Colloid stability.
Lyophobic sols. Stabilization of colloids.
Lyophilic and lyophobic sols

• Sols (lyosols) are dispersed colloidal size particles in a liquid medium (=solid/liquid dispersions)

• These sols can be
  • Lyophilic: strong interactions exist between the particles and the solvent (the particles are wetted)
    - Thermodynamically stable
  • Lyophobic: little or no interactions between the particles and the solvent (partially wetted or unwetted particles)
    - Thermodynamically unstable
    - Can be kinetically stable or unstable
Solutions and dispersions

- Mixing is **spontaneous**.
- Mixing is **reversible**.
- Thermodynamically **stable**.
- Inhomogeneities on molecular levels.

Properties of the real solutions are **independent on the way** these solutions are prepared.

- Mixing is **non-spontaneous** (requires mechanical energy).
- Mixing is **irreversible**.
- Thermodynamically **unstable** (requires a stabilizing agent) and unmix spontaneously.
- Inhomogeneities on large length scales compared to molecular dimensions.

Properties of the colloidal dispersions are strongly **dependent on the way** they are prepared → for repeatability, empirical preparation procedures are followed.
Thermodynamical stability

- Solutions are _thermodynamically stable_
  - Gibbs energy of the components before mixing is higher than after mixing ($\Delta G < 0$)
- Dispersions are _thermodynamically unstable_
  - The Gibbs energy increases by mixing ($\Delta G > 0$)
  - But if unmixing is slow enough → _kinetically stable_ dispersions
In an unstable system the particles may adhere to one another and form aggregates of increasing size that may settle out under the influence of gravity. An initially formed aggregate is called a floc and the process of its formation flocculation. The floc may or may not separate out. If the aggregate changes to a much denser form, it is said to undergo coagulation. An aggregate usually separates out either by sedimentation (if it is more dense than the medium) or by creaming (if it less dense than the medium). The term’s flocculation and coagulation have often been used interchangeably. Usually coagulation is irreversible whereas flocculation can be reversed by the process of deflocculation.
Coagulation or flocculation

a) The suspended particles settle out and form a firm, dense mass (cake). The cake cannot be redispersed by gentle agitation.

b) The suspended particles form light, fluffy agglomerates held together by strong van der Waals forces. The flocculated particles settle rapidly forming a loosely adhering mass with a large sediment height. Gentle agitation will easily resuspend the particles. Weak flocculation requires strong adhesion and a zeta potential of almost zero.
Strength of interparticle forces

**Encounters** between particles occur as a result of **Brownian motion** and stability of a suspension is determined by the interaction between particles during these encounters.

Stability depends on the **balance of attractive and repulsive interactions**.

**Attraction** comes from van der Waals forces between particles.

**Repulsion** is a consequence of interaction between **similarly charged** electric double layers and/or **particle-solvent affinity**. Repulsion prevents particles to get close enough and attach.
Stability of lyophobic sols

- Lyophobic sols are thermodynamically unstable.
- However, there are stabilizing factors → kinetical stability can be attained.
- Whether aggregation does or does not occur depends on the balance of attractive and repulsive forces.

\[ \vec{F} = \vec{F}_A + \vec{F}_R \]

- For stabilization to occur, the repulsive forces must dominate.
Electrostatic and steric stabilization

$V_R$  
Electrostatically stabilized

$V_S$  
Sterically stabilized

All particles naturally attract each other. Electrical charges or attached polymer layers screen the attraction.
There is attraction between atoms/molecules even in vacuum ($V_A$: attraction potential)

$$V_A(r) = \frac{\text{const}}{x^6}$$

Dispersion attraction between atoms/molecules is additive so it effects in case of macroscopic bodies too.

The attraction depends on the geometry of the particles

$$V_A(x) = -\frac{A}{12\pi x^2}$$

$A$ is the Hamaker constant (or attraction parameter)
The attraction of bodies arises from London (dispersion) attraction of molecules (all molecules act independently).

- The effect is *additive*: one molecule of the first colloid has a van der Waals attraction to each molecule in the second colloid, *the total force is the sum of all forces*.
- An *attractive energy curve* is used to indicate the variation in van der Waals force with distance \( (x) \) between the particles.
Effective Hamaker constant

The Hamaker constant \( A \) in vacuum depends on material properties: density, polarizability.

An attractive energy or attractive potential curve is used to indicate the variation in van der Waals force with distance between the particles.

\[
V_A(x) = -\frac{Ar}{12x}
\]

\[A_{\text{eff}} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2\]

Order of magnitude \(10^{-20} - 10^{-21} \text{ J}\)

The effective Hamaker constant \( A_{\text{eff}} \) also depends on the dispersion medium.
Particles of the same charge

Most of the time the shear plane is close enough to the Stern plane, so we can consider \( \zeta \approx \Psi_{St} \)

\[
\Psi = \Psi_{St} e^{-\kappa(x - x_{OHP})}
\]

OHP: outer Helmholtz plane = Stern plane
The loosely held countercharges form “electric double layers”. The electrostatic repulsion results from the **interpenetration** of the diffuse part of the double layer around each charged particle.

