



Colloids

1. Terminology, definitions, clasification

Colloid systems (or simply colloids) – dispersions systems, mostly bi-components, looking as physically uniform, but if fact they are not molecularly dispersed.

Thus, although colloid is a substance microscopically dispersed evenly throughout another one, it consists of **two separate phases: a dispersed phase** (or internal phase) and **a continuous phase** (or dispersion medium, solvent).

The size of dispersed phase is between **1nm – 1000 nm** (1 μ m). They are in the range between molecular size (that in solutions) and mechanical dispersions (suspensions). They can be mono-dispersed or poly-dispersed.

Colloidal systems may be solid, liquid, or gaseous. They can be classified as shown in Table 1.

Table 1. Classification of colloid systems

Continuous phase	Internal phase	Name	Examples
Gas	Gas	Does not exist, all gases are mutually miscible	
	Liquid	aerosol	fog, mist, hair sprays
	Solid	solid aerosol	smoke, cloud, air particulates
Liquid	Gas	foams, sols	whipped cream, shaving cream, detergent foam
	Liquid	lyosols, emulsoids	milk, mayonnaise, hand cream, gelatins, proteins
	Solid	lyosols, suspensoids	pigmented ink, blood, metal sols, sulfides, $\text{Me}(\text{OH})_y$, Me_xO_y
Solid	Gas	solid foams	aerogels, styrofoams, pumice, gas occlusions in minerals
	Liquid	solid foams, gels	agar, gelatin, jelly, silicagel, opal
	Solid	solid sols	cranberry glasses, microcosmic salt bead, NaCl crystals impured with colloidal metallic Na particles.

2. Occurrence of colloid systems

In living nature: proteins, pectins, carbohydrates.

In animate nature: clays, fog, smog, volcanic ash.

Synthetic colloidal substances: soaps, dyes, colloidal sulphur, hydroxides of metals.

Chemical compounds having molecules of colloidal size: macromolecules, starch, cellulose, rubber, keratin, collagen, polymers (polystyrene, poly(vinyl chloride), polyamides, polycarbonates, polyurethanes)

The most popular are colloidal systems with a liquid as the dispersing phase – called colloidal solutions (liosols or sols):

⇒ **hydrosols** – water is a dispersing phase,

⇒ **organosols** – organic liquid is a dispersing phase.

Depending on *the interactions between the dispersed phase and the dispersing phase* colloids are classified:

⇒ **liophobic (hydrophobic)** – the colloidal particles are not solvated (or hydrated – in the case of water) by a dispersing phase,

⇒ **liophilic (hydrophilic)** – are strongly solvated (hydrated) and therefore are stable and less sensitive to coagulating agents.

2. Occurrence of colloid systems

Colloids can be also classified as:

- ⇒ **Phase colloids** – the colloidal particles are larger than the individual chemical molecule or atom which forms the particle, e.g. sol of gold or silver, metal oxides, emulsions.
- ⇒ **Molecular colloids** – they are dispersed molecularly in a solvent but size of the molecules is sufficiently large (macromolecules) to behave as the colloidal system. The molecules may not have electric charge, e.g. proteins, gelatine, polymers.
- ⇒ **Association colloids (micellar)** – they consist of associated molecules forming micelles, e.g. sodium dodecyl sulphate (SDS), Fig. 2.1.

