

Interfacial Phenomena II

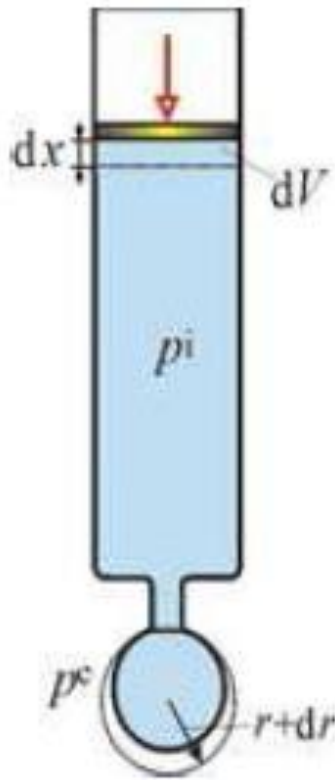
The equilibrium in systems with phase interface

In each system, spontaneous actions take place to establish equilibrium. The sum of the energies of all phase interfaces in the system is reduced by:

- **Reducing the surface** (curvature) of the phase interfaces
- **Changing of phase interfaces** to different phase interfaces which are energetically more advantageous (wetting, spreading)
- **Adsorption**, i.e. a change in composition on the interface, which leads to the reduction of the interfacial energy

Reducing the energy of the system by minimization of the area of the phase interface

Curvature of the phase interface (e.g. liquid droplets, bubbles, etc.) affects the properties of the system.



$$p^i \cdot dV = p^e \cdot dV + \gamma \cdot dS$$

$$p^i - p^e = \gamma \cdot dS / dV = \gamma \cdot (1/R_1 + 1/R_2)$$

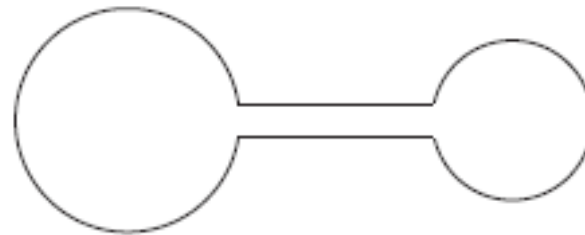
$$\gamma = dW / dS$$

R – radius of curvature

Laplace equation

spherical drop or bubble ($R_1 = R_2 = r$): $p^i - p^e = 2\gamma / r$

$$p^i = p^e + 2\gamma / r$$



γ_1	=	γ_2
r_1	>	r_2
P_1	<	P_2

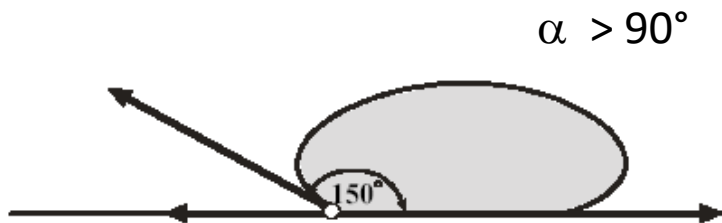
Biophysics: effect of surface tension on inflation and deflation of lung alveoli.

Reducing the energy of the system by changing of the phase interface

Interfaces solid-liquid (wetting)

If the surface tension of the solid is greater than the sum of the surface tension of the liquid and the **interfacial tension** of the solid-liquid, liquid wets the solid surface: $\sigma_s > \sigma_l + \sigma_{sl}$

If it is true $\sigma_s < \sigma_l + \sigma_{sl}$, the drop of liquid takes on a solid surface the equilibrium shape, characterized by the **wetting angle** α .



$\alpha = 180^\circ$

$\alpha > 90^\circ$

$\alpha < 90^\circ$

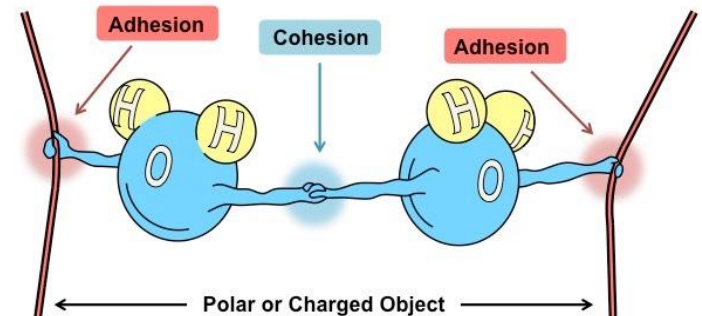
$\alpha = 0^\circ$

perfect non-wetting

poor wetting

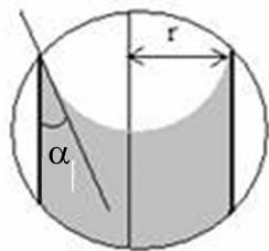
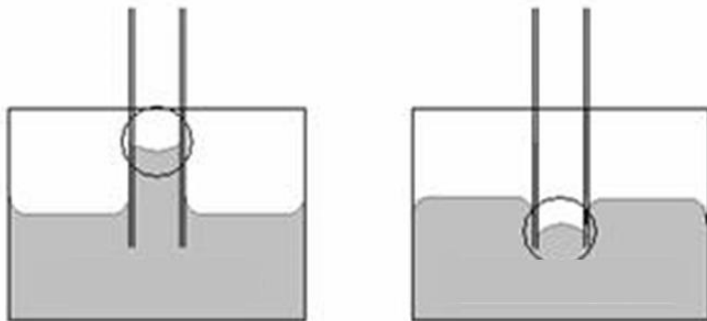
good wetting

perfect wetting

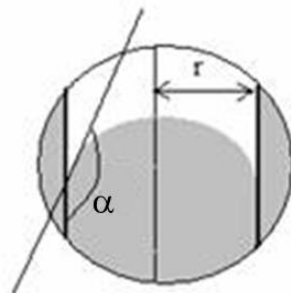


Interfaces solid-liquid (wetting – capillary actions)

