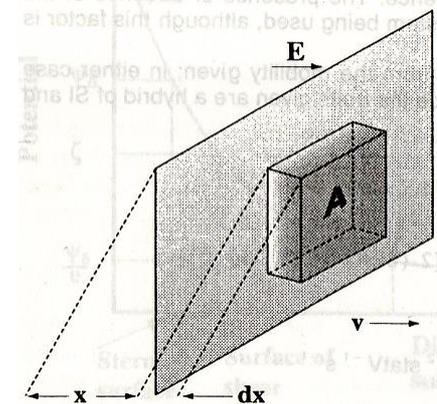
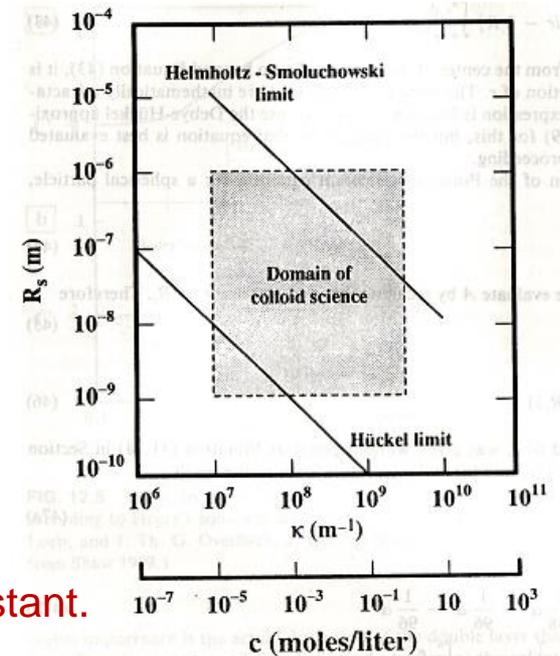
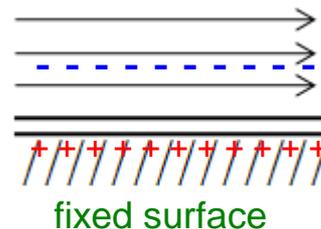
$$-E\epsilon \frac{d\psi}{dx} = \eta \frac{dv}{dx} + \text{constant} \quad \begin{array}{l} d\psi/dx = 0 \text{ and } dv/dx = 0 \\ \text{at } x = \infty \rightarrow \text{constant} = 0. \end{array}$$

$$-E\epsilon\psi = \eta v + \text{constant} \quad \begin{array}{l} \psi = 0, v = 0 \text{ at } x = \infty \\ \rightarrow \text{constant} = 0. \end{array}$$

$\psi = \zeta, v = -v_E$ at the surface of shear

$$E\epsilon\zeta = \eta v_E$$

$$u_E = \frac{v_E}{E} = \frac{\zeta\epsilon}{\eta}$$



Deviation from the two limits

The Henry equation

Assume that

1. $\mathcal{E} = \mathcal{E}(\text{external}) + \mathcal{E}(\text{particle}) + \mathcal{E}(\text{DDL})$: mutual distortion neglected.
Ionic atmosphere is not distorted.
2. Debye-Hückel approximation valid:
low ψ_d (< 26 meV) limit.
3. ε and η are constant throughout the mobile part of the DL.

- **Surface and bulk conductance** affect the distribution of \mathbf{E} field near to the surface of the charged particle

$$u_E = \frac{\zeta \varepsilon}{1.5 \eta} [1 + \lambda F(\kappa a)] \quad \lambda = (k_0 - k_1) / (2k_0 + k_1)$$

k_0 : bulk conductivity
 k_1 : particle conductivity

- $F(\kappa a) = 0 \sim 1$; 0 for $\kappa a \ll 1$ and 1 for $\kappa a \gg 1$
- For non-conducting particles, $\lambda = 1/2$ and u_E reduces to

$$u_E = \frac{\zeta \varepsilon}{1.5 \eta} f(\kappa a) \quad f(\kappa a) = 0 \sim 1.5$$