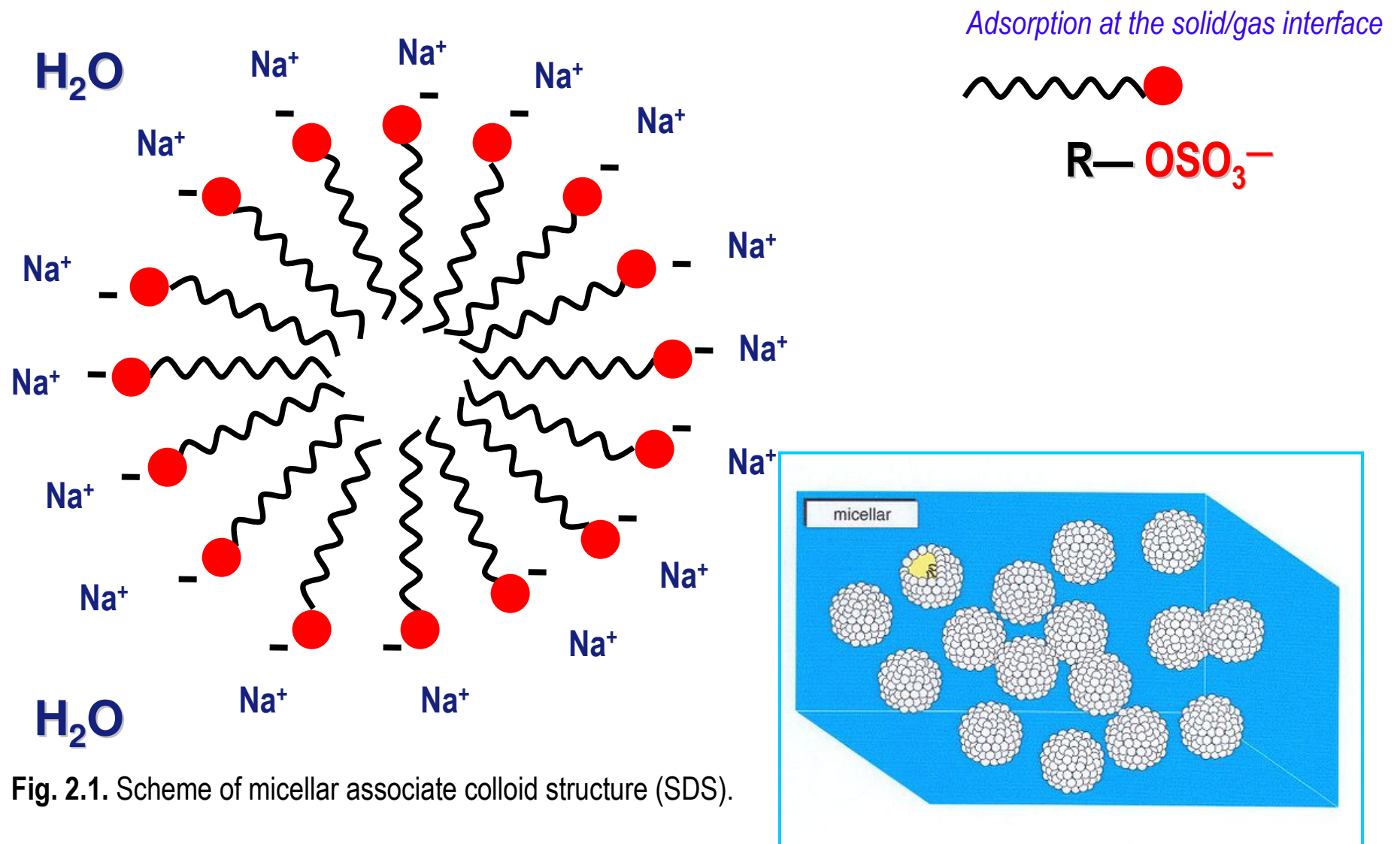


Fig. 2.1. Scheme of micellar associate colloid structure (SDS).

Fig. 2.2. Schematic of a micellar solution showing spherical micelles distributed in water (solvent) and having no long range positional order. [http://en.wikipedia.org/wiki/Micellar_solutions]

3. Methods for colloids preparation

There are **two groups of colloids preparation**: by **dispersion** and **condensation**.

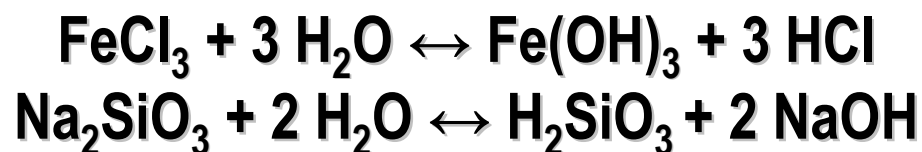
Dispersion methods

- a) **Mechanical grinding** – in colloidal mill (low efficiency)
- b) **Dispersion in electric arc** (sols of metals), by ultrasounds, irradiation
- c) **Peptization** – conversion of freshly precipitated sediment into sol with help of a suitable electrolyte.

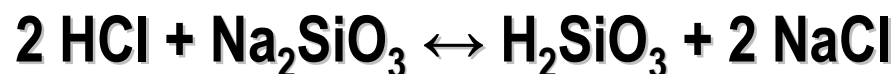
3. Methods for colloids preparation

Condensation methods (mostly chemical methods)

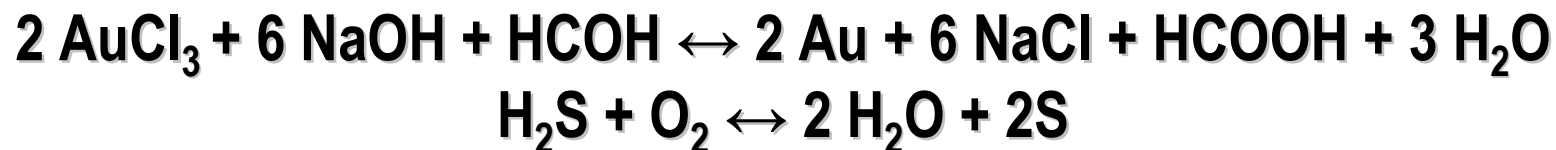
a) **Salt hydrolysis** – at elevated temperatures hydrosols of hydroxides and oxides and silicic acid can be obtained:



b) **Exchange reactions** – under suitably chosen conditions colloidal substance can be obtained:



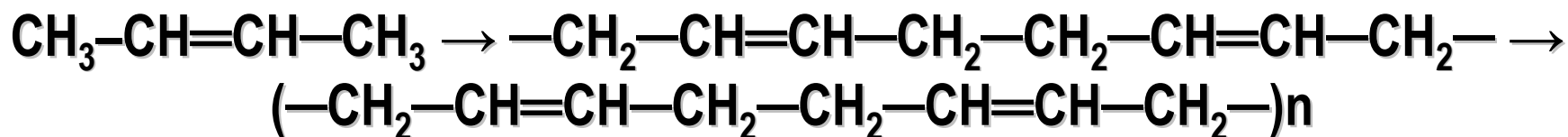
c) **Redox reactions:**



3. Methods for colloids preparation

Condensation methods (mostly chemical methods)

d) **Polymerization reaction**, e.g. polymerization of divinyl to rubber:



or polymerization of formaldehyde to polyoxymethylene:



e) **Reduction of solubility** – by adding a dispersing medium (solvent) in which the colloidal component is less soluble causes formation of this component sol, for example by dropping sulphur solution in ethanol to water.