An important case of the equilibrium at the solid-liquid interface is the behavior in thin tubes (capillaries), in which the level of liquid is set higher (**capillary elevation**) or lower (**capillary depression**) than the surrounding liquid level .



concave meniscus



convex meniscus

During capillary elevation, the liquid rises to a level at which the surface and the gravitational force of the liquid will be in equilibrium

$$h = (2 \cdot \sigma \cdot \cos \alpha) / (\rho \cdot r \cdot g)$$

r – capillary radius

g – gravitational acceleration

ρ – density of the liquid

Used for the determination of surface tension of liquids (glass capillaries almost perfectly wetted, $\cos \alpha = 1$).

Biophysics: capillary action allows the water to rise into the upper parts of plants .

Sample problem

The trunk and leaves of a tree can be considered a system of capillaries. **Calculate the capillaries diameter**, if a 41 m tall tree does not dry out. Assume that the water perfectly wets the walls of the capillaries; the surface tension of the water is 70 mN m^{-1} and its density is 1 g cm^{-3} .

$$h = (2 \cdot \sigma \cdot \cos \alpha) / (\rho \cdot r \cdot g)$$

$$r = (2 \cdot \sigma \cdot \cos \alpha) / (\rho \cdot h \cdot g)$$

$$r = 2 \cdot 0.070 / 1000 \cdot 41 \cdot 9.81$$

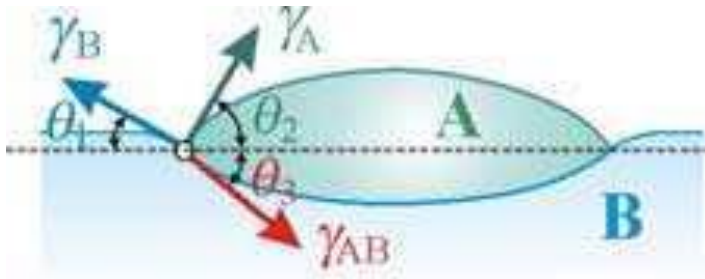
$$r = 3.48 \cdot 10^{-7} \text{ m}$$

$$d = 0.7 \text{ } \mu\text{m}$$



Interfaces liquid-liquid

The behavior of drop of liquid on the surface of another liquid (immiscible) is similar to the behavior of a drop of liquid on the solid surface.



$$\gamma_B > \gamma_A + \gamma_{AB}$$
$$\gamma_B < \gamma_A + \gamma_{AB}$$

drop spreads out
drop takes equilibrium shape

Cohesive and adhesive forces

Cohesion - forces between the liquid (A-A). Work of cohesion $W_c = 2 \gamma_A$

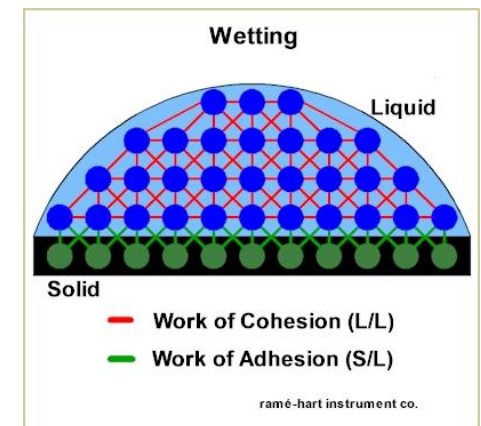
Adhesion - forces between the molecules of the two phases (A-B).

Work of Adhesion $W_a = \gamma_A + \gamma_B - \gamma_{AB}$

Liquid A is spread

(or solid surface is wetted) when:

$W_a > W_c$



Reducing the energy of the system by adsorption on the phase interface

For multi-component systems, energy is also reduced by changing concentration on the phase interface - **adsorption**. Adsorption typically means **positive adsorption**, in which the concentration of a particular component in the phase interface is higher than in the condensed phases.

Adsorption versus Absorption



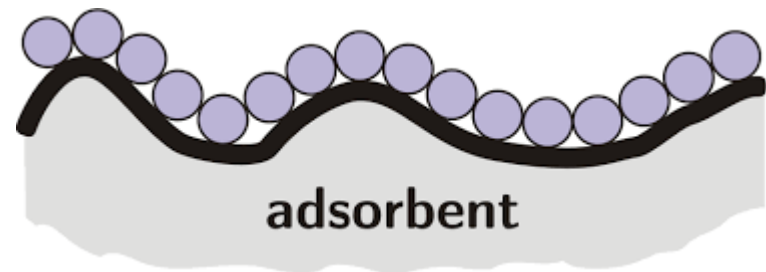
Adsorption on a movable (gas-liquid or liquid-liquid) and solid phase interface (gas-solid or liquid-solid).

Reducing the energy of the system by adsorption at the phase interface

Adsorption is a spontaneous process, in which, as with any spontaneous process, Gibbs energy decreases.

