

Electrokinetic Phenomena

Frank Simon

Leibniz Institute of Polymer Research Dresden
Hohe Straße 6, D-01069 Dresden, Germany, frsimon@ipfdd.de

In the year 1803, the German medical doctor and librarian Ferdinand Friedrich von Reuss^[a] (1778^[b]-1852) was invited by M.N. Muraviev, the curator of Lomonossow's Moscow University to hold the chair of chemistry at the Physical-Mathematical Faculty. Inspired by Alessandro Volta's work on electricity, Reuss carried out some electrolysis experiments in a beaker, but also on the banks of the Moscow river. In order to study the influence of barrier layers on electrolysis, he applied an electric voltage (provided by a Volta column) to sand and clay layers and observed the movement of water through the barrier layers. In 1809, Reuss' studies were published (with the date 1808) in the journal *Mémoires de la Société Impériale des Naturalistes de l'Université Impériale de Moscou* [1]. The 200 years old publication describes the discovery of the two electrokinetic phenomena electro-osmosis and electrophoresis.

Definition of electrokinetics

Electrokinetics are the sciences of the generation of an electric current by moving a non-conductor and the movement of non-conductors caused by an electric field.

Electrokinetic phenomena are observed on the interface of two interacting phases, such as a solid, which is in contact with a liquid. An essential requirement for the observation of electrokinetic phenomena is the formation of an *electrochemical double layer* at the interface. The *electrochemical double layer* can be considered as space charge, and external electrical fields cause a movement of the fluid phase(s). Materials having a large specific surface, such as colloidal particles, fine-porous solids, capillaries etc. are favorites to study their electrokinetic properties.

Well-known electrokinetic phenomena are

- *Electrophoresis*, movement of electrically charged particles (solid, liquid or gaseous) in an electric field, with is filled with a liquid as second phase.
- *Sedimentation potential* (reverse electrophoresis), generation of an electrical potential by the movement of a solid or liquid particles in a liquid caused by e.g. particles' sedimentation or centrifugation.
- *Electro-osmosis*, movement of a liquid along a solid or liquid surface driven by an electric field.
- *Streaming potential* and *streaming current* (reverse electro-osmosis), generation of an electrical potential and current by the movement of a liquid along a solid or liquid surface.
- *Electro-capillarity*, changing the surface tension of a liquid during electrical charging.
- *Electro-acoustic effects*, alternating movement of colloidal particles, caused by applying ultrasonic vibrations or an electrical field generates an electric potential or alternating shock waves (electro-acoustic wave).

^a Reuss is the English transcription of the German aristocracy name *von Reuß*. During Reuss' stay in Moscow his name of was translated and used in Russian language *Fedor Fedorovich Reuss* (Федор Федорович Рейсс). Sometimes, the Russian was transcribed as *Reiss*.

^b Sometimes, Feb. 18, 1788 is published as Reuss' birthday.

Electrochemical double layer and double layer models

An insoluble solid, which is dipped in an aqueous electrolyte solution forms a solid/liquid interface. The interface is characterized by a different chemical potential μ of the two interacting phases and a charge distribution, which is different from the bulk of the two phases. Free-ly moveable charge carriers (e.g. solvated ions) can be adsorbed on the solid surface. There, they can remain or initiate surface reactions, such as the dissociation of Brønsted-acid surface groups, the partly desorption of surface-bonded ions and the substitution of ions having a higher or lower number of charges (isomorphic substitution). In presence of an organic liquid, which does not contain ions, electrons can be transferred from the solid to the liquid phase (or vice versa) and charge-up the interface.

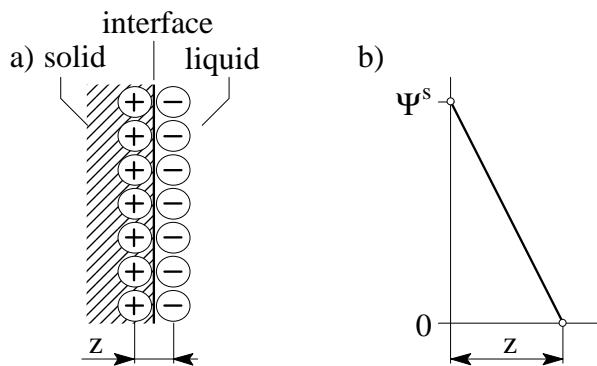


Fig. 1: Model of the electrochemical double layer according to Helmholtz's condenser model (a) and the potential Ψ in dependence on the distance z , $\Psi = \Psi(z)$ (b); Ψ^s = surface potential.

From the excess of charges (regarded to the zero charge or charge neutrality of the bulk phase) at the solid/liquid interface an electric potential Ψ arises. The excess of charges at the interface is called *electrochemical double layer (DL)*. In 1859, the *DL* was postulated by Quincke who discovered the streaming potential as well as streaming current and wanted to explain his and Reuss' electrokinetic phenomena [2]. The first *DL* model was developed by Helmholtz [3]. Helmholtz transferred his findings of the behavior of a simple plate condenser to the solid/liquid interface (Fig. 1, eq. 1).

$$\sigma^s = -\frac{\Psi^s \cdot \epsilon_0 \cdot \epsilon_r}{z} \quad (1)$$

(with σ^s = surface charge density, Ψ^s = surface potential, z = distance, ϵ_0 = permittivity of the free space, ϵ_r = dielectric number)

The model by Helmholtz does not consider the mobility of the ions solved in the liquid phase. They can be attracted by the solid surface, but this directed force is simultaneously disturbed by the non-directed Brown's molecular movement. According to Gouy and Chapman a cloud of ions is situated near the solid surface (Fig. 2) [4, 5]. The charge distribution in this ion cloud is controlled by the attraction of the ions by the solid surface. The attraction lowers with increasing the distance z , and the influence of the Brown's molecular movement. In contrast to Helmholtz's assumption the ions in the cloud are not highly ordered. Hence, the ion cloud is called *diffuse layer (diff)*. The Poisson equation (2) describes the correlation between potential Ψ and space charge density ρ for each point in the space.

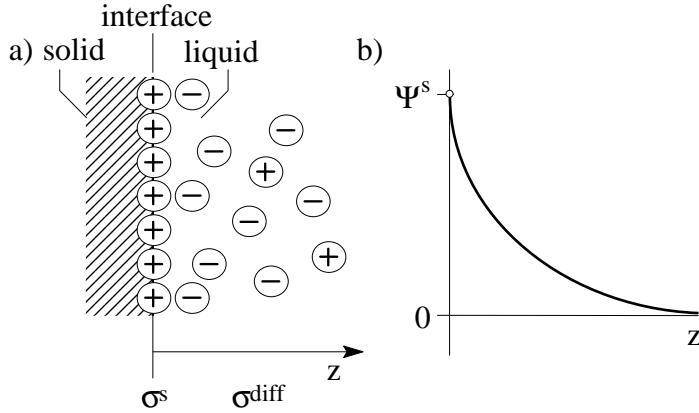


Fig. 2: Model of the electrochemical double layer according to Gouy and Chapman (a) and the potential Ψ in dependence on the distance z , $\Psi = \Psi(z)$ (b); Ψ^s = surface potential, σ^s = surface charge density, σ^{diff} = charge density of the diffuse layer.

$$\frac{d^2\Psi}{dz^2} = -\frac{\rho}{\epsilon_0 \cdot \epsilon_r} \quad (2)$$

(with Ψ = potential, z = distance, ρ = space charge density, ϵ_0 = permittivity of the free space, ϵ_r = dielectric number)

In order to get an expression describing the charge densities on the solid surface (σ^s) and the diffuse layer (σ^{diff}) equation (2) has to be integrated considering the boundary conditions that $\Psi = 0$ at $z = \infty$ (in that case $d\Psi/dz|_{z \rightarrow \infty} = 0$ and $\rho|_{z \rightarrow \infty} = 0$) and $\Psi = \Psi^s$ at $z = 0$ ^[c]. The unwieldy parameter space charge density ρ can be substituted by the concentration (c_i) of excess charge carriers situated in the diffuse layer (eq. 3)

$$\rho = F \cdot [v \cdot c_{\oplus} - v \cdot c_{\ominus}] \quad (3)$$

(with F = Faraday constant, v = valency, c_{\oplus} = concentration of cations, c_{\ominus} = concentration of anions)