4. Properties of colloidal systems

Optical properties

The most characteristic property are Brownian movements (motions) which are random movements of particles suspended in a fluid (i.e. a liquid - water or a gas - air) system.

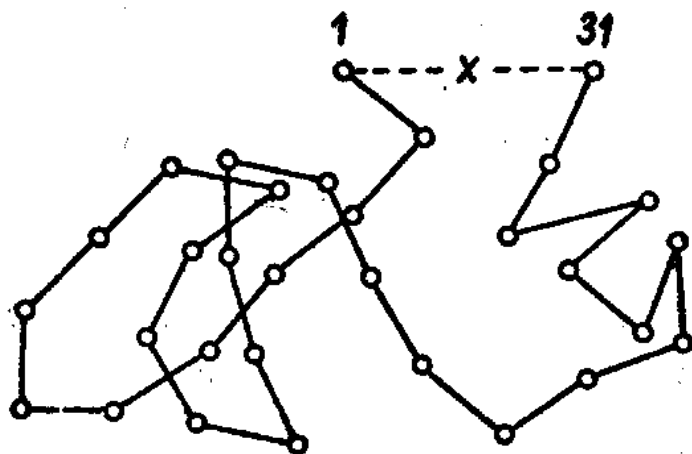


Fig. 4.1. Brownian 1 – 31 subsequent movements of colloidal particle through

The theory of Brownian motion based on the kinetic theory of matter was elaborated by **Einstein** and **Smoluchowski**.

The resulting equation correlates average square distance (movement) $\overline{(\Delta x)^2}$ at identical time intervals.

$$\overline{(\Delta x)^2} = \frac{RT}{N} \frac{t}{3\pi\eta r} \Rightarrow \overline{\Delta x} = \sqrt{\frac{RT}{N} \frac{t}{3\pi\eta r}} \quad (1)$$

where $\overline{\Delta x}$ is average projection path of the particle on the axis x, η is viscosity of the medium, r is radius of the moving particle, t is time, N is Avogadro's number.

For example: $T = 293$, $r = 1\text{nm}$, $\eta = 0.010\text{ cP (g m}^{-1}\text{ s}^{-1})$, $\overline{\Delta x} = 6.5 \cdot 10^{-6}\text{ cm}$.

Tyndall effect (or Tyndall scattering), named after the 19th century physicist John Tyndall) – is caused by reflection of light by very small colloidal particles in a transparent medium.

If the wavelength of the light is larger than the particle size, the light beam thrown on a colloidal, visually transparent system is scattered by the particles present there as the dispersed phase.

The dispersed light can be observed from side view normal to the throwing light. In liquids the Tyndall effect can be observed by using a laser pointer when directed on a sol, such as colloidal silver chloride, then the beam of the laser can be easily seen as it travels through the liquid.

It is similar to the Rayleigh scattering, in that the intensity of the scattered light depends on the fourth power of the frequency, so blue light is scattered more strongly than red light.

In other words, the longer-wavelength light is more transmitted while the shorter-wavelength light is more reflected via scattering.

Tyndall effect

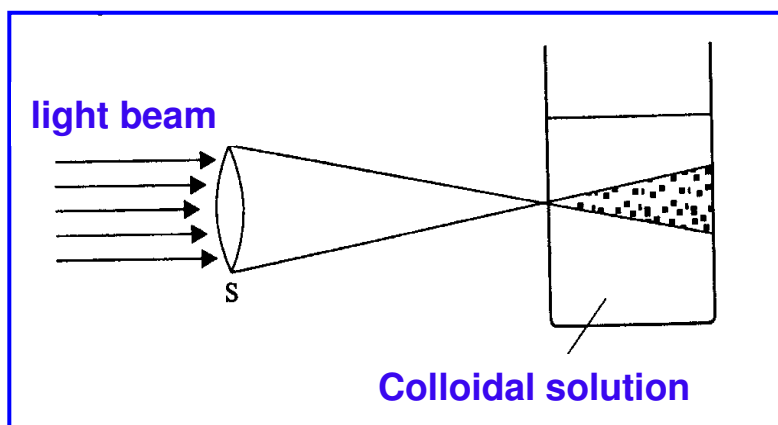


Fig. 4.2. Scheme of Tyndall effect

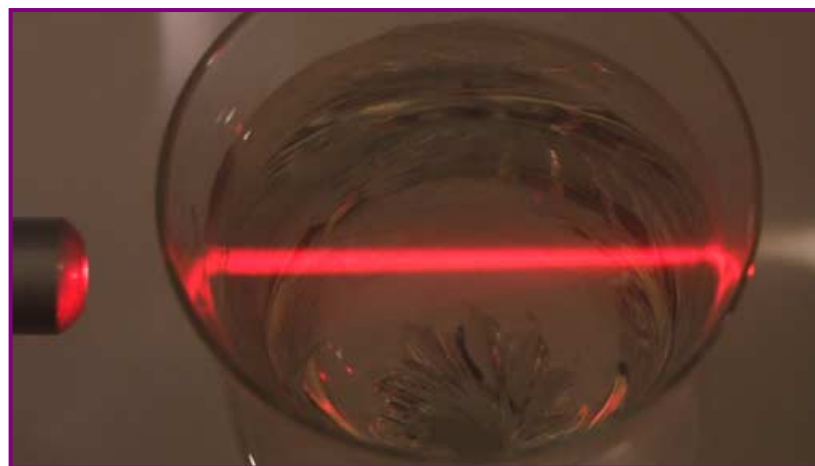


Fig. 4.3. Tyndall effect can be seen here using a laser pointer.