The gas molecules can only carry two-dimensional motion on the surface of the adsorbent and therefore lose one translational degree of freedom during adsorption -> decrease in entropy occurs. This implies that the heat of adsorption is negative ($\Delta_{\text{ads}}H = \Delta_{\text{ads}}G + T \cdot \Delta_{\text{ads}}S$).

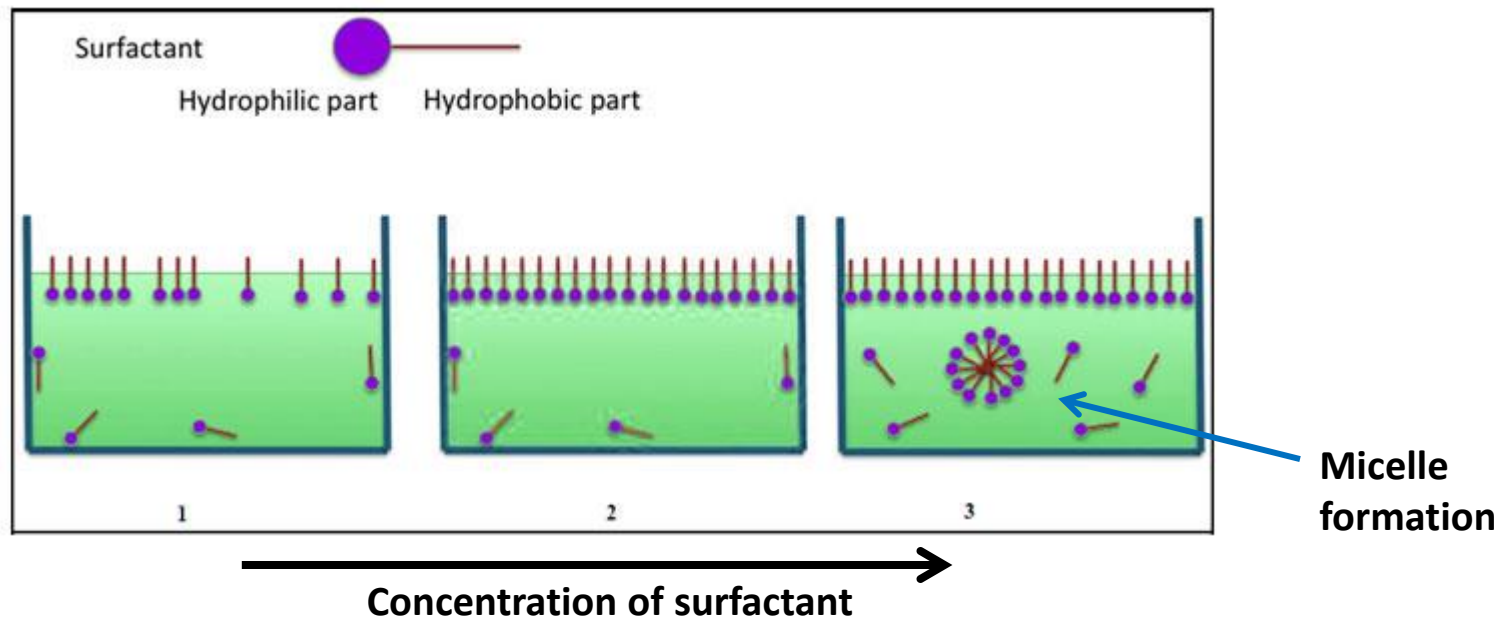
Adsorption is always an exothermic process and the adsorbed amount (at constant pressure) decreases with increasing temperature.



Interfaces liquid-gas

The concentration of the solute is higher in the surface layer than inside the solution - **adsorption at the liquid surface**.

Model of saturated monolayer: The molecules of the solute are closely arranged so that their hydrated polar groups are orient into the aqueous phase and the hydrocarbon chains are directed outside the aqueous phase.



Interfaces solid-gas and solid-liquid

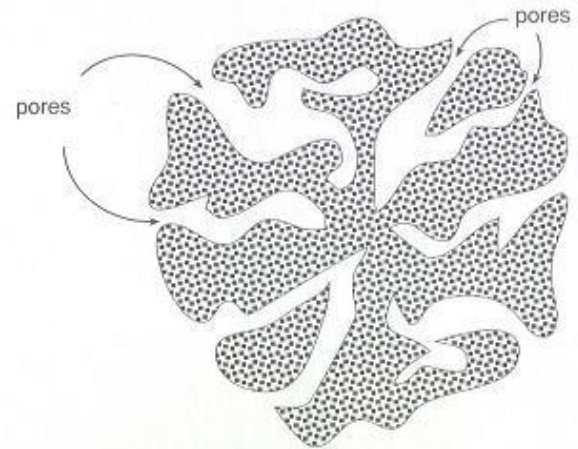
The surfaces of solids: unlike liquid, the surface of solids is rough both in microscale and macroscale. **The surface of solids is not homogeneous** and the force acting in the plane of the surface differs in different locations, and is also different in different directions.

Surface and structure of the pores affects properties of the porous material (adsorption strength, permeability, reactivity).

Specific surface - surface area per unit of mass (m^2/g).

The outer surface - geometric surface of particle (the visible part of the surface).

The inner surface - surface of the pores and cracks that permeate the particle.



Interfaces solid-gas and solid-liquid

Adsorbent - solid particles with a large adsorption capacity (i.e. large specific surface).