If Brown's molecular movement controls the concentration of the cations and anions in the diffuse layer, their concentrations (c_i) can be expressed by the Boltzmann distributions (4a and 4b).

$$c_{\oplus} = c^{\infty} \cdot \exp\left[-\frac{z \cdot F \cdot \Psi}{R \cdot T}\right] \quad (4a)$$

$$c_{\ominus} = c^{\infty} \cdot \exp\left[-\frac{z \cdot F \cdot \Psi}{R \cdot T}\right] \quad (4b)$$

(with c^{∞} = bulk concentration of ions, z = stoichiometric number, it is the ions' valency v considering the sign of the ions' charge: $v \cdot [+1]$ for cations and $v \cdot [-1]$ for anions, Ψ = potential, R = gas constant, T = absolute temperature [K])

For monovalent ions the integration of eq. 2^[d] gives:

$$\sigma^{\text{diff}} = \sqrt{8 \cdot \epsilon_0 \cdot \epsilon_r \cdot c^{\infty} \cdot R \cdot T} \cdot \sinh\left[\frac{F \cdot \Psi^s}{2 \cdot R \cdot T}\right] \quad (5)$$

^c or $(d\Psi/dz)|_{z=0} = -\sigma^s/[\epsilon_0 \epsilon_r]$.

^d All integration steps are provided in Ref. [6].

The fundamental condition of charge neutrality requires $\sigma^{\text{diff}} = -\sigma^s$.

Equation (5) can be used to approximate the effective thickness of the electrochemical double layer. The effective thickness of the electrochemical double (d) can be defined as the z-position where the potential $\Psi = (1/e)$ ($e = \text{Euler's number}$). With the condition $\Psi = (1/e)$ equation (5) can be developed as progression with eq. (6) as the first term. For the approximation all further terms are neglected.

$$\sigma^{\text{diff}} = F \cdot \Psi \cdot \sqrt{\frac{2 \cdot \epsilon_0 \cdot \epsilon_r \cdot c^\infty}{R \cdot T}} \rightarrow \Psi = \frac{\sigma^{\text{diff}}}{T} \cdot \sqrt{\frac{R \cdot T}{2 \cdot \epsilon_0 \cdot \epsilon_r \cdot c^\infty}} \quad (6)$$

The distance d can be calculated by the solution of eq. (7), where the differential quotient $(d\Psi/dz)|_{z=0}$ can be substituted by $(-\sigma^s/[\epsilon_0 \cdot \epsilon_r]) = \sigma^{\text{diff}}/[\epsilon_0 \cdot \epsilon_r]$, the second boundary condition used to integrate eq. (2)

$$\left(\frac{d\Psi}{dz} \right)_{z=0} = \frac{\Psi}{d} \quad (7)$$

Finally, for monovalent ions we get:

$$d = \frac{1}{F} \cdot \sqrt{\frac{R \cdot T \cdot \epsilon_0 \cdot \epsilon_r}{2 \cdot c^\infty}} = \frac{1}{\kappa} \quad (8)$$

As can be seen in eq. (8), the effective thickness of the electrochemical double layer d equals the reciprocal of the Debye Hückel radius (κ). A low ion concentration gives an expanded double layer, while an increase of the ion concentration reduces the effective double layer thickness. This effect is called *compression of the electrochemical double layer*.

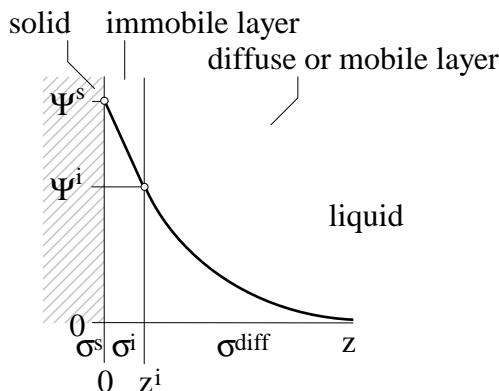


Fig. 3: Potential Ψ in dependence on the distance z , $\Psi = \Psi(z)$ (b) for an electrochemical double layer according to Stern; Ψ^s = surface potential, Ψ^i = potential at the distance z^i , σ^s = surface charge density, σ^i = charge density of the immobile layer, σ^{diff} = charge density of the diffuse layer.

In 1924, Otto Stern combined the two models described above and created the first double layer model [6], which was suited to explain the electrokinetic phenomena. Later the Stern's model was multifariously modified and extended. Today, the so-called *GSCG model* (Gouy-Chapman-Stern-Grahame model [7]) is generally accepted to explain charging processes taking place on a solid/liquid interface and explaining the resulting electrokinetic phenomena.

According to Stern, freely moveable ions solved in the liquid phase were attracted by surface forces and irreversibly adsorbed on the solid surface. A so-called immobile layer with a thickness of z^i is formed. This assumption corresponds to the model by Helmholtz. However, the irreversibly adsorbed ions do not fully compensate the oppositely charged carrier on the solid surface. Hence, a diffuse layer as described by Gouy and Chapman is formed to compensate the excess charges (Fig. 3). The fundamental charge neutrality is given by the sum of all charge densities $\sigma^s + \sigma^i + \sigma^{diff} = 0$. The surface charge density σ^s is given by Helmholtz's condenser model (eq. 9a) and the charge density of the diffuse layer confirms the Gouy-Chapman approach (eq. 9b).

$$\sigma^s = -\frac{\epsilon_0 \cdot \epsilon_r}{z^i} \cdot (\Psi^s - \Psi^i) \quad (9a)$$

$$\sigma^{diff} = \sqrt{8 \cdot \epsilon_0 \cdot \epsilon_r \cdot c^\infty \cdot R \cdot T} \cdot \sinh \left[\frac{F \cdot \Psi^i}{2 \cdot R \cdot T} \right] \quad (9b)$$

(with Ψ^i = potential at the z^i plane)

The charge density of the immobile layer σ^i corresponds to the number (n_j) of excess charges in the plane z^i (eq. 10 is only valid for monovalent ions, for other ions their valence v_j has to be multiplied with n_j).

$$\sigma^i = e_0 \cdot (n_\oplus - n_\ominus) \quad (10)$$

(with e_0 = elementary charge, n_\oplus = number of cations, n_\ominus = number of anions)

Ions of the liquid phase can be adsorbed (n^{ads}) or be dissolved in the liquid's bulk phase (n^{solv}). The transport of an ion from the liquid's bulk phase to the plane z^i (Fig. 3) requires a amount of energy, the specific adsorption potential (ϕ , eq. 11).

$$\phi = \phi_\oplus + e_0 \cdot \Psi^i \quad (11a)$$

$$\phi = \phi_\ominus - e_0 \cdot \Psi^i \quad (11b)$$

(with e_0 = elementary charge, ϕ_\oplus = specific adsorption potential of cations, ϕ_\ominus = specific adsorption potential of anions, Ψ^i = potential at the z^i plane)

As discussed for the Gouy-Chapman model the ion distribution near the solid/liquid interface can be expressed by a Boltzmann approach (eq. 12).

$$\frac{n^{ads}}{n^{solv}} = \frac{n^{ads,max} - n^{ads}}{n^{solv,max} - n^{solv}} \cdot \exp \left[-\frac{\phi}{k_B \cdot T} \right] \quad (12)$$

(with $n^{ads,max}$ = maximum number of ions, which can be adsorbed in the immobile layer, $n^{solv,max}$ = maximum number of ions, which are solved in the liquid phase, k_B = Boltzmann constant)

Eqs. (11) and (12) were combined and put in eq. (10). It gives a practicable expression for the charge density of the immobile layer (σ^i). Multiplying the equation with the Loschmidt constant (N_L) we get molar values ($N = n_j \cdot N_L$; $F = e_0 \cdot N_L$; $\Phi_j = \phi_j \cdot N_L$; $R = k_B \cdot N_L$), (eq. 13):

$$\sigma^i = F \cdot N \cdot \left[\frac{1}{1 + \frac{1}{x} \cdot \exp \left[\frac{\Phi_\oplus + F \cdot \Psi^i}{R \cdot T} \right]} - \frac{1}{1 + \frac{1}{x} \cdot \exp \left[\frac{\Phi_\ominus - F \cdot \Psi^i}{R \cdot T} \right]} \right] \quad (13)$$

(with x = molar fraction of the dissolved ions, $x = n^{\text{solv}} / (n^{\text{solv}} - n^{\text{solv,max}})$; Φ_{\oplus} = non-electrostatic or intrinsic adsorption free enthalpy of cations, Φ_{\ominus} = non-electrostatic or intrinsic adsorption free enthalpy of anions)

Equation (13) seems to be very useful to characterize a solid surface, which is in contact with an aqueous solution. It contains the two very important parameters Φ_{\oplus} and Φ_{\ominus} controlling the adsorption behavior of ions and the charge formation mechanism on the solid surface. The two parameters describe the non-electrostatic or intrinsic adsorption free enthalpies for the ions dissolved in the solution. If ions are adsorbed on the surface an additional term considering the electrostatic interactions also contribute to the driving force of adsorption. The knowledge of the two parameters Φ_{\oplus} and Φ_{\ominus} is fundamental to describe the the chemical equilibrium of the solid/liquid system (see Chapter *Interpretation of electrokinetic measurements*).