The glass on the left contains 5 ppm of colloidal silver and the one on the right is from the tap after the bubbles have settled out.

[<http://silver-lightning.com/tyndall/>]; [www.silverwell.com.au/Making-CS.html]

5. Methods of colloids purification

Dialysis and electro dialysis

These are the methods of purification of colloidal systems.

The separation of smaller molecules from larger ones or of dissolved substances (electrolytes) from colloidal particles in a solution by selective diffusion through a semi-permeable membrane.

For example, ions can move through the membrane (diffuse) but larger colloidal particles cannot pass.

The 'impurities' slowly diffused out of the bag leaving behind pure colloidal solution. The distilled water is changed frequently to avoid accumulation of the impurities, otherwise they may start diffusing back into the bag. Heating and stirring speed up the process.

Dialysis and electro dialysis

Nevertheless, still the ordinary process of dialysis is slow. To increase the process of purification by dialysis the electric field can be applied. This process is called electro dialysis.

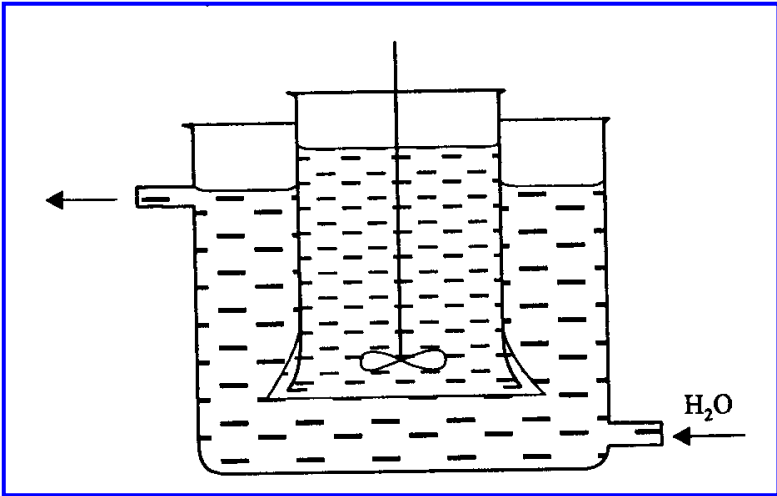


Fig. 5.1. Scheme of flow dialyser

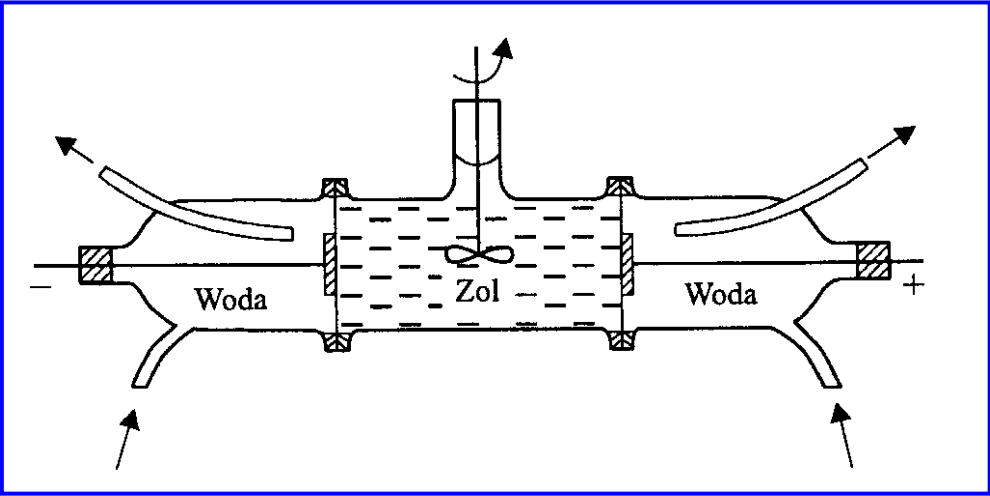
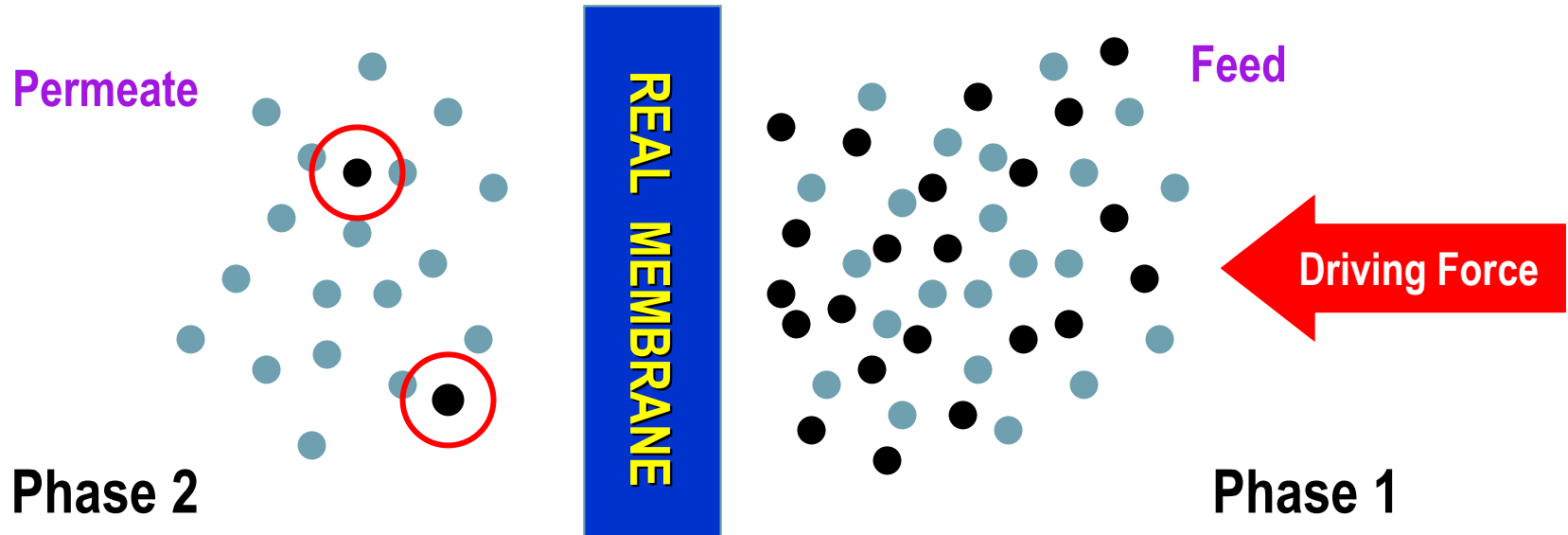
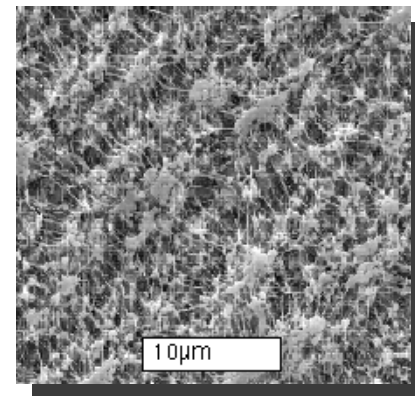


Fig. 5.2. Scheme of electro dialysis

Ultrafiltration - Sol particles can pass through the ordinary filter (**membrane**) whose pores *Colloids* are larger (more than 1μ) than the size of sol particles. However, by special preparation technique the pores can be diminished and then the treated filter may retain colloidal particles and allow the true solution particles to escape.



A membrane can be defined as a barrier (not necessarily solid) that separates two phases as a selective wall to the mass transfer, making the separation of the components in a mixture possible.



Ultracentrifugation

