Kinetic Properties

Electrokinetic (Zeta) Potential

Elektrical double-layer can be formed by several different mechanisms: adsorption of ions from the solution (typically when the ions is present also in the solid phase), ionization of surface functional groups, ion exchange between ions of similar size but of different valence, crystal splitting. Charged surface attracts ions of the opposite sign. Closest to the surface is the **Stern layer**, composed solely from the ions of opposite sign with respect to the solid phase and bound to the surface by electrostatic forces as well as by adsorption (van der Waals interaction). **Diffuse layer** is composed of both positive and negative ions with the surplus of ions opposite to the charge of the solid phase, contributing to the overall neutralization of the solid phase charge. Electrical potential decreases linearly from the surface through the Stern layer and then non-linearly in the diffuse layer, asymptotically to zero potential. Description of electrical potential in the diffuse layer is obtained from the **Gouy-Chapman theory**

$$E = E_0 \exp(x/l)$$

$$l = \left(\frac{\varepsilon_r \varepsilon_0 k_B T}{e^2 1000 N_A \sum (c_i z_i^2)} \right)^{1/2} = \left(\frac{\varepsilon_r \varepsilon_0 k_B T}{e^2 2000 N_A} \right)^{1/2} I^{-1/2}$$

l is the effective thickness of the double-layer, E_0 Stern layer potential, $e = 1{,}602 \cdot 10^{-19}$ J is the elementary charge, z_i the respective ion charge, c_i its (molar) concentration, $k_B = 1{,}38 \cdot 10^{-23}$ J/K is the Boltzmann constant, $N_A = 6{,}023 \cdot 10^{23}$ is the Avogadro constant, $\varepsilon_0 = 8{,}854 \cdot 10^{-12}$ is the permittivity of vacuum, ε_r is the relative permittivity or dielectric constant (for water and dilute aqueous solutions at 25°C $\varepsilon_r = 78{,}5$). Rising concentration of electrolyte squeezes the diffuse layer until the surface charge is completely neutralized by the Stern layer (called under these circumstances the Helmholtz layer).

If the solution is moving with respect to the solid phase, part of the diffuse layer slips, leaving a potential between the electrode and the bulk solution, called the electrokonetic potential (**ζ-potential**), which depends on the interfacial configuration (size and shape of the surface relative to the flow direction of the electrolyte).

Diffusion

Different concentration of a compound in different parts of the system leads to the spontaneous transport from the place with higher concentration to the place with lower concentration (diffusion). Driving force for diffusion other than concentration difference can be also the pressure difference (pressure diffusion) or temperature difference (thermodiffusion). Diffusion flux J (the amount of the compound that passes through unit area per unit of time perpendicular to the direction of diffusion) follows from the **Fick's first law**

$$J = \frac{dn_i}{S d\tau} = -D_i \frac{dc_i}{dx}$$

where S is the area, x is the coordinate in the direction of diffusion flow and D_i **diffusion coefficient**.

Estimation Methods: Diffusion coefficient can be estimated by the Chapman-Enskog approximation, based on the kinetic theory of gases. Parameters needed for estimation are related to the intermolecular potential parameters, expressed e.g. by the Lennard-Jones or Stockmayer potential functions. The method is described e.g. in Hirschfelder J.O., Curtiss C.F., Bird R.B.: Molecular Theory of Gases and Liquids, Wiley, New York, 1967 (and following editions).

Diffusion in fluids, especially in dispersion systems, can be described by the **Einstein-Stokes** equation

$$D_i = \frac{k_B T}{6\pi\eta^\circ r_i}$$

where η° is the solvent viscosity and r_i the particle radius (mean or effective hydrodynamic radius is used in case of polydispersion systems).

Osmosis

Two dispersion mixtures with different concentrations posses a spontaneous tendency to equilibrate the concentration in all parts of the systems. If they are divided by semipermeable membrane (permeable to the solvent, but not to the solute), solvent molecules flow from the region with lower solute concentration to the the other side of the membrane, until the concentrations are equal. Suppresing this spontaneous flow requires additional pressure at the side with lower-concentration solution. This is the **osmotic pressure**, π

$$\pi = -\frac{RT}{V_1}\ln a_1$$

where V_1 and a_1 are molar volume and activity of the solvent, respectively. Approximation for dilute solution is called **van't Hoff equation** or **Morse equation**

$$\pi = RTc_2$$

where c_2 is the solute concentration.

Viscosity

Viscosity is the resistance of a fluid to shearing flow. Shear velocity ($\tau_{xy} = F_x / S$ where F_x is the force in the direction of the flow) follows from the **Newton's law**

$$\tau_{xy} = -\eta\frac{dv_x}{dy}$$

where v_x is the flow speed, y is the coordinate perpendicular to the flow direction and η is a constant called dynamic viscosity (unit Pa·s). Kinematic viscosity is defined as $\upsilon = \eta / \rho$, where ρ is the fluid density.

Estimation Methods: Dynamic viscosity can be also estimated from the Chapman-Engskog approximation (see above). Several structure-activity relationships (group contribution methods) were developed mainly for organic fluids, see e.g. the monograph
Poling B.E., Prausnitz J.M., O'Connell J.P.: The Properties of Gases and Liquids, 5th Edition, McGraw-Hill, New York, 2002.
Einstein equation can be applied in case of dilute dispersion systems

$$\eta = \eta^\circ\left(1 + 2{,}5\varphi\right)$$

where φ is the volume fraction of the dispersion (mass fraction and density of the dispersion particles must be known for its calulation).