The estimation of the two parameters describing the ion adsorption requires the determination of the potential at the plane between the immobile and diffuse layer $\Psi^i(z^i)$. Electrokinetic methods are established to measure a potential (ζ), which is around Ψ^i .

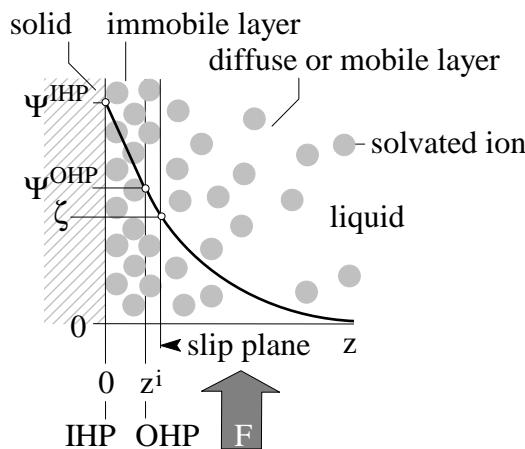


Fig. 4: Schematic build-up of the electrochemical double layer in the frame of electrokinetics. The block file shows an external force F , which is applied to move the liquid relative to the solid.

Electrokinetic potential – zeta-potential

Fig. 3 schematically shows the build-up of an electrochemical double layer. According to Stern, the layer consists of an immobile and a diffuse layer. The immobile layer is between the *inner Helmholtz plane* (IHP) and the *outer Helmholtz plane* (OHP). In Fig. 3, the position of the *outer Helmholtz plane* is indicated by z^i . The solid surface ($z = 0$) can be considered as *inner Helmholtz plane*^[e] (hence, $\Psi^i = \Psi^{\text{IHP}}$). Sometimes, the two planes are also called *Stern plane*.

In order to reach a relative movement between the solid and the liquid phase an external force (F) is applied. In such an electrokinetic experiment the liquid has to move along the solid. Ions are firmly adsorbed in the *immobile layer* remain on the solid. Ions in the diffuse layer are transported with the liquid (Fig. 4). The relative movement requires a *slip plane* between the immobile and mobile part of the electrochemical double layer. The exact position of the

^e Many scientists differentiate *surface* and *inner Helmholtz plane*. In thermodynamics and reality, a surface is not a mathematical line, it is rather a thin volume consisting of the solid and liquid phase. All agree that the *inner Helmholtz plane* must be very near the *surface*.

slip plane is not clear [8]. It cannot be the *outer Helmholtz plane* because ions and their solvation shell have a geometric extent; however the *slip plane* must be very near the *outer Helmholtz plane*.

The potential in the *outer Helmholtz plane* Ψ^{OHP} equals the potential Ψ^i at the z^i position in the Stern model. Hence, in eq. (13) Ψ^i can be substituted by Ψ^{OHP} . If it is assumed that the *slip plane* is very close to the *outer Helmholtz plane* the potential Ψ^{OHP} can be approximated by ζ ($\Psi^i = \Psi^{\text{OHP}} \approx \zeta$), where ζ is the potential in the *slip plane*. According to Freundlich, the potential of the *slip plane* is called *zeta-potential* [9] or electrokinetic potential. It can be indirectly determined by carrying out an electrokinetic experiment (see Chapter *Electrokinetic experiments*). The zeta-potential gives a very relevant information about the build-up of the electrochemical double layer because it reflects the mechanical equilibration of the force of ions' adhesion on the solid surface and the applied external force (F).

It is very important to point out that the *zeta-potential* is neither a property of a solid surface nor a property of a liquid or solution. It results from the coexistence of two phases and reflects the properties of the interphase formed between a solid and liquid phase. If the properties of the liquid phase, e.g. an aqueous electrolyte solution is changed (e.g. variation of the ion strength, pH value, concentration of surfactants etc.), the equilibrium between the solid and the solution is newly adjusted and a changed zeta-potential value will be determined (eq. 14).

$$\zeta = \zeta(\text{solid/liquid}; c^\infty; \text{pH}; \dots) \quad (14)$$

Electrokinetic experiments

Electrokinetic experiments require the coexistence of two phases, usually a solid and a liquid phase. As mentioned above, during the experiment a relative movement between the solid and liquid phase has to be generated by an external force. Table 1 summarizes common electrokinetic experiments and informs about the force driving the relative movement between the solid and liquid phases (the electro-acoustic experiments will be separately discussed). Mostly, the shape of the solid sample (e.g. powder, sheet, fibers etc.) determines the selection of the suitable experiment. The electrokinetic experiments deliver measured values, which can be used as received or can be converted into the corresponding zeta-potential values.

Table 1: Survey of electrokinetic experiments (electro-acoustic experiments are not included)

	Electric force	Mechanic force
Liquid is immobile, solid is mobile	Particle electrophoresis	Sedimentation and centrifuge potential
Solid is immobile, liquid is mobile	Electro-osmosis	Streaming potential and streaming current

Particle electrophoresis / micro-electrophoresis

Solid particles are suspended in a liquid. During the electrophoresis experiment the suspension must be stable and no sedimentation of particles should take place. The particle concentration should be low that no turbidity or opacity is observed^[f]. The size of the particle must allow to observe them by microscopic techniques^[g]. In a measuring cell equipped with two

^f For highly concentrated suspensions electro-acoustic experiments can be successfully employed.

^g A special technique, using a so-called *mass transport analyzer* determine the mass of the solids transported from the anode space to the cathode space or vice versa.

electrodes an electric field is applied to the suspension (Fig. 5). If the electric force F_{el} is in an equilibrium with the friction force F_{fr} ($F_{el} = F_{fr}$)^[h], a particle having a radius r moves with the constant *electrophoretic velocity* v_e (eq. 15). The velocity v_e can be determined by measuring the particle's way and the time or directly by laser anemometry.

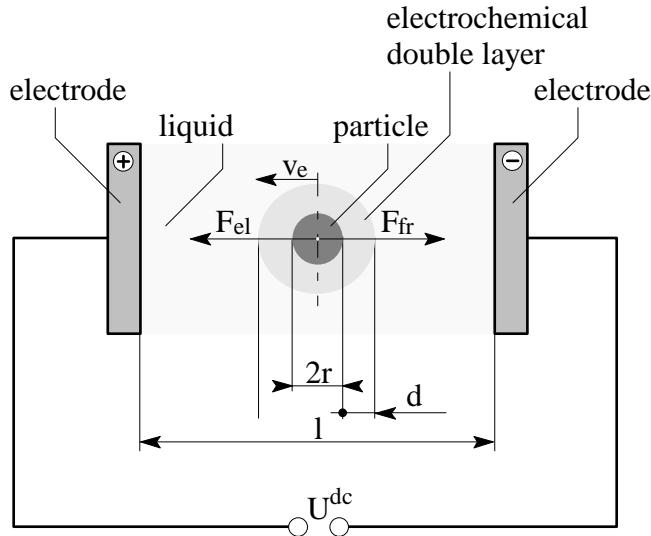


Fig. 5: Principle of the particle electrophoresis: Particles are suspended in a liquid. The electrical field between the electrodes causes a particle movement. The velocity of the particles v_e is measured. (With r = radius of the particle, d = effective thickness of the electrochemical double layer, F_{el} = electric force, F_{fr} = friction force, U^{dc} = applied d.c. voltage, l = distance between the electrodes)

$$v_e = -\frac{2}{3} \cdot \frac{\epsilon_0 \cdot \epsilon_r \cdot E \cdot \zeta}{\eta} \quad (15a)$$

$$v_e = -\frac{2}{3} \cdot \frac{\epsilon_0 \cdot \epsilon_r \cdot U^{dc} \cdot \zeta}{\eta \cdot l} \quad (15b)$$

$$v_e = -\frac{2}{3} \cdot \frac{\epsilon_0 \cdot \epsilon_r \cdot E \cdot \zeta}{\eta} \cdot f[\kappa \cdot r] \quad (15c)$$

$$v_e = -\frac{\epsilon_0 \cdot \epsilon_r \cdot E \cdot \zeta}{\eta} \quad (15d)$$