The sol particles do not set out under the action of gravity because of kinetic impacts of the molecules of the medium. However, using high speed centrifugal machines having 15,000 or more revolutions per minute the colloidal particle can be settled. Such machines are known as ultracentrifuges.

6. Electrical charge of colloidal particles

The electrical charge of colloidal particles, similarly to their solvation (hydration) causes stabilization of the colloidal system.

Mechanisms leading to formation of electrical charge on the particle:

- ◆ ion adsorption,
- ◆ ionization of the surface groups,
- ◆ dissolution of ions from the colloidal particle surface into the solution.

Ion adsorption – usually different ions adsorb on the particle surface in different amounts. It leads to formation of net electric charge – in most case negative one. This is because cations are more strongly hydrated. The adsorbing ions are often constituents of the colloidal particle, like H^+ i OH^- .

Ionization of the surface groups – the groups, like $-COO^-$ or $-NH_3^+$ forms on the surface of polymers or proteins.

The ionization degree strongly depends on the pH. The pH value at which there is no net charge on the particle surface is called **point of zero charge (pzc)**.

6. Electrical charge of colloidal particles

Dissolution of ions – in the case of colloids that can dissociate, like AgI, the Ag^+ and I^- ions dissolve into the solution in nonequivalent amounts.

The dissolved amounts depend on the concentration of these ions in the solution and it is determined by the solubility product (SP) of the compound,

for AgI: $\text{SP}_{\text{AgI}} = a_{\text{Ag}^+} \cdot a_{\text{I}^-} = 10^{-16}$.

Here, if $\text{pAg} = 5.5$ ($\text{pI} = 10.5$) then the AgI surface possesses no net charge, i.e. pzc occurs:

$$[\text{Ag}^+]_r = 10^{-5.5} \quad [\text{I}^-]_r = 10^{-10.5} \quad \Rightarrow \quad \text{pAg}_{\text{pzc}} = 5.5$$

Ag^+ and I^- ions are called potential determining ions.