An electrostatic repulsion curve is used to indicate the energy that must be overcome if the particles are to be forced together.

\[ V_R(x) = \Psi_0^2 e^{-\kappa x} \]
The Balance of Repulsion & Attraction (DLVO theory)

Notice the secondary minimum. The system flocculates, but the aggregates are weak. This may imply reversible flocculation.

The point of maximum repulsive energy is called the energy barrier. Energy is required to overcome this repulsion. The height of the barrier indicates how stable the system is. The electrostatic stabilization is highly sensitive with respect to surface charge ($\zeta \sim \psi \sim \text{pH}$) and salt concentration ($\kappa, z$).

$$\gamma = \frac{e^{-\frac{ze \Psi_{\text{St}}}{2kT}} - 1}{e^{-\frac{ze \Psi_{\text{St}}}{2kT}} + 1}$$

$$V_T = V_A + V_R$$

$$V_A(x) = -\frac{Ar}{12x}$$

$$V_R(x) = r(kT)^2\gamma^2z^{-2}e^{-\kappa x}$$
Van der Waals attraction will predominate at small and at large interparticle distances. At intermediate distances double layer repulsion may predominate, depending on the actual values of the forces. In order to agglomerate, two particles on a collision course must have sufficient kinetic energy due to their velocity and mass, to “jump over” this barrier.
An increase in electrolyte concentration leads to a compression of the double layer ($\kappa$ increase) and so the energy barrier to coagulation decreases or disappears. If the barrier is cleared, then the net interaction is all attractive, and as a result the particles coagulate. This inner region is after referred to as an energy trap since the colloids can be considered to be trapped together by van der Waals forces.

Ionic strength: $I_1 < I_2 < I_3 < I_4 < I_5$
Inverse Debye length: $\kappa_1 < \kappa_2 < \kappa_3 < \kappa_4 < \kappa_5$
Critical coagulation concentration

What concentration of salt \( (n_0) \) eliminates the repulsive barrier?

If the potential energy maximum is large compared with the thermal energy, \( kT \) of the particles, the system should be stable; otherwise, the system should coagulate.

<table>
<thead>
<tr>
<th>As(_2)S(_3) (−ve sol)</th>
<th>AgI (−ve sol)</th>
<th>Al(_2)O(_3) (+ve sol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>LiNO(_3)</td>
<td>NaCl</td>
</tr>
<tr>
<td>NaCl</td>
<td>NaNO(_3)</td>
<td>KCl</td>
</tr>
<tr>
<td>KCl</td>
<td>KNO(_3)</td>
<td>KNO(_3)</td>
</tr>
<tr>
<td>KNO(_3)</td>
<td>RbNO(_3)</td>
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</tr>
<tr>
<td>K acetate</td>
<td>(AgNO(_3))</td>
<td></td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>Ca(NO(_3))(_2)</td>
<td>K(_2)SO(_4)</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>Mg(NO(_3))(_2)</td>
<td>K(_2)Cr(_2)O(_7)</td>
</tr>
<tr>
<td>MgSO(_4)</td>
<td>Pb(NO(_3))(_2)</td>
<td>K(_2) oxalate</td>
</tr>
<tr>
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<td>Al(NO(_3))(_3)</td>
<td>K(_3)[Fe(CN)(_6)]</td>
</tr>
<tr>
<td>1/3Al(_2)(SO(_4))(_3)</td>
<td>La(NO(_3))(_3)</td>
<td></td>
</tr>
<tr>
<td>Al(NO(_3))(_3)</td>
<td>Ce(NO(_3))(_3)</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.1 FLOCCULATION CONCENTRATIONS IN millimoles PER dm\(^3\) FOR HYDROPHOBIC SOLS\(^{116}\)

(By courtesy of Elsevier Publishing Company)

Counterion valency c.c.c (in mol/l) \( \sim Z^{-6} \)

c.c.c. is the concentration of salt that just eliminates the repulsive barrier.
The Schulze–Hardy Rule states:
the critical coagulation concentration (c.c.c.) inversely depends on the sixth power of the charge on the ions.

\[
c_{\text{monovalent}} : c_{\text{divalent}} : c_{\text{trivalent}} = 1 : 2^{-6} : 3^{-6} = 1 : 0.015 : 0.0014
\]

Figure 8.2. The influence of electrolyte concentration \( \kappa \) on the total potential energy of interaction of two spherical particles\(^{118, 121}\)

\[
a = 10^{-7} \text{ m} \quad T = 298 \text{ K} \\
A = 10^{-19} \text{ J} \quad s = R/a (R = \text{distance} \\
\psi_0 = 25.6 \text{ mV} = \frac{kT}{e} \quad \text{between centres of spheres)
\]
Strength of interparticle forces – Rates of coagulation