(with E = electric field strength, ζ = zeta-potential, ϵ_0 = permittivity of the free space, ϵ_r = dielectric number of the liquid^[i], η = viscosity of the liquid^[i], U^{dc} = applied d.c. voltage, l = distance between the electrodes, $f[\kappa \cdot r]$ = correction function explained below, the quotient v_e/E is called *electrophoretic mobility*, u_e)

Equation (15a) is known as Hückel equation [10]. It is valid for particles with $r \ll d$, where d can be calculated according to eq. (8). A more general equation (eq. 15c) was derived by Hen-

^h Electrical force is given by $F_{el} = -E \cdot Q = -E \cdot C \cdot \zeta$ (with E = electric field strength; C = capacity; $\zeta = \Psi$ = potential), where $C = 4 \cdot \pi \cdot r \cdot \epsilon_0 \cdot \epsilon_r$. The friction force F_{fr} is given by the Stokes' law $F_{fr} = 6 \cdot \pi \cdot v_e \cdot r \cdot \eta$ (with η = viscosity).

ⁱ The use of the liquid's parameter is not fully correct. More correct is the use of the values valid for the slip plane. These values can be only approximated by models (see the IUPAC Report recommended at the end of this paper).

ry [11]. It contains a function $f[\kappa \cdot r]$ considering the ratio between the particles' radii and the effective thickness of the electrochemical double layer, $d = 1/\kappa$. In the case of $r \approx d$ (usually given in moderately concentrated aqueous electrolyte solutions, e.g. $c^\infty > 1 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$, containing monovalent ions) the function $f[\kappa \cdot r]$ approximates the factor 3/2. The corresponding equation (15d) is called Smoluchowski equation [12].

Electro-osmosis

The stream of a liquid through a capillary tube may be driven by an applied voltage. In the case of an equilibrium between electric force F_{el} and the friction force F_{fr} ($F_{el} = F_{fr}$)^j the liquid streams with a constant velocity through the capillary (Fig. 6). Along the *slip plane* the electrochemical double layer is sheared by the streaming liquid.

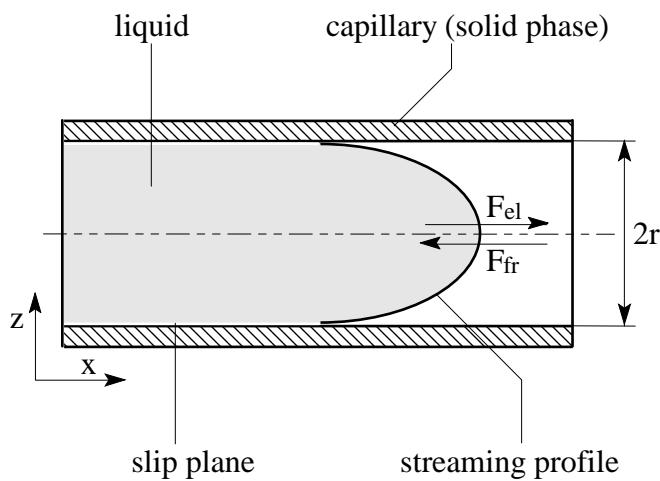


Fig. 6: Principle of the electro-osmosis: A liquid streams through a capillary driven by an electric field. The volume stream \dot{V} of the liquid is measured. (With r = radius of the capillary, F_{el} = electric force, F_{fr} = friction force)

The integrations of the Poisson equation (eq. 2) and Fick's Second Law (see footnote j) give an expression for the streaming velocity in x-direction, v_x (eq. 16a):

$$v_x = -\frac{\epsilon_0 \cdot \epsilon_r \cdot E \cdot \zeta}{\eta} \quad (16a)$$

$$\dot{V} = \frac{V}{t} = -\frac{\epsilon_0 \cdot \epsilon_r \cdot U^{dc} \cdot \zeta \cdot q}{\eta \cdot L} \quad (16b)$$

The velocity of the streaming liquid can be substitute by the volume stream ($\dot{V} = v_x \cdot q$, where q is the capillary's cross-section). The volume stream (\dot{V}) can be easily measured by measuring a transported liquid volume (V) per time (t). The electric field strength (E) is the

^j Electrical force is given by $F_{el} = -E \cdot Q = -E \cdot V \cdot \rho$ (with E = electric field strength; V = volume; ρ = space charge density, see eq. 2). The friction force F_{fr} is given by Fick's second law

$F_{fr} = -\eta \cdot V \cdot \left[\frac{dv_x}{dx} \Big|_{x+dx} - \frac{dv_x}{dx} \Big|_x \right]$ (with η = viscosity, V = volume; v_x = velocity in x-direction, x, z = coordinates). For eq.'s (2) integration the potential at the slip plane is $\Psi = \zeta$, and $\Psi = 0$ in the liquid's bulk phase (hence, $d\Psi/dz = 0$). For integration Fick's Second Law, in the slip plane the velocity v_x is $v_x|_{SP} = 0$, in the liquids bulk phase $v_x = v_x$.

quotient of the applied d.c. voltage (U^{dc}) and the length of the capillary (L). Using these substitutions the corresponding Smoluchowski equation can be deviated from eq. (16a).

It is necessary to note, that eqs. (16a) and (16b) are only valid for a single capillary. Electro-osmosis experiments are usually carried out on bundles of fibers or compact powder samples. These solids form diaphragms having unknown effective cross-sections (q) and capillary lengths (L). However, the ratio L/q (also called *cell constant*) can be experimentally determined, and in this way it is possible to use eq. (16b) also for studies on diaphragm-forming solids (e.g. fibers or fine powders). Ref. [13] summarizes different methods to determine the *cell constant* of a porous system.

A very comfortable method to determine the *cell constant* (L/d) and consider the increased solid's surface conductivity (χ^s) was suggested by Fairbrother and Mastin [14]. According to the Ohm's laws the applied d.c. voltage is $U^{dc} = R_x \cdot I$ (with R_x = electric resistance in the electro-osmosis measuring cell filled with the measuring liquid, I = current) and $R_x = 1/\chi \cdot L/q$ (with χ = specific conductivity, L/q = *cell constant*). In the diaphragm the specific conductivity (χ) is composed by the electrolyte's conductivity (χ^∞) and the surface conductivity (χ^s): $\chi = \chi^\infty + \chi^s$. The surface conductivity can be neglected if the diaphragm is filled with a highly concentrated electrolyte solution, such as a $0.1 \text{ mol} \cdot \text{l}^{-1}$ KCl solution. In that case, the *cell constant* is given by $(L/q)^{0.1 \text{ M KCl}} = R^{0.1 \text{ M KCl}} \cdot \chi^{0.1 \text{ M KCl}}$. However, a highly concentrated electrolyte solution is not suitable to carry out electro-osmosis experiments because the ion concentration in the bulk phase and the electrochemical double layer is not different and no potential can be expected between the solid and the liquid phase. The *cell constant* (L/q^x) of diaphragm filled with a diluted electrolyte solution, such as a $1 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ KCl solution is given by $(L/q)^x = R^x \cdot \chi^x$. The electric resistances $R^{0.1 \text{ M KCl}}$, R^x (in the filled electro-osmosis measuring cell) and the conductivity $\chi^{0.1 \text{ M KCl}}$ the can be easily measured^[k]. The *cell constant* is a geometric parameter and independent of the applied electrolyte concentration: $(L/q)^{0.1 \text{ M KCl}} = (L/q)^x$. Hence the conductivity of a diaphragm filled with a diluted electrolyte solution can be expressed by $\chi^x = (R^x)/(R^{0.1 \text{ M KCl}} \cdot \chi^{0.1 \text{ M KCl}})$. With the first Ohm's law we get the *Fairbrother-Mastin approach* (16c):

$$\dot{V} = -\frac{\epsilon_0 \cdot \epsilon_r \cdot I \cdot \zeta}{\eta} \cdot \frac{R^{0.1 \text{ M KCl}} \cdot \chi^{0.1 \text{ M KCl}}}{R^x} \quad (16c)$$

(with I = electric current).