Physical adsorption

Molecules are bound to a solid surface by **physical forces** (van der Waals) that act between all particle types. Physical adsorption **is not specific** and is being on the whole surface of the solid.

Chemisorption

The molecules are bonded to the surface molecules of the adsorbent by **chemical bond formation**; chemisorption is **very specific** - the bond can occur only between certain molecules.

Adsorption on the interface solid - gas

When the solid is in contact with the gas, the gas molecules are always trapped on solid surface - adsorption (increasing the concentration of molecules of a substance on the phase interface).

The properties that affect the adsorption of gases on solids:

1. **Specific surface**
2. **Type of gas**
3. **The heat of adsorption** - the energy released when gas is adsorbed on a solid surface. Exothermic process. Physical adsorption - the released heat is low (about 5 kcal mol^{-1}), chemisorption - the formation of chemical bonds, the released heat is high (about $20\text{-}100 \text{ kcal mol}^{-1}$).
4. **Effect of temperature** - physical adsorption decreases with increasing temperature (Le Chatelier's principle), chemisorption can increase with temperature (activation energy).

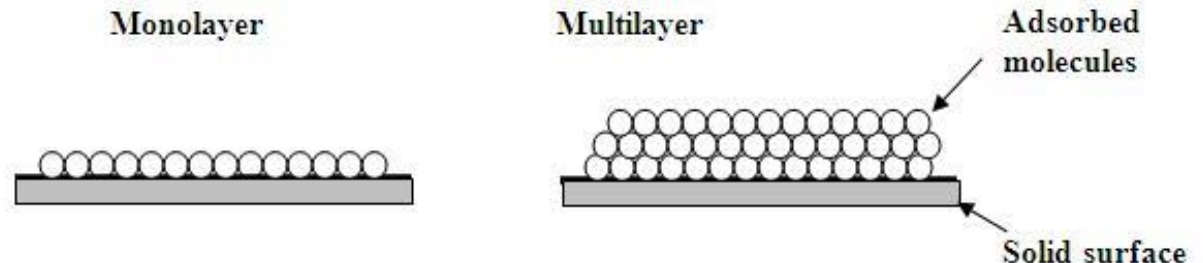
Adsorption on the interface solid - gas

The properties that affect the adsorption of gases on solids:

5. **Reversibility** - physical adsorption is reversible (adsorption / desorption), chemisorption is irreversible.

6. **Influence of pressure** – increasing pressure leads to a higher physical adsorption; reducing pressure leads to desorption. Chemisorption - the effect of pressure is negligible.

7. **The thickness of the adsorbed layer** - physical adsorption may lead to multilayer adsorption, chemisorption is monolayer (additional layers may be bound by physical forces).



Kinetics of adsorption

During adsorption the following steps occurring:

1. diffusion to the outer surface of the adsorbent
2. diffusion in pores to the inner surface of the adsorbent
3. adsorption

The slowest process determines the kinetics of adsorption.

Physical adsorption – diffusion in pores is the slowest process in porous adsorbents.

Chemisorption – chemical reaction is the slowest process.

$$k = A \cdot \exp(-E_a/RT)$$

Arrhenius equation

k - adsorption rate constant

E_a - activation energy of adsorption

A - frequency factor of adsorption

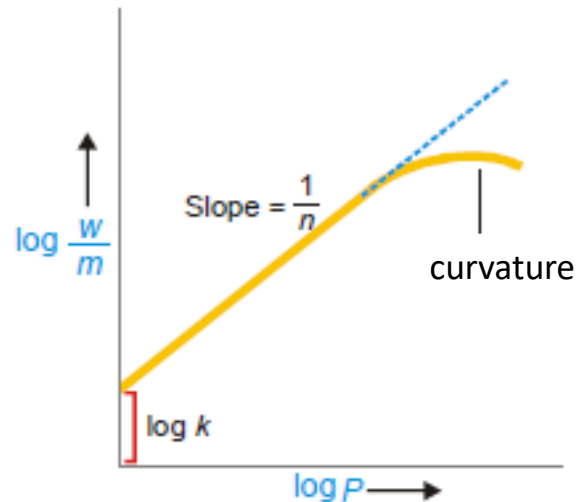
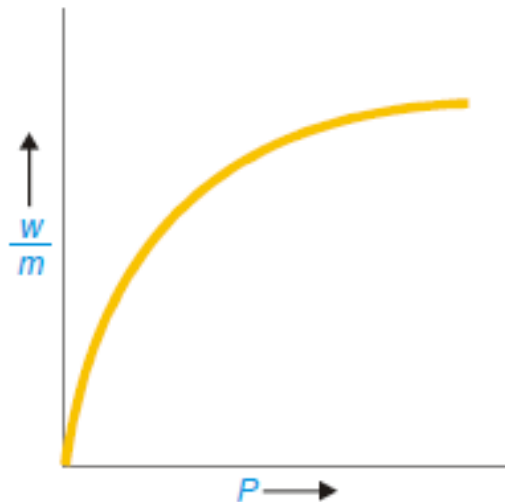
Freundlich isotherm

dependence of adsorbed amount (w/m) at equilibrium pressure p at a constant temperature:

$$w/m = k \cdot p^{1/n} \quad k, n \text{ are constants}$$

linear equation :

