Polymer solutions

Model of the ideal chain:
- beads are connected by flexible bonds/angles/torsions
- beads far enough do not interact (by solvent-mediated effective interaction)

Better models:
- repulsive forces \(\rightarrow\) excluded volume (beads do not overlap)
- attractive forces \(\rightarrow\) “negative excluded volume” (beads are “sticky”)

Electrokinetic phenomena

- electroosmosis – motion of an ionic solution through a porous material or capillary induced by an applied electric field (electroosmotic flow); if pressure is applied against: electroosmotic pressure
- reversed: flow of the solution produces an electroosmotic potential
- electrophoresis – motion of a colloid particle in an ionic solution induced by an applied electric field
- reversed: sedimentation potential or current

Different is the electrocapillarity, change of the surface tension with applied voltage (e.g., mercury)
movie: jchemed.chem.wisc.edu

Electroosmosis

Smoluchowski (also Helmholtz–Smoluchowski) equation:
\[
v = \frac{\epsilon \zeta}{\eta} E
\]

Eq. (1) also holds for electrophoresis provided that the particles are large enough and distant (\(\gg \lambda\)); for small particles \(\rightarrow\) ionic conductivity.
Eqs. (1) and (2) are used to measure the \(\zeta\) potential
Colloid stability requires \(|\zeta| > 40 \text{ mV}\).

Izoelectric point: the concentration of ions or pH so that \(\zeta = 0\) (\(\approx\) a particle is not charged) – typical for polyelectrolytes (proteins with both \(-\text{NH}_2\) and \(-\text{COOH}\)). Smallest repulsion – best folded

Example. Small cavities in a solution of soap move towards the anode

Emulsions

Types:
- O/W (oil-in-water): less polar liquid (oil) in a more polar liquid (water)
- W/O (water-in-oil)

Examples: milk, mayonnaise, cutting fluids (for metals)

Most properties given by the continuous phase (medium): conductivity, wetting, dissolution of dyes

Concentrated emulsions must be stabilized by an emulsifier – surfactant, e.g., lecithin (phosphatidylcholine)

Instability: flocculation (aggregation, elst. bound), coalescence (of droplets), creaming (sedimentation), Ostrwald ripening

Double layer

Two layers of a surfactant; cell membrane = phospholipide double layer (glued together by the hydrophobic ends, usually 2D liquid)

vesicle – liquid inside, artificial: liposome, drug transport

Langmuir–Blodgett films
more (double) layers, usu. 2D crystal

- model of biomembrane, glucose sensor, microelectronics, anti-reflective coating
Phase transition classification

- 1st order: slope change of $G$, discontinuity in enthalpy, density (crystallization, vaporization, ...)
- 2nd order: Ehrenfest: discontinuity in enthalpy, density; higher derivatives modern: higher derivatives diverge ("continuous") (critical point [CP], Curie point, lambda-transition He)
- 3rd order ("continuous"): e.g., Kosterlitz–Thouless (some 2D systems): all derivatives continuous $f(\alpha) = 1 - \alpha^{1/4}$ pro $\alpha > 0$

Glass transition = viscosity $> 10^{12} \text{Pa s}$ – not a phase transition
Micelle crystallization (to a laminar/fibrilar phase) is 1st order phase transition

Foams

- Gas in liquid
  - wet foams (spherical cavities, "bubbles")
  - dry foams (polyhedra, 12–14)
- Gibbs–Plateau channels
- Plateau rules (see lecture 10)

Stabilized by surfactants
destabilization: gravity, evaporation, Ostwald ripening, film rupture
Dry foams (styrofoam)

Aerosols

- Liquid dispersion: fog (10 nm – 10 µm)
- Solid dispersion: smoke (to 10 µm), dust (above 10 µm)

Destabilization:
- sedimentation (stabilized by sun radiation: heated)
- coagulation (stabilized by el. charge)

Particle charge: (electro)spaying (nozzle, wind+sea), ionization by UV, grinding of ionic crystals
Aerosol of flammable dust may explode (flour, coal)

Gels

Connected 3D network of the dispersed phase (and the medium), do not flow
Generally **lyogel**, in water **hydrogel**, (dried) xerogel

reversible gel: gel swelling

sometimes reversibility refers to the sol → gel process
gelatinization of macromolecule solutions:
- cross-linking by chemical bonds
- association (vdW, H-bonds)
- crystalline links
- geometric (entanglement)
destabilization of (lyophobic) sols with linking (not coagulation)
older gels: syneresis (swelling of the structure – yoghurt)

Aerogel = xerogel with a very low density (supercritical drying), silica gel to 1.9 g dm$^{-3}$; alumina; aerographite 0.18 g dm$^{-3}$ – ultimate tensile strength 1 kPa
Use: insulation, adsorbent, Cherenkov detector

Atmospheric aerosols

- clouds
  - nucleation of droplets around dust, ions, salts ($\left(\text{NH}_4\right)_2\text{SO}_4$ most typical)
polarizable anions at surface of droplets
- solid aerosols
  - most stable $\approx 300$ nm:
    - smaller particles diffuse fast and get adsorbed
    - larger particles sediment particles < 10 µm (PM10, aerodynamic diameter) are not filtered in the nose, may penetrate to alveoli and (smaller ones) to the blood

- smog (c smoke and fog):
  - London (reduction) type (smoke, fog, SO$_2$): sox = volcanic smog
  - photochemical (ox.) smog (L.A.): NO$_x$ + VOC + hv → O$_3$ + ...

stratosphere
- soot (does not sediment because heated)
- volcanic ash, SO$_2$ → SO$_4^{2-}$ (→ cooling)

nuclear winter (soot), volcanic winter (ash, SO$_4$)