Streaming potential and streaming current

The streaming potential/streaming current experiment can be considered as the reverse electro-osmotic experiment. During the electro-osmosis an electric force is applied to move a liquid through a diaphragm. In the streaming potential/streaming current experiment an electrical potential and an electrical current is generated by a streaming liquid along a solid phase. The force to drive the liquid stream is usually produced by a pressure difference ($\Delta p = p_1 - p_0$, with p_1 = filling pressure and p_0 = outlet pressure) (Fig. 7).

In the state of equilibrium the generated streaming current I_{ss} must equal a reverse current I_R (eq. 17a). The streaming current I_{ss} is given by the sum of the transported charges per time, which is controlled by the volume stream ($dV/dt = \dot{V}$) of the liquid and the space charge density (ρ) along the solid/liquid interphase (eq. 17b).

$$I_{ss} = I_R \quad (17a)$$

^k In the electro-osmosis measuring cell the surface conductivity contributes to the conductivity. Hence, the conductivity of the dilute electrolyte solution (χ^x) cannot be exactly measured.

$$I_{ss} = - \int_0^r \rho \frac{dV}{dt} \quad (17b)$$

With eq. 2 we get:

$$I_{ss} = \epsilon_r \cdot \epsilon_0 \cdot \int_0^r \frac{d^2\Psi}{dz^2} \frac{dV}{dt} \quad (17c)$$

If the capillary is flown by a laminar liquid flow, the volume stream in a hollow cylinder, which is the typical shape of a capillary, can be calculated by the Hagen-Poiseuille law (eq. 17d). It bases on the equilibrium of the friction force (F_{fr}) and hydrostatic force (F_{stat})^[1].

$$\frac{dV}{dt} = - \frac{(r-z) \cdot \pi \cdot dz \cdot \Delta p \cdot (2 \cdot r \cdot z - z^2)}{2 \cdot \eta \cdot L} \quad (17d)$$

Eq. (17d) can be introduced in eq. (17c). The streaming current is only generated along the solid/liquid interphase near the capillary wall. Hence, z can be neglected. The integration of the increment $r \cdot (d^2\Psi/dz^2) dz$ from 0 to r and the substitution of the potential Ψ by ζ gives:

$$I_{ss} = - \frac{\Delta p \cdot \pi \cdot \epsilon_r \cdot \epsilon_0 \cdot \zeta}{\eta \cdot L} \quad (17e)$$

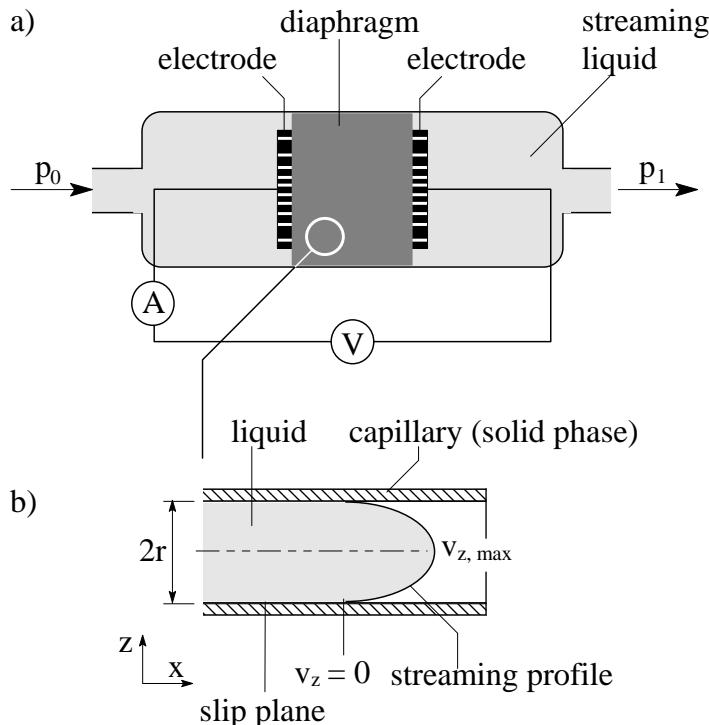


Fig. 7: Experimental set-up (a) to measure the streaming potential and streaming current on a diaphragm consisting of a bundle of capillaries (the two electrodes are perforated). Fig. 7b visualizes the laminarly streaming liquid in a single capillary.

¹ With $F_{fr} = F_{stat}$ we get for a streaming layer in the height z : $-2 \cdot \eta \cdot (r-z) \cdot \pi \cdot L \cdot (dv_z/dz) = (r-z)^2 \cdot \pi \cdot \Delta p$ (where L is the length of the streaming layer). The differential equations can be integrated from 0 to v_z and from 0 to z . Then, the velocity of the streaming layer in z position is given by: $v_z = -\Delta p / (4 \cdot \eta \cdot L) \cdot (2 \cdot r \cdot z - z^2)$. The volume stream in a hollow cylinder is given by: $dV/dt = 2 \cdot (r-z) \cdot \pi \cdot dz \cdot v_z$. With the expression for v_z from the Hagen-Poiseuille law we get: $dV/dt = -(r-z) \cdot \pi \cdot dz \cdot \Delta p \cdot (2 \cdot r \cdot z - z^2) / (2 \cdot \eta \cdot L)$ (17d).

According to Ohm's law the reverse current is $I_R = U/R$, where the resistance R can be expressed by the geometric ratio (or *cell constant*) L/q and the electric conductivity (χ). The capillary's cross section is $q = r^2 \cdot \pi$. Combining eqs. (17a) and (17e) we get the Smoluchowski equations to calculate the zeta-potential from streaming current and streaming potential measurements (eqs. 18). The two Smoluchowski equations are only valid for a single capillary. The use of capillary bundles (diaphragms) and the consideration of surface conductivity requires the same procedure explained in the Chapter *Electro-osmosis*. For studying sample surfaces with the method described here it is recommended to measure both the streaming potential ($U/\Delta p$) and the streaming current ($I/\Delta p$)^[m].

$$\frac{U}{\Delta p} = -\frac{\epsilon_r \cdot \epsilon_0 \cdot \zeta}{\eta \cdot \chi} \quad (18a)$$

$$\frac{I}{\Delta p} = -\frac{\epsilon_r \cdot \epsilon_0 \cdot q \cdot \zeta}{\eta \cdot L} \quad (18b)$$

(with η = viscosity of the liquid^[i], χ = specific conductivity, L = length of the capillary, q = cross section of the capillary, L/q = *cell constant*).

Electro-acoustic phenomena

In order to determine the zeta-potential of suspensions having a high fraction of solid particles (volume fraction of particles ca. 20 vol-%) the *electrokinetic sonic amplitude* (ESA) effect is used. A second way is the measurement of the *ultrasonic vibration potential* (UVP), which is also called CVP = *colloidal vibration potential* [15].

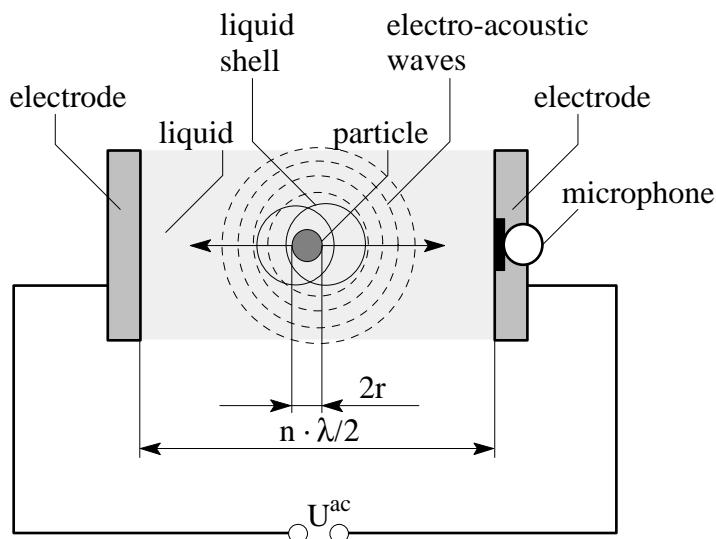


Fig. 8: Principle of the *electrokinetic sonic amplitude* measurement: Particles are suspended in a liquid. The alternating electrical field between the electrodes causes a relative particle movement towards the liquid. The amplitudes of the emitted electro-acoustic waves were recorded as ESA signals by a microphone. (With U^{ac} = applied a.c. voltage with frequencies between 0.1 and 1 MHz, n = natural number, λ = wave length of the externally applied field.)