For insoluble oxides and hydroxides the potential determining ions are H^+ i OH^- .

As a consequence of the net electric charge there is **the electrical double layer** presence around the particle.

The electrical double layer

Because of the presence of the electrical double layer there is electric potential difference between the charged surface and the bulk solution. The potential drop between the adsorption layer and bulk solution is called electrokinetic potential (the zeta potential), see Fig. 6.1.

It can be determined experimentally with the help of **electrokinetic phenomena**.

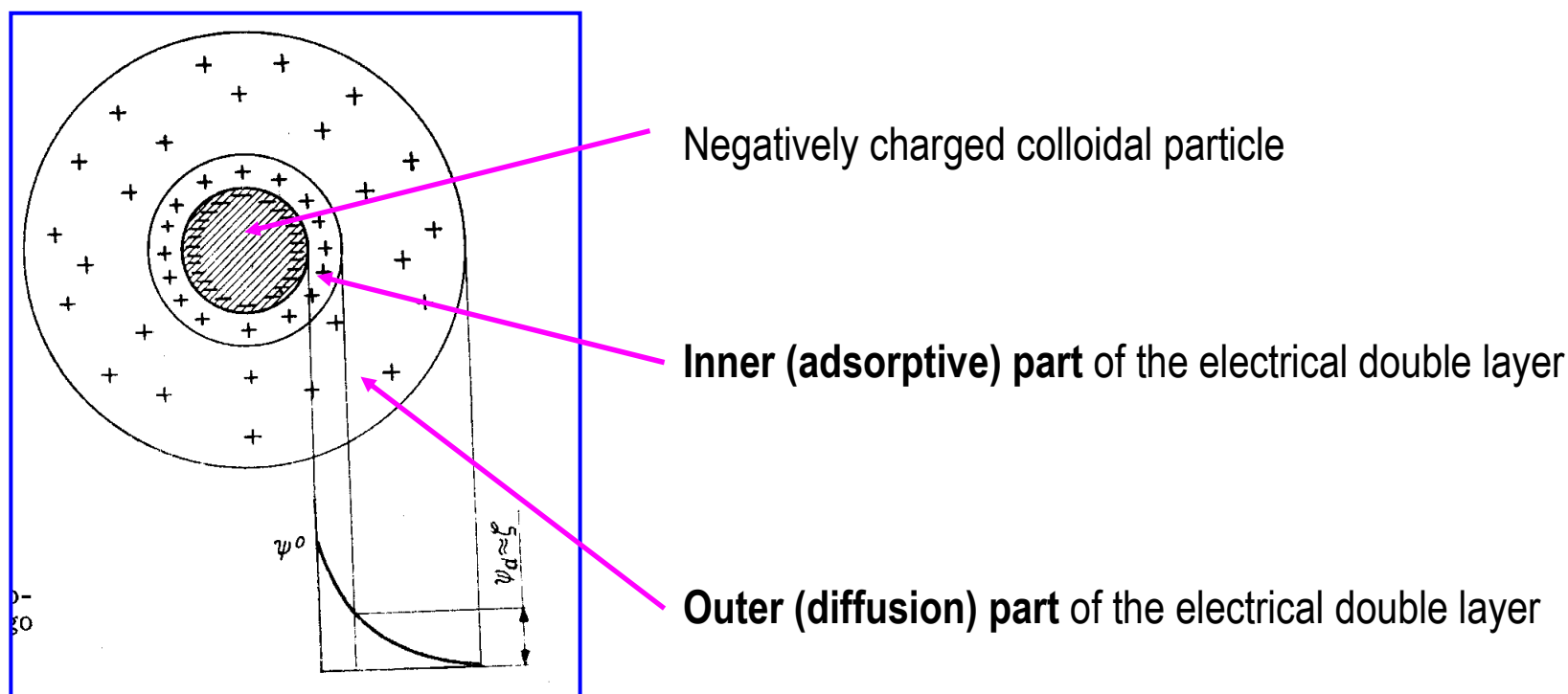


Fig. 6.1. Structure of electrical double layer around a colloidal particle.

7. Stability of colloidal systems – coagulation

One of the most important physico-chemical properties of colloidal particles is **their tendency to aggregate**.

This is caused by **attractive van der Waals forces** acting between the particles.

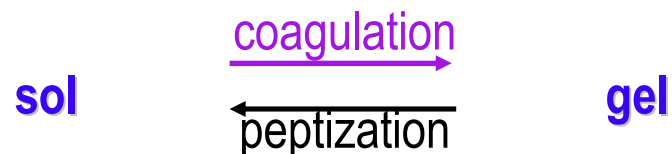
On the other hand, principal repulsive forces are electrostatical ones acting between the same charged particles.

Also hydration (solvation) forces between the particle and the solution stabilize the system.

The liophobic (hydrophobic) sols are stabilized by repulsive the double layer forces.

Therefore they are sensitive to the electrolyte addition, which often already at its low concentration causes destabilization of the system and removing the colloidal particles from the dispersing phase.

This process is called **coagulation**, which means transition from a sol to gel form.



The added electrolyte causes neutralization of the colloidal particle charge due to the ions adsorption. The most efficient coagulation takes place at the point of zero charge (the charge is zero, $\sigma = 0$) or at the isoelectric point (the zeta potential is zero, $\zeta = 0$).