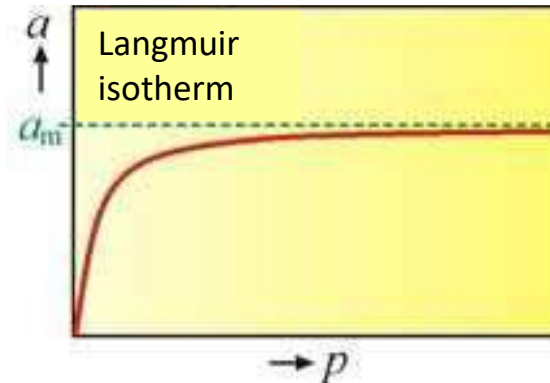
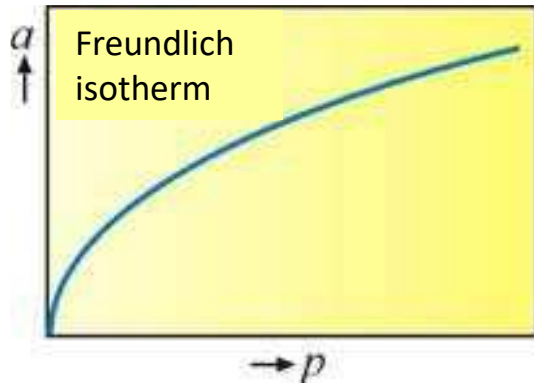
$$\log w/m = \log k + 1/n \log p$$



Limitation: **valid at low pressures**, at higher pressures deviations from linearity.

Langmuir isotherm

Adsorption at higher equilibrium pressures (concentrations) describes better Langmuir isotherm.



$$a = a_m \cdot (k \cdot p) / (1 + k \cdot p)$$

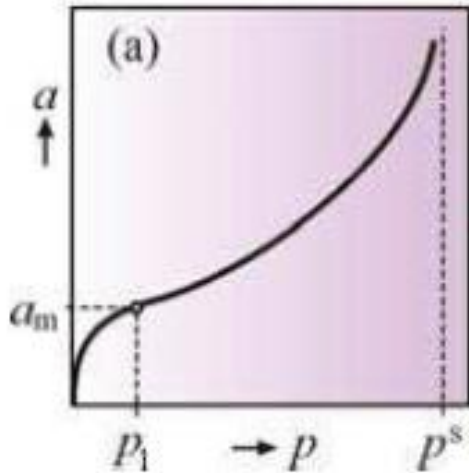
k – adsorption coefficient (it depends on temperature, adsorbent and the adsorbed gas); a_m – maximum adsorption capacity

linear equation:
$$\frac{1}{a} = \frac{1}{a_m \cdot k} \cdot \frac{1}{p} + \frac{1}{a_m}$$

Limitation: **Langmuir equation is suitable for monolayer adsorption.**

BET isotherm

Description of adsorption on planar surfaces (multiple adsorption layers.)



$$a = a_m \cdot \frac{C \cdot p_{\text{rel}}}{(1 - p_{\text{rel}})} \cdot \left(\frac{1 - (x+1) \cdot p_{\text{rel}}^x + x \cdot p_{\text{rel}}^{x+1}}{1 + (C-1) \cdot p_{\text{rel}} - C \cdot p_{\text{rel}}^{x+1}} \right)$$

a – adsorbed amount

a_m – maximum adsorption capacity (at full coverage of the surface by molecular monolayer)

C – constant (depending on the adsorption and condensation heat)

p_{rel} – the ratio of the equilibrium pressure to the saturated vapor pressure of the adsorbate

x – number of layers ($x \rightarrow 1$: Langmuir isotherm)

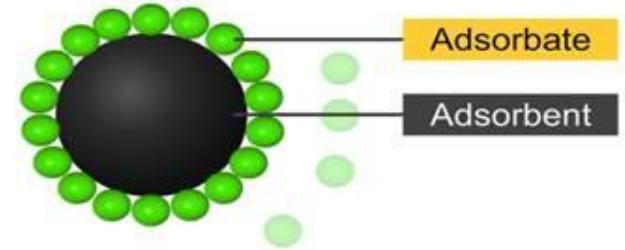
Application of adsorption isotherms: **determination of specific surface of adsorbents**

Adsorption on the interface solid - liquid

Adsorption from solutions – is manifested by the change in the composition of the solution.

S/L adsorption follows the same principles as adsorption of gases on solids:

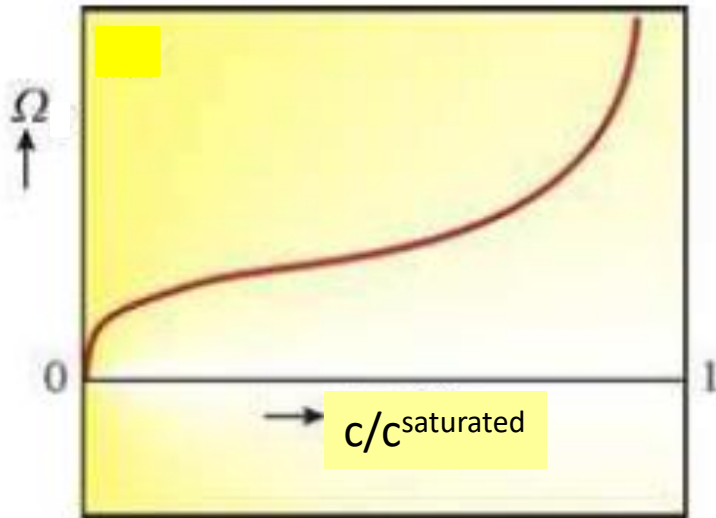
1. Certain adsorbents adsorb some solute effectively than other
2. Increase in temperature decreases the rate of adsorption (exothermic process)
3. Increase of the specific surface increases the adsorption
4. During the adsorption is established equilibrium between adsorbed amount and concentration of the adsorbate in solution



Molecular adsorption

Whole molecules are adsorbed (or both types of ions in the same extent). Molecular adsorption usually involves physical force – physical adsorption.