^m The quotients were determined from measuring the potential (U) and the current (I) values in dependence on the pressure (Δp), which is applied on the diaphragm. The slopes of the graphs $U = U(\Delta p)$ and $I = I(\Delta p)$ must be constant.

For ESA measurements an alternating electrical field (frequencies between 0.1 and 1 MHz) is applied on a suspension (Fig. 8). The field force generates an alternating movement of the liquid's molecules and the suspended particles. If particles and liquid have different densities, the velocity of particles and liquid's molecules is different and a relative movement of particles towards the liquid can be observed. The relative movement between liquid and particle shears the diffuse part of the electrochemical double layer near the solid surface. This is the same scenario as described for particle electrophoresis. In contrast to the micro-electrophoresis experiment, during the ESA measurement the external electrical field is alternating and the particle's direction of movement is also alternating. As response acoustic waves are generated. The pressure amplitudes (ESA in Pa/[V·m]) and the frequency of the emitted acoustic waves are recorded by a microphone. From the ESA signal the *electrophoretic mobility* (u_e) can be calculated (eq. 19a). Shifts in the frequency can be used to determine the main particle diameter.

$$u_e = -\frac{\text{ESA}}{\phi \cdot \Delta\rho_{sl} \cdot c_s} \quad (19a)$$

(with ϕ = volume fraction of the suspended particles, $\Delta\rho_{sl}$ = amount of the difference between the liquid's and particle's density, c_s = velocity of sound in the suspension).

As described for micro-electrophoresis experiments the *electrophoretic mobility* (u_e) can be used to calculate the zeta-potential. However, the alternating field requires a modification of the Henry equation (15c) with an additional complex function G compensating the periodic speed-up and retardation of the suspended particles (eq. 19b). Function G depends on the angular frequency (ω) of the applied electrical field. More information can be found in Ref. [15].

$$u_e(\omega) = -\frac{2}{3} \cdot \frac{\epsilon_0 \cdot \epsilon_r \cdot \zeta}{\eta} \cdot f[\kappa \cdot r] \cdot G[\omega] \quad (19b)$$

The second electro-acoustic method, the measurement of the *ultrasonic vibration potential* (UVP) can be considered as reversal to the ESA experiment. Via the microphone alternating acoustic waves are applied. They generate a relative movement between the solid and the liquid phase and shears the diffuse part of the electrochemical double layer. The shift between particle and its liquid shell is connected with a lateral separation of opposite charge centers. The so formed dipole alternates with the frequency of the applied acoustic waves. The generated potential is tapped by the electrodes.

The advances of the electro-acoustic methods is their application to study turbid and highly concentrated suspensions, sludge or ceramic slurries. The size of the suspended particles could range from a few nanometers to about 100 μm . Stirring the suspension does not effect the measurement.

Interpretation of electrokinetic measurements

As mentioned above, electrokinetic phenomena are always related to two-phases systems, where mostly one phase is a liquid and the second phase a solid. The build-up of the electrochemical double layer is the result of the properties of the *two* interacting phases. Hence, zeta-potential values are never material constants or material properties neither for the solid nor the liquid. The zeta-potential can be considered as a *probe* to get information about the real double layer's build-up and can be successfully used to characterize the surface properties of the solid *in contact* with a liquid phase. To get qualitative and quantitative information of the kind of interactions between the solid surface and the liquid the properties, such as pH value or the concentration of salt ions (c^∞_{ions}) or other dissolved substances (c^∞_{solv}) were varied. The determined zeta-potential is the response on changes in the electrochemical double layer's build-up. Hence, for interpretation electrokinetic measurements it is necessary to record and discuss functions, such as $\zeta = \zeta(\text{pH})$, $\zeta = \zeta(c^\infty_{\text{ions}})$ or $\zeta = \zeta(c^\infty_{\text{solv}})$.

Charge formation and charge formation mechanisms on solid surfaces

Fig. 9 schematically shows functions $\zeta = \zeta(\text{pH})$. The shape of three of them is very typical for surfaces having Bønsted acidic or/and Bønsted basic sites. The fourth function was recorded from a surface does not have dissociable surface groups, but adsorption centers for hydronium (H^+) and hydroxyl (OH^-) ions. The strong dependence of the zeta-potential values on the concentration of hydronium (H^+) and hydroxyl (OH^-) ions (expressed as pH value) make sure that H^+ and OH^- are *potential-determining ions* (pdi). Obviously, these ions control the charge density in the *slip plane*. Dissolved ions, which are not specifically adsorbed on the solid surface are called *indifferent ions*. These ions do not control the surface potential.

If hydronium ions (H^+) are adsorbed on suitable surface sites (Bønsted basic groups) the surface charge becomes positive and the corresponding zeta-potential values have plus signs (Fig. 9a). The increase of the hydroxyl ion concentration propagates the deprotonation of the positively charged surface sites. The zeta-potential values decreases, cut the zero line at $\text{pH} = \text{pH}_{\text{IEP}}$ (see below) and become negative as a result of OH^- ion adsorption (Fig. 9a).

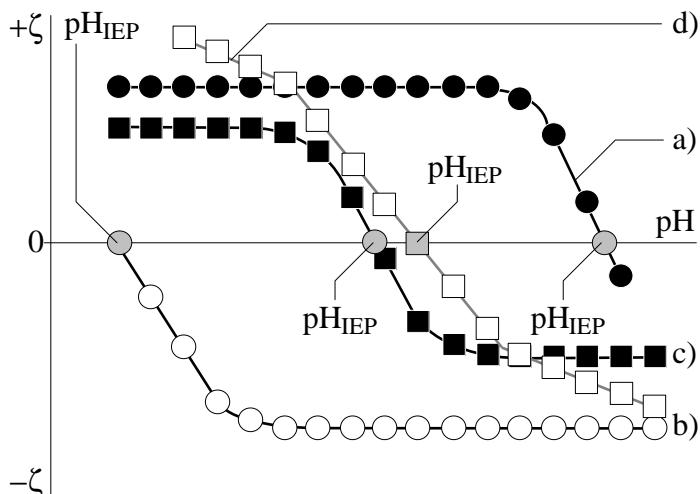


Fig. 9: Typical shapes of $\zeta = \zeta(\text{pH})$ plots for sample surfaces endowed with Bønsted basic sites (a), Bønsted acidic sites (b), coexisting Bønsted acidic and basic sites (c). Plot (d) is typical for *inert* surfaces having neither Bønsted acidic nor basic sites. The meaning of pH_{IEP} (isoelectric point) at $\zeta = 0$ is explained below.

Bønsted acidic sites attract hydroxyl ions (OH^-), which initiate dissociation reactions in a second step. The formed negative surface charges cause zeta-potential values with minus signs (Fig. 9b). With increasing the pH value the progress of dissociation reactions increases the amount of the zeta-potential values. However, on a sample surface the number of dissociable Bønsted acidic sites is limited. If all dissociable Bønsted acidic sites are dissociated the zeta-potential remains constant and a plateau of the function $\zeta = \zeta(\text{pH})$ is observed (Fig. 9b).

Fig. 9c shows a typical function $\zeta = \zeta(\text{pH})$ of a sample surface containing Bønsted acidic as well as Bønsted basic sites. Its amphoteric character can be identified by the two clearly pronounced plateau levels indicating the hydronium ions adsorption and the dissociation of the basic functionalities.