Rates of coagulation can be measured by the change in the number of particles, Smoluchowski equation:

\[-\frac{dN}{dt} = 8\pi DaN^2 = k_d N^2\]

If there is an energy barrier, \( V_{\text{max}} \) to coagulate then a fraction (\( \alpha \)) of collisions is unsuccessful, so the rate of coagulation slower, \( k_s \).

\[\alpha \approx \exp \left(-\frac{V_{\text{max}}}{kT}\right)\]

\( k_d \) is the rate of the diffusion limited aggregation or rapid coagulation (no barrier, \( V_{\text{max}} = 0 \))

The stability ratio: \[ W = \frac{k_d}{k_s} \]

The stability of dispersion is increased by: increase in particle radius, increase in electrokinetic potential (\( \zeta > 25\text{mV} \)), decrease in Hamaker constant, decrease in the ionic strength, decrease in temperature.

\( t \): time, \( N_p \): number of single particles per unit volume, \( D \): diffusion coefficient, \( k_d \): rate constant, \( k_B \): Boltzmann constant, \( T \): temperature, \( V_{\text{max}} \): maximal rate of aggregation
Elementary acts of coagulation:

\[ N \text{ decreases with time, while their size increases.} \]

\[ VN = \text{constant} = V_0 N_0 \quad V \sim 1/N \]

\[ -\frac{dN}{dt} = kN^2 \quad \rightarrow \quad \frac{1}{N} - \frac{1}{N_0} = k t \]

If all flocculation rate constants are the same

\[ N / N_0 = \frac{1}{1 + kN_0 t / 2} \]

Rate can be measured through decreasing the total number -dN/dt or increasing the average volume, dV/dt for example by turbidity as a function of time.

Turbidity~ \( V^2 N \sim V (VN) \sim V \text{ constant} \)

http://apricot.polyu.edu.hk/~lam/dla/
Steric stabilization

Electrostatically stabilized

Sterically stabilized

All particles naturally attract each other.
Electrical charges or attached polymer layers screen the attraction.
Lyophilic macromolecules as stabilizers

Protective action of adsorbed macromolecules (natural or synthetic)

\[ V_S = V_M + V_{VR} \]

Polymer thickness

Work is required to push the particles closer together than their polymer layers keep them apart.
Steric stability

One factor of steric stabilization is the tail size.

$V_S + V_A \quad $ Steric + attractive interaction

Compression (Volume restriction)

Steric repulsion

Long tail

Short tail

Only 1 minimum: flocculation

One factor of steric stabilization is the tail size.
Steric stabilization by surface bound polymers is:

- not sensitive to surface charge and salt concentration
- works also in non-aqueous media
- works also in concentrated dispersions

Disadvantage: more difficult to prepare.

\[ V_T = V_A + V_S \]
\[ V_R = 0 \]
How to avoid coagulation

The stabilizing polymer must be in a good solvent environment

\[ V_S = V_M + V_{VR} \]

\[ V_T = V_A + V_S \]

Segments in the tail can move freely or can not, the interaction between segments themselves is stronger or smaller than than interaction between the segments and the solvent.
Sterically stabilized dispersions are stable when the polymer is soluble – the one phase regions.

- The worse the solvent, the more unstable the colloidal dispersion. Cross-over from stabilization to flocculation: \( \theta \) solvent, \( \theta \) temperature

**Configuration of adsorbed polymers**

- Homopolymers
- Random copolymers
- Block copolymers: Two or three segments are common.
- Grafted polymers: Polymers may be attached to or grown from the surface.

*Chemical adsorption*
Steric + electrostatic stabilization

It can be achieved by polyelectrolytes, gelatin, protein... or by charged surface + neutral polymers (caution about zeta potential)

\[ V_T = V_A + V_R \]

Plane of shear \( \Rightarrow \zeta \) potential

\[ V_T = V_A + V_R + V_S \]

Plane of shear is pushed out, farther
Bridging flocculation

Good adsorbent, good solvent, (very) low polymer density, (very) long polymers

The long polymers ‘bind’ the colloids together in open flocs. Application: water purification (in practice, a few ppm of cationic polyelectrolyte is added, since most natural colloid surfaces are negative)
The isoelectric point of casein is 4.6. Lyophilic sols’ stability comes from solvation + charge. If solvation interaction alone is strong enough the colloids stay stable at its isoelectric pH if it is not they coagulate at their isoelectric pH.

Gelatin is stable at its isoelectric condition so called isostable colloids, but it can be precipitated with much more salt or dehydration agent (acetone, alcohol).

Casein is unstable at this isoelectric pH where there is no charge, this is an isolabile protein. Casein precipitates at iep where there is no repulsion.

The isoelectric point of casein is 4.6.

The fermentation of milk sugar (lactose) produces lactic acid, which acts on milk protein to give yoghurt its gel-like texture.