Adsorption isotherms



total adsorption:

$$\Omega = V_0 \cdot (c_0 - c) \quad [\text{mol}]$$

V_0 – the initial volume of the solution per 1 g of adsorbent

c_0 – concentration of the substance in the solution before adsorption

c – concentration of the substance in the solution after adsorption

$c/c^{\text{saturated}}$ – the relative concentration (ratio of equilibrium concentration to the concentration of a saturated solution)

The theoretical expression is more complex than for gases:

- Freundlich type equation
- Langmuir type equation

Molecular adsorption

The relationship between the properties of the system and adsorptivity:

1. **Polarity**: Polar substances are well adsorbed on polar adsorbents from nonpolar solutions and vice versa.
2. **Solubility**: Solute is adsorbed the more, the less it is soluble in a given solvent.

Pharmaceutical and industrial applications:

1. **Adsorption chromatography** (polar solid phase e.g. silica gel; eluent nonpolar e.g. hexane, benzene)
2. **Adsorption of toxic substances and impurities** (medicine, ecology)
3. **Drug carriers** (used e.g. for poorly soluble drugs)
4. **Drying process** (desiccants)
5. **Heterogeneous catalysis** (reactive molecules adsorbed on the surface of the catalyst)

Ion exchange adsorption

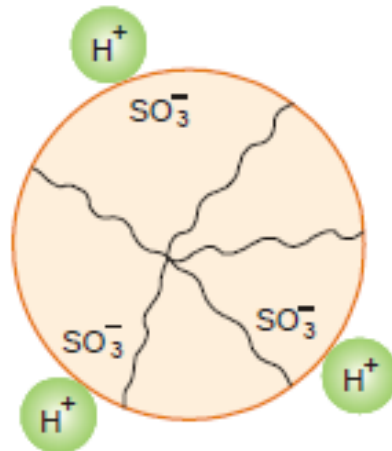
Preferably is adsorbed one of the ions from electrolyte .

The adsorbent replaces the ions adsorbed by the solution with other ions which release it into the solution.

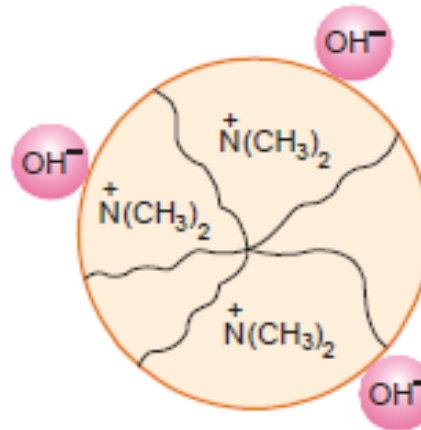
The **cation exchanger** – Polymers containing acidic functional groups.



The **anion exchanger** – polymers containing basic functional groups.



Cation exchange resin

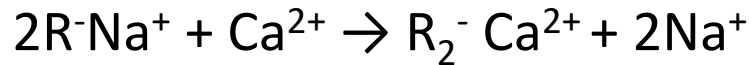


Anion exchange resin

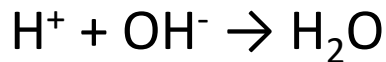
Ion exchange adsorption

Applications:

1. **Water softening** (removal of Ca^{2+} and Mg^{2+}) – industry (preventing the formation of limescale)



2. **Production of deionized water** – industry, pharmacy
- use of cation exchangers and anion exchangers



3. **Drugs based on ion exchange**

Cation exchangers: adjusting the electrolyte balance in the body (edema treatment).

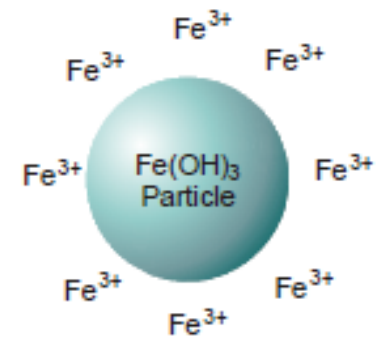
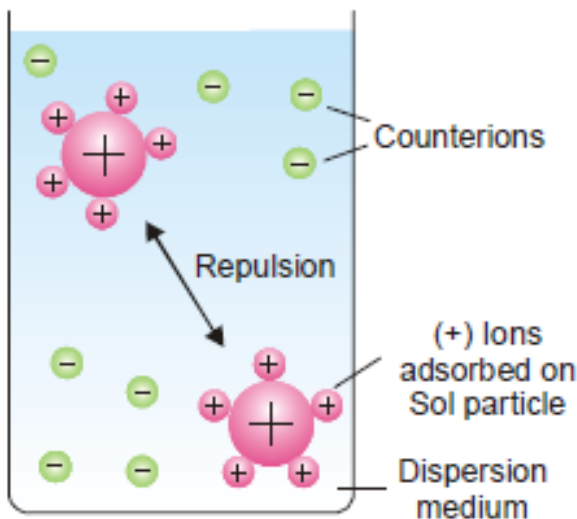
Cation and anion exchangers: treatment of intoxication.