Surfaces do not have Bønsted acid or base groups, such as many fluoropolymers, polyolefins and many other polymers are characterized by curves $\zeta = \zeta(\text{pH})$ as shown in Fig. 9d (gray line). Positive zeta-potential values result from the adsorption of hydronium ions. With increasing the pH value the increased number of OH^- ions compensate the positive surface charge. The zeta-potential values decreases. At higher pH values the preferential OH^- adsorption turns the surface net charge and the zeta-potential is negative. Of course, on the sample surface the number of adsorption sites is limited and the zeta-potential values should reach a plateau value. But all H^+ and OH^- ions are wrapped by a water shell. On the hydrophobic surface the water molecules cannot be stabilized. Adsorbing ions oust their water molecules and increase more and more the surface charge density and the corresponding zeta-potential^[n].

As mentioned above, ion adsorption and dissociation reactions charge a solid surface. The charging mechanism can be studied by carrying out electrokinetic experiments in depends of pH. For such experiments an equilibrium between the solid and liquid phase is required and vice versa the pH-dependence of the calculated zeta-potential values contains information on the solid/liquid equilibrium (see Chapters *Single acid site dissociation model* and *Molar free enthalpies of ion adsorption, adsorption enthalpy and adsorption entropy*).

Isoelectric point and point of zero charge

In Fig. 9 each function $\zeta = \zeta(\text{pH})$ is characterized by a pH value where the zeta-potential equals zero. This pH value is called *isoelectric point* ($\text{pH}_{\text{IEP}} = \text{pH}|_{\zeta=0}$). In electrokinetic experiments pH_{IEP} cannot be directly determined because all equations available to calculate the zeta-potential are discontinuous for $\zeta = 0$. Hence, pH_{IEP} must be determined by interpolation. According to its definition the zeta-potential is the potential in the *slip plane* (see Chapter *Electrokinetic potential – zeta-potential*). Following the established double layer models the ion concentration of a *potential-determining ion* species j in the *slip plane* (c_j^{SP}) can be described by a Boltzmann approach (eq. 4, if H^+ and OH^- are *potential-determining ions*, c_j can be expressed by pH, $\text{pH} = -\log_{10}[c_j]$).

$$c_j^{\text{SP}} = c_j^\infty \cdot \exp\left[-\frac{z_j \cdot F \cdot \zeta}{R \cdot T}\right] \quad (4c)$$

At the pH_{IEP} (where $\zeta = 0$) the exponential function is one and c_j^{SP} equals the ion concentration in the bulk of the liquid (c_j^∞). At pH_{IEP} the surface can be uncharged and the *outer Helmholtz plane* does not contain an excess neither of positively nor negatively charged ions. In that case, the pH_{IEP} equals the *point of zero charge* (pH_{pzc} , see below). But, at pH_{IEP} the

ⁿ The zeta-potential value can have a plus or minus sign. In both cases the potential is considered as a maximum value because a potential is the always the difference between two levels. At $[x_{\max}, \zeta_{\max}]$ the difference becomes a maximum independently on the sign.

inner Helmholtz plane (which can be considered as the solid surface) can also be charged and the immobile ions in the *outer Helmholtz plane* completely compensate the surface charges. If dissolved salt cations or anions contribute to the charge compensation (as *potential-determining ions* besides the *potential-determining H⁺* or OH⁻ ions) pH_{IEP} and pH_{pzc} are different. The role of the accompanying salt ions can be tested by electrokinetic measurements in dependence on the salt concentration, such as pH-dependent measurements in 1·10⁻⁵, 1·10⁻⁴, 1·10⁻³ and 1·10⁻² mol·l⁻¹ KCl. Shifted pH_{IEP} values indicate a specific adsorption and *potential-determining properties* of the electrolyte cations and/or anions.

The *point of zero charge* (pH_{pzc}) is known from the colloidal chemistry. According to Nernst's equation, the *point of zero charge* describes the state of an completely *uncharged* solid surface ($\Psi^s = 0$), which is in contact with an aqueous electrolyte solution. It does not describe the charge distribution in a *slip plane* or in the *outer Helmholtz plane*. Usually, the pH_{pzc} values were determined by potentiometric titration experiments, which do not require a relative movement between the solid and the liquid phase. Potentiometric titrations are very useful to study adsorption/dissociation equilibria and determine the number of surfaces sites, which can be charged. Comparisons of pH_{IEP} and pH_{pzc} allow to explain the mechanisms of solid surface charging.

Single acid site dissociation model [16]

Many solid surfaces consisting of functional groups having a Bønsted acidic character. Hence, most materials can be found in the nature are characterized by a negative surface charge if they are in contact with aqueous solutions of low or moderate pH values. The dissociation equilibrium of the Bønsted acidic sites (A^s-H) is described in the following equation:



The dissociation equilibrium (20) is characterized by the dissociation constant K_a[†]:

$$K_a^\dagger = \frac{[A^\ominus]^s \cdot [H_3O^\oplus]^{SP}}{[A-H]^s} \rightarrow \frac{[A-H]^s}{[A^\ominus]^s} = \frac{[H_3O^\oplus]^{SP}}{K_a^\dagger} \quad (21a)$$

(with [A[⊖]]^s = activity of the dissociated Bønsted acidic sites, [H₃O[⊕]]^{SP} activity of hydronium ions in the Stern plane, [A-H]^s = activity of the Bønsted acidic surface sites)

According to eq. (4c in the Chapter *Isoelectric point and point of zero charge*) the activity of hydronium ions in the Stern plane can be expressed by a Boltzmann approach (eq. 21 b) and K_a[†] can be transformed into the corresponding pK_a value (eq. 21 c).

$$[H_3O^\oplus]^{SP} = [H_3O^\oplus]^\infty \cdot \exp\left[-\frac{F \cdot \zeta}{R \cdot T}\right] = \exp[-2.3 \cdot pH] \cdot \exp\left[-\frac{F \cdot \zeta}{R \cdot T}\right] \quad (21b)$$

$$K_a^\dagger = \exp[-2.3 \cdot pK_a] \quad (21c)$$

The degree of dissociation α is the ratio of the activity of dissociated Bønsted acidic surface sites [A[⊖]]^s and the activities of all Bønsted acidic surface sites ([A[⊖]]^s + [A-H]^s):

$$\alpha = \frac{[A^\ominus]^s}{[A-H]^s + [A^\ominus]^s} \rightarrow \frac{1}{\alpha} = \frac{[A-H]^s}{[A^\ominus]^s} + 1 = \frac{[H_3O^\oplus]^{SP}}{K_a^\dagger} + 1 \quad (22a)$$

With eqs. (21b) and (21c) we get:

$$\alpha = \frac{1}{1 + \exp\left[-2.3 \cdot (\text{pH} - \text{pK}_a) - \frac{F \cdot \zeta}{R \cdot T}\right]} \quad (22b)$$

The sum of all charge densities in the electrochemical double layer must be zero (condition of charge neutrality):

$$\sigma^{\text{diff}} + \sigma^{\text{IHP}} + \sigma^{\text{OHP}} = \sigma^{\text{diff}} + \sigma^{\text{SP}} = 0 \quad \rightarrow \quad -\sigma^{\text{diff}} = \sigma^{\text{SP}} \quad (23)$$

In the case of univalently charged surface sites $A^{\Theta,s}$ the charge density in the Stern plane (σ^{SP}) can be expressed by the product of the number of the dissociated species $\alpha \cdot N_a$ and their charge e_0 (with N_a = number of acidic surface sites, e_0 = elementary charge). Employing the Gouy-Chapman approach ($\Psi^i \approx \zeta$) the charge density in the diffuse layer (σ^{diff}) can be expressed by:

$$\sigma^{\text{diff}} = \sqrt{8 \cdot \epsilon_0 \cdot \epsilon_r \cdot c^\infty \cdot R \cdot T} \cdot \sinh\left[-\frac{F \cdot \zeta}{2 \cdot R \cdot T}\right] = \alpha \cdot N_a \cdot e_0 \quad (24)$$

As mentioned in the Chapter *Charge formation and charge formation mechanisms on solid surface* the dissociation of Bønsted acidic surface sites are propagated with increasing the pH value in the liquid phase. If all dissociable groups are dissociated ($\alpha = 1$) the zeta-potential values remain constant and a plateau [$\zeta^{\text{const}} = \zeta(\text{pH})|_{\alpha=1}$] can be observed (Fig. 9b). From eq. (24) we get:

$$N_a = \frac{1}{e_0} \cdot \sqrt{8 \cdot \epsilon_0 \cdot \epsilon_r \cdot c^\infty \cdot R \cdot T} \cdot \sinh\left[-\frac{F \cdot \zeta^{\text{const}}}{2 \cdot R \cdot T}\right] \quad (25)$$