- In reality, two mutual distortion effects exist:
1) **electrophoretic retardation** and 2) **relaxation effect**

$$u = \frac{\varepsilon}{\eta} \left(\zeta + 5 R_s^3 \int_{\infty}^{R_s} \frac{\psi}{r^6} dr - 2 R_s^3 \int_{\infty}^{R_s} \frac{\psi}{r^4} dr \right) \quad (43)$$

where r is the radial distance from the center of the particle. To go beyond Equation (43), it is necessary to know ψ as a function of r . The resulting expressions are mathematically intractable unless a relatively simple expression is used for ψ . We may use the Debye-Hückel approximation given by Equation (19) for this, but the constant in that equation is best evaluated somewhat differently before proceeding.

We return to the solution of the Poisson-Boltzmann equation for a spherical particle, Equation (19), with $B = 0$:

$$\psi = \frac{A \exp(-\kappa r)}{r} \quad (44)$$

In the present development we evaluate A by recalling that $\psi = \zeta$ when $r = R_s$. Therefore

$$A = R_s \zeta \exp(\kappa R_s) \quad (45)$$

and Equation (44) becomes

$$\psi = \frac{R_s \zeta}{r} \exp[-\kappa(r - R_s)] \quad (46)$$

This equation, with ψ_0 instead of ζ , was given without proof as Equation (11.38) in Section 11.4c. Combining Equations (43) and (46) and integrating leads to the result

$$u = \frac{2 \varepsilon \zeta}{3 \eta} f(\alpha) \quad (47a)$$

where

$$f(\alpha) = \left(1 + \frac{1}{16} \alpha^2 - \frac{5}{48} \alpha^3 - \frac{1}{96} \alpha^4 - \frac{1}{96} \alpha^5 - \left[\frac{1}{8} \alpha^4 - \frac{1}{96} \alpha^6 \right] \exp(\alpha) \int_{\infty}^{\alpha} \frac{e^{-t}}{t} dt \right) \quad \text{with} \quad \alpha = \kappa R_s < 1 \quad (47b)$$

For $\kappa R_s > 1$, the function $f(\alpha)$ becomes (see Hunter 1981)

$$f(\alpha) = \left(\frac{3}{2} - \frac{9}{2} \alpha^{-1} + \frac{75}{2} \alpha^{-2} - 330 \alpha^{-3} \right) \quad (47c)$$

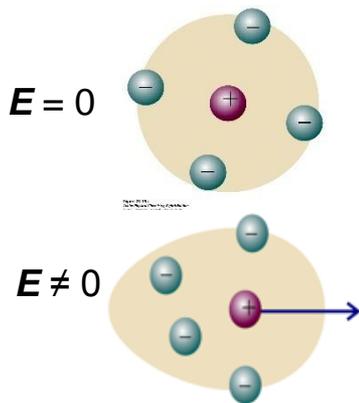
The above result (Equations (47a)–(47c)) is known as *Henry's equation*. Two specific assumptions underlying its derivation should be pointed out:

1. The ion atmosphere is undistorted by the external field.
2. The potential is low enough to justify writing $e\psi/k_B T < 1$, which is equivalent to requiring that $\psi < 25$ mV (Section 11.2b).

It should also be noted that in the limit of $\kappa R_s \rightarrow 0$, Equation (47a) reduces to the Hückel equation, and in the limit of $\kappa R_s \rightarrow \infty$, it reduces to the Helmholtz-Smoluchowski equation. Thus the general theory confirms the idea introduced in connection with the discussion of Figure 12.1, that the amount of distortion of the field surrounding the particles will be totally different in the case of large and small particles. The two values of C in Equation (40) are a direct consequence of this difference. Figure 12.5a shows how the constant C varies with κR_s (shown on a logarithmic scale) according to Henry's equation.