Nicorette - ion-exchange resin to control the rate of release of nicotine

Electrical properties of the interface

The generation of electrical charge at the phase interfaces of heterogeneous systems (**colloids**) affects their stability. Some mechanisms of formation of electrical charge:

1. dissociation of functional groups in surface layers
2. preferential dissolution of one of the ions in the crystal lattice
3. adsorption one type of ions



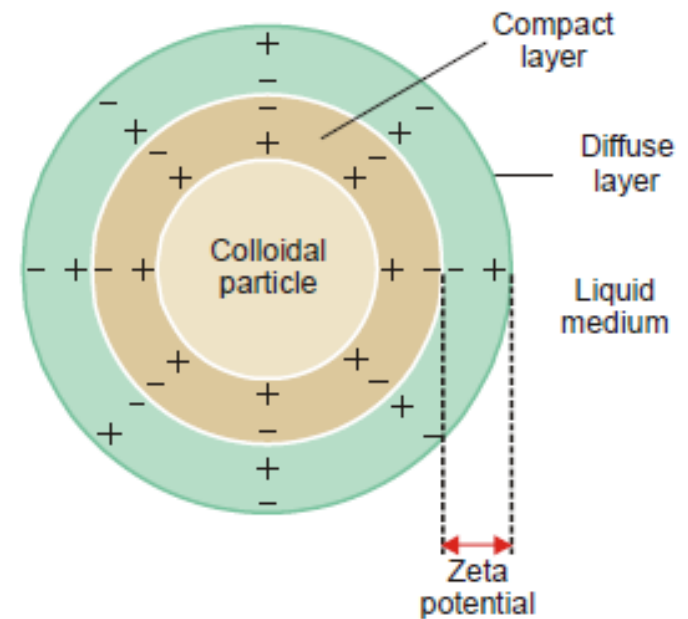
Mutual repulsion between similarly charged particles prevents the formation of aggregates – **important for the stability of colloidal systems.**

Electrical double layer

Stern model

The outer layer is bonded to the inner mainly by **adsorptive forces**. The rest of charge of the inner layer is neutralized by ions, which are bound by **electrostatic forces** (form a diffusion layer).

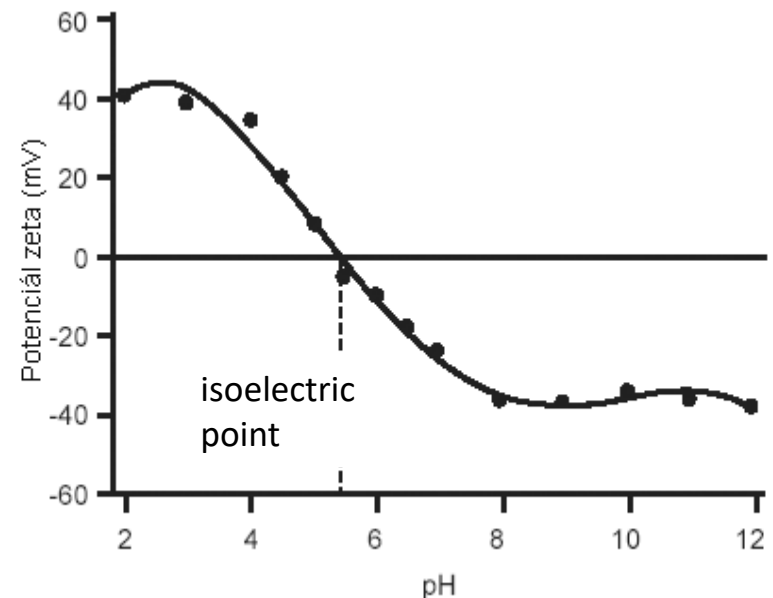
When particle is moving relative to the liquid, the inner layer and the part of outer layer which is bonded by adsorptive forces are moved together with particle. The rest of diffuse double layer is moved with the liquid. There is a difference in potential between the compact layer and the bulk of solution across the diffuse layer - **zeta potential**.