Eq. (25) can be used to calculate the number of Bønsted acidic surface sites on a solid surface. For the determination of N_a electrokinetic experiments in dependence on pH are required. The combination of eqs. (22b), (24) and (25) gives an equation, which can be used to calculate the acid strength of a solid surface:

$$\frac{\sqrt{8 \cdot \epsilon_0 \cdot \epsilon_r \cdot c^\infty \cdot R \cdot T} \cdot \sinh\left[-\frac{F \cdot \zeta^{\text{const}}}{2 \cdot R \cdot T}\right]}{1 + \exp\left[-2.3 \cdot (\text{pH} - \text{pK}_a) - \frac{F \cdot \zeta}{R \cdot T}\right]} = \sqrt{8 \cdot \epsilon_0 \cdot \epsilon_r \cdot c^\infty \cdot R \cdot T} \cdot \sinh\left[-\frac{F \cdot \zeta}{2 \cdot R \cdot T}\right] \quad (26a)$$

$$\text{pK}_a = \text{pH} + 0.434 \cdot \left\{ \frac{F \cdot \zeta}{R \cdot T} + \ln \left[\frac{\sinh\left[-\frac{F \cdot \zeta^{\text{const}}}{2 \cdot R \cdot T}\right]}{\sinh\left[-\frac{F \cdot \zeta}{2 \cdot R \cdot T}\right]} - 1 \right] \right\} \quad (26b)$$

The knowledge of the zeta-potential plateau value (ζ^{const}) and the use of pairs of variates [pH; ζ] from electrokinetic measurements gives a function $\text{pK}_a = \text{pK}_a(\text{pH})$. A solid surface endowed with Bønsted acidic surface sites can be considered as a polyacid. Each acidic surface group has a corresponding pK_a value. The pK_a value of the most acidic surface group can be considered as *intrinsic* or non-electrostatic pK_a value of the solid surface. During the dissociation of this most acidic group one negative surface charge is generated. This charge influences the adsorption of the second OH^- ion, which is necessary to dissociate the second surface group. The additional electrostatic repulsion (electrostatic interaction) shifts the pK_a value for the second dissociation slightly to a higher value. The high number of dissociable surface

sites and the number of negative surface charges increasing with the dissociation's progress results in the pH-dependence of pK_a .

Molar free enthalpies of ion adsorption, adsorption enthalpy and adsorption entropy

Electrokinetic experiments can be carried out in dependence on the concentration of a salt or an other substance (e.g. ionic surfactants) dissolved in water. Fig. 10 shows typical functions $\zeta = \zeta(x)$, where x is the molar fraction of the dissolved ions.

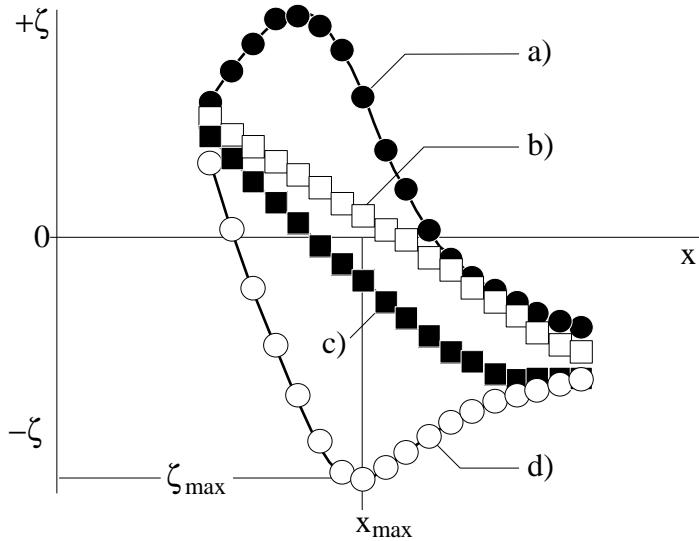


Fig. 10: Typical shapes of $\zeta = \zeta(x)$ plots in dependence on the valence of electrolyte ions [valence of cations : valence of anions = 4 : 1 (a); 3 : 1 (b); 2 : 1 (c); 1 : 1 (d)]. Figure according to Jacobasch [17].

Some of the $\zeta = \zeta(x)$ functions shown in Fig. 10 are characterized by the appearing of a turning point [x_{\max} , ζ_{\max}]^[n, page 15]. In the literature, the real existence of a turning point is very controversially discussed. According to the simple Stern theory a different number of ions near the solid surface and the liquid's bulk phase is required to generate an electrical potential. In a liquid, which is not able to provide charge carriers electrokinetic phenomena cannot be observed. Liquids with a high concentration of ions have nearly the same number of ions in their bulk phase as present in the electrochemical double layer. A potential cannot be generated and no electrokinetic phenomena are observed (compression of the electrochemical double layer). Between the two ultimate states (no any charge carriers vs. to much charge carriers) where the zeta-potential has to be zero, the zeta-potential is different of zero and must pass a turning point.

Ions adsorbed in the immobile layer contribute to the charge density (σ^i) of that layer. In eq. (13) the potential (Ψ^i) in the z^i layer can be approximated by the zeta-potential (ζ):

$$\sigma^i = F \cdot N \cdot \left[\frac{1}{1 + \frac{1}{x} \cdot \exp\left[\frac{\Phi_{\oplus} + F \cdot \zeta}{R \cdot T}\right]} - \frac{1}{1 + \frac{1}{x} \cdot \exp\left[\frac{\Phi_{\ominus} - F \cdot \zeta}{R \cdot T}\right]} \right] \quad (13a)$$

The turning points [x_{\max} , ζ_{\max}] in the $\zeta = \zeta(x)$ functions are characterized by $(d\zeta/dx) = 0$. The differentiation of eq. (13a) gives two eqs. (27a) and (27b) containing the non-electrostatic adsorption free enthalpies of cations (Φ_{\oplus}) and anions (Φ_{\ominus}) [6].

$$\Phi_{\oplus} + \Phi_{\ominus} = 2 \cdot R \cdot T \cdot \lg [x_{\max}] \quad (27a)$$

$$\Phi_{\oplus} - \Phi_{\ominus} = 2 \cdot F \cdot \zeta_{\max} \quad (27b)$$

In the state of equilibrium the *molar adsorption free enthalpy* of the ion species j ($\Delta_{\text{ads}}G_j^{\ominus}$) is the sum of the ions' non-electrostatic or *intrinsic* adsorption free enthalpy (Φ_j) and the electrostatic contribution $v_j \cdot F \cdot \zeta$, where ζ depends on pH and concentration (x) of the liquid phase.

$$\Delta_{\text{ads}}G_j^{\ominus}(pH, x)|_{\text{eq}} = \Phi_j + v_j \cdot F \cdot \zeta(pH, x) \quad (28)$$

$$\Delta_{\text{ads}}G_j^{\ominus}(pH, x)|_{\text{eq}} = -R \cdot T \cdot \ln [K_{\text{ads}}^{\dagger}]_{\text{eq}} \quad (29)$$

Van't Hoff's reaction isotherm (eq. 29) shows the relationship between the *molar adsorption free enthalpy* and the equilibrium constant K_{ads}^{\dagger} . As mentioned above (Chapter *Single acid site dissociation model*) the dependence of the zeta-potential on the concentration of the *potential-determining ions*, e.g. pH and/or x, results in a concentration dependence of the *molar adsorption free enthalpies* and the equilibrium constants.

Employing the fundamental thermodynamic potential function (eq. 30) the *molar adsorption enthalpy* ($\Delta_{\text{ads}}H_j^{\ominus}$) as well as the *molar adsorption entropy* ($\Delta_{\text{ads}}S_j^{\ominus}$) of the ion species j can be determined from temperature-dependent electrokinetic experiments.

$$\Delta_{\text{ads}}G_j^{\ominus} = \Delta_{\text{ads}}H_j^{\ominus} - T \cdot \Delta_{\text{ads}}S_j^{\ominus} \quad (30)$$

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