Deviation from Henry equation

- Electrophoretic retardation:
Ionic atmosphere moves to the opposite direction, resulting in an enhanced viscous drag.
- Relaxation: nonsymmetrical Ionic atmosphere, forcing the particle in the opposite direction.
- Surface conductivity
- $\psi_d \sim \zeta > 26 \text{ meV}$.
- Deviation occurs in the mid-range of κa and for a high counter-ion charge number.



$$e\zeta/kT = 2 \text{ in each case}$$

$$q_0 = (2e^2 N_A c z^2 / \epsilon k T)^{1/2} a$$

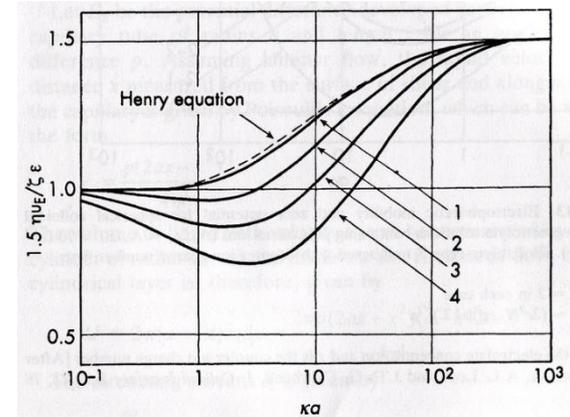


Figure 7.12 Electrophoretic mobility and zeta potential for spherical colloidal particles in 1-1 electrolyte solutions ($\Lambda_+ = \Lambda_- = 70 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). The curves refer to $e\zeta/kT = 1, 2, 3$ and 4 (i.e. $\zeta/\text{mV} = 25.6, 51.2, 76.8$ and 102.4 at 25°C) [After P.H. Wiersema, A.L. Loeb and J.Th.G. Overbeek, *J. Colloid Interface Sci.*, **22**, 78 (1966)]

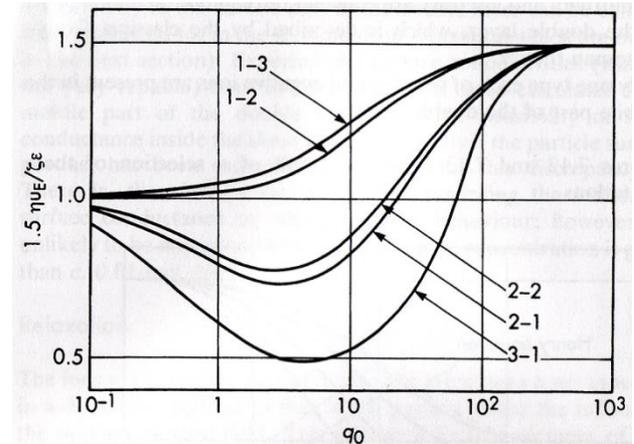


Figure 7.13 Electrophoretic mobility and zeta potential for spherical colloidal particles in electrolyte solutions containing polyvalent ions ($\Lambda_+/z_+ = \Lambda_-/z_- = 70 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). Electrolyte type is numbered with counter-ion charge number first:

Poiseuille's equation

$$v_x = \frac{p(2ax - x^2)}{4\eta l}$$

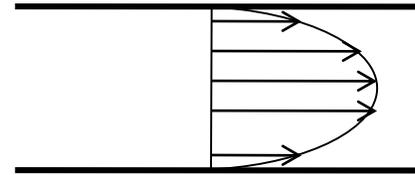
$$\begin{aligned} dJ &= 2\pi(a - x)v_x dx \\ &= \frac{2\pi p(2ax - x^2)(a - x)dx}{4\eta l} \end{aligned}$$

streaming current

$$I_s = \int_0^a \rho dJ = \frac{\pi \epsilon p a^2}{\eta l} \int_0^a x \frac{d^2 \psi}{dx^2} dx$$

$$\psi = \zeta \text{ at } x = 0 \text{ and } \psi = 0,$$

$$d\psi/dx = 0 \text{ at } x = a$$



$$I_s = \frac{\epsilon p A \zeta}{\eta l}$$

$$E_s = \frac{I_s l}{k_0 A}$$

$$E_s = \frac{\epsilon p \zeta}{\eta k_0}$$

$$E_s = \frac{\epsilon p \zeta}{\eta \left(k_0 + \frac{2k_s}{a} \right)}$$