Electrical double layer

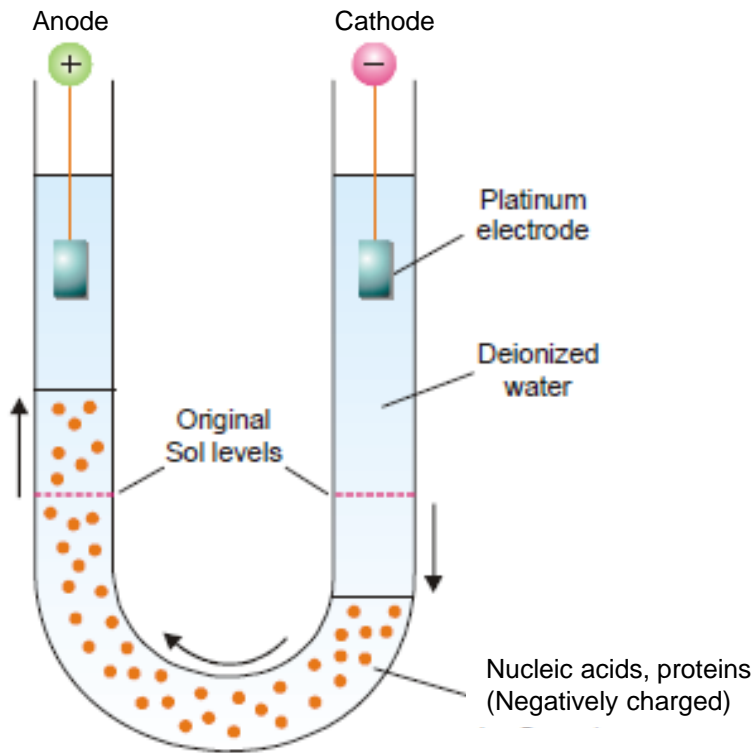
Zeta potential

- Size of zeta potential indicating the potential **stability** of the colloidal system.
- If all particles in the suspension have a large negative or positive zeta potential, then they will tend to repel each other (don't aggregated). The boundary between stable and unstable suspensions is generally taken at either +30 mV or -30 mV.
- The sign of the zeta potential is strongly influenced by the addition of electrolyte.
- Zeta potential is strongly affected by **pH** (affecting dissociation).



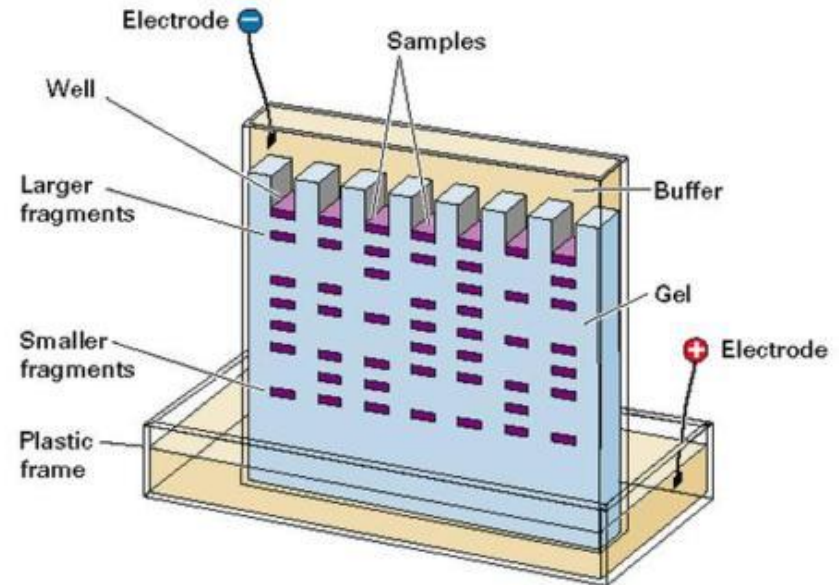
Electrokinetic phenomena

Electrophoresis



Electromigration separation methods:

- gel electrophoresis
- capillary gel electrophoresis

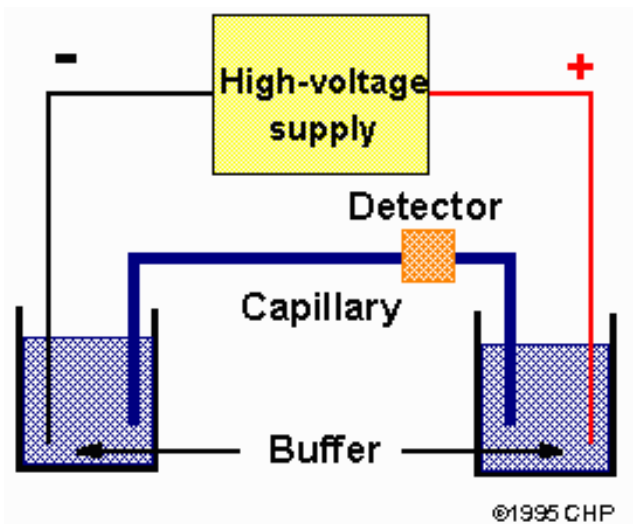


Gel electrophoresis is a method for **separation and analysis** of macromolecules (**DNA, RNA and proteins**) and their fragments, based on their size and charge. Shorter molecules move faster through the pores of the gel.

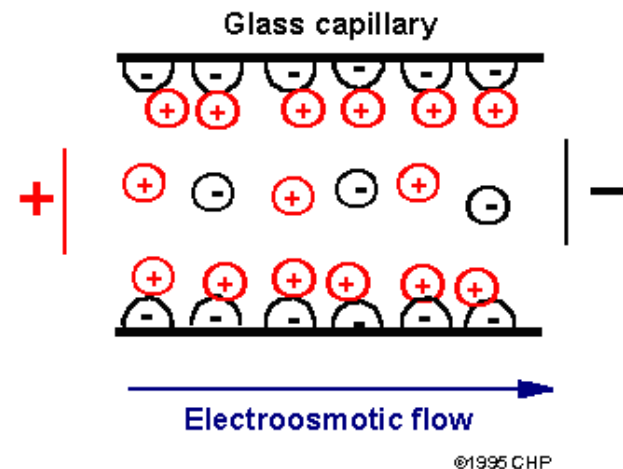
Electrokinetic phenomena

Electromigration separation methods:

- **capillary electrophoresis**



Electroosmosis: the motion of liquid induced by an applied potential across a capillary tube.



Capillary electrophoresis allows the separation of positively and negatively charged particles, but also uncharged particles (due to the **electroosmotic flow**).