The two parameters can occur simultaneously.

DLVO theory

Derjaguin and **L**andau, and **V**ervey and **O**verbeek independently elaborated the theory of stability of colloidal systems.

The theory allows calculation of the interaction energy changes upon approaching two particles each other.

Nowadays it is known as **the DLVO theory**.

It compares the attractive van der Waals–London forces, ΔG_{121}^{LW} , and the electrostatical repulsive ones, ΔG_{121}^{EL} , interacting upon overlapping of the double layers of two particles approaching each other.

The total interacting energy can be expressed as follows:

$$\Delta G_{121}^{TOT} = \Delta G_{121}^{LW} + \Delta G_{121}^{EL} \quad (1)$$

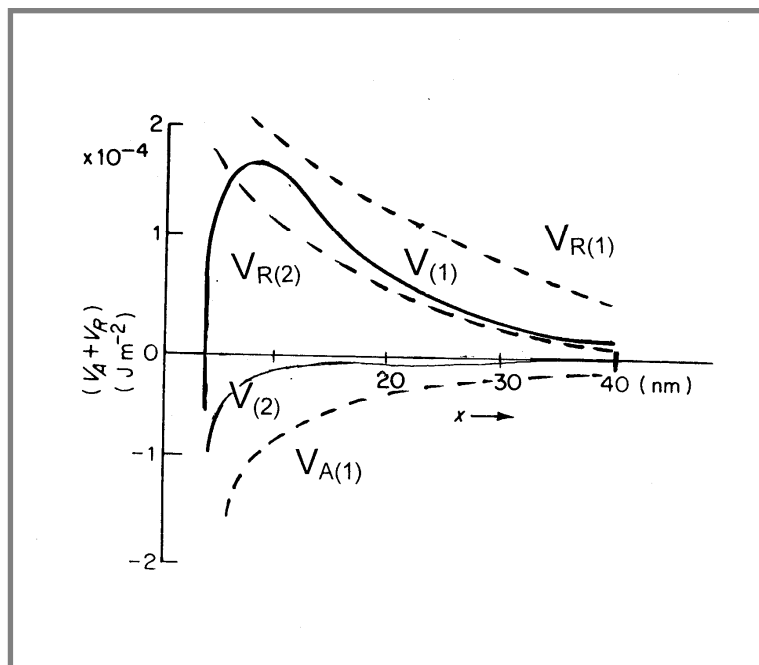


Fig. 7.1. Changes of the potential energy of interaction between two particles as a function of the distance between them.

$V_{(1)}$ – strong repulsion – weak attraction (maximal repulsion in mean distances), stable dispersion

$V_{(2)}$ – strong attraction – weak repulsion (coagulation) in all distances the attractive forces dominate.

If at a given temperature the energy maximum exceed the thermal energy (kT), **the system should be stable.**

In sufficiently large distances between the particles there appears so called **secondary minimum** on the energy curve and if it is enough large in comparison to kT then the colloidal particles can form well-spaced flocks (**aggregates**).

In the case of liophilic (hydrophilic) colloids, the situation is more complicated because other factors play a role in the system stability, like energy of the ion desorption, dehydration, entropic and bridging effects, which are difficult to describe their effects mathematically.

In such systems small addition of an electrolyte practically does not affect the system stability.

At high electrolyte concentration the effect of 'salting out' appears and they can be sedimented.

The added ions cause desolvation (dehydration) of the colloidal particles and simultaneously experience hydration.

Thus this process greatly depends upon the energy of hydration of the ions.

The cations and anions form liotropic series:

cations: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Be}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Rb}^+ > \text{Cs}^+$

and anions: $\text{citric}^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{J}^- > \text{CNS}^-$

Extended DLVO theory

The DLVO theory does not describe well stability of the hydrophilic system. Therefore some extension of this theory has been proposed that takes into account structural interactions involving solvation, hydration and/or hydrophobic interactions that originate from specific polar and nonpolar interactions appearing in such systems.

One of such approaches comes from van Oss, Good and co-workers.

The total energy of interactions between two different particles (1) and (2) dispersed in medium (3) may be expressed as the sum of three components.

- ◆ **Electrostatic interactions (EL)**, resulting from the presence of the electrical double layer.
- ◆ **Lifshitz-van der Waals (LW) interactions**, mostly London dispersion interactions.
- ◆ **Solvation interactions**, which according to van Oss and co-workers' concept may result of Lewis acid-base electron-donor and electron-acceptor (**AB**) interactions between the contacting phases.

Extended DLVO theory

The first two interactions are expressed by **the classical DLVO theory**, and the third component of the total interactions was introduced to explain the AB interactions between hydrophilic and hydrophobic particles in the polar environment.

The total energy of interactions can be written:

$$\Delta G_{132}^{\text{TOT}} = \Delta G_{132}^{\text{EL}} + \Delta G_{132}^{\text{LW}} + \Delta G_{132}^{\text{AB}} \quad (2)$$

As follows from this model free acid-base energy (AB) of the interactions in the polar environment may exceed even 100 times those of dispersion interactions (LW) and ca. **10 times** the electrostatic interactions (EL).

Effect of added substances on colloid stability

The addition of hydrophilic substance (sol) can improve stability of the hydrophobic colloidal system due to its adsorption on the colloidal particles.

This phenomenon preventive from the coagulation of a liophobic sol (by the addition of a liophilic colloid) is called **sol protection or protection of colloids**.

The adsorbed particles can increase the electric surface charge and potential and/or decrease van der Waals interactions.

If the stabilizing agent is a macromolecule polymer, then its molecule tails can stretch outward the bulk solvent and on the particles approaching each other ordering of the tails can occur.

As a result the entropy ΔS decreases and if the change in enthalpy ΔH is small, then the Gibbs free energy ΔG change is positive:

$$\Delta G = \Delta H - T\Delta S > 0$$

This prevents from coagulation of the system and the effect is called **steric stabilization** or **entropy stabilization**.

It should be mentioned about three more phenomena found in colloidal systems.

- ◆ Small addition of a liophobic sol to a colloidal system can make it sensitive to coagulation by the electrolyte addition – this phenomenon is named sensibilization.
- ◆ Reversal conversion of a fixed gel into a fluidal sol form (liosol) by mechanical force (stirring, shaking) which after a time again becomes gel is called tixotrophy, e.g. $\text{Fe}(\text{OH})_3$, clays.
- ◆ A similar phenomenon that consists in separation (extraction) of a gel from the colloidal system is called **syneresis**, e.g. separation of whey from sour milk.

Emulsions

1. Types of emulsions

An emulsion is a mixture of two or more immiscible liquids.

In emulsion both the dispersed and continuous phases are liquid where one liquid (the dispersed phase) is dispersed in the other (the continuous phase).

Two types of emulsions can be distinguished:

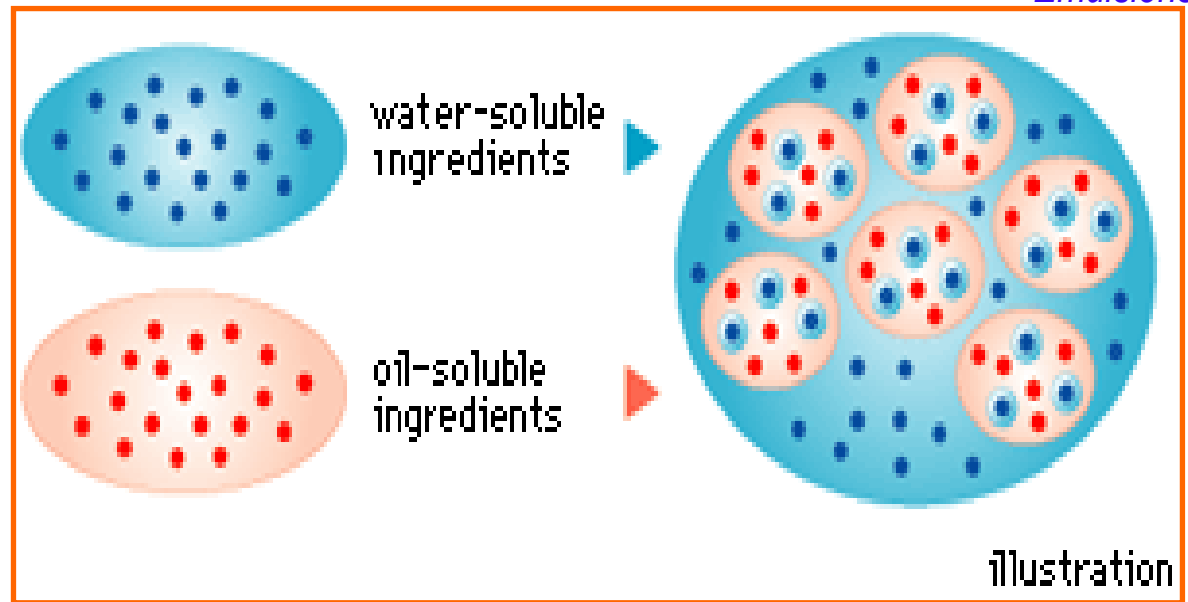
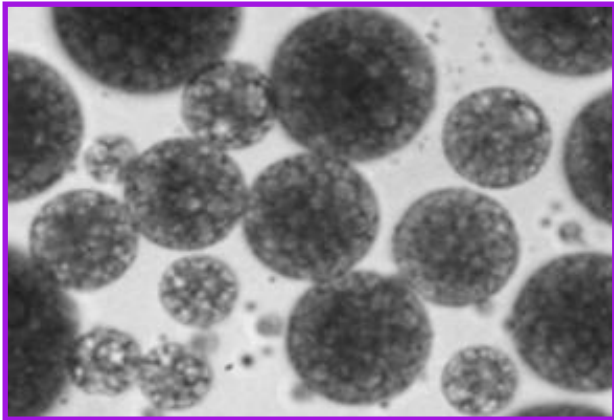
Oil – in – water (**O/W**) and water – in –oil (**W/O**).

In O/W emulsion oil is dispersed in water which is the continuous phase and in W/O type emulsion it is reverse, water is dispersed in oil.

There are also multiple emulsions of the types: water/oil/water, w/o/w and oil/water/oil.

Some examples are shown in Fig. 1.1.

Emulsions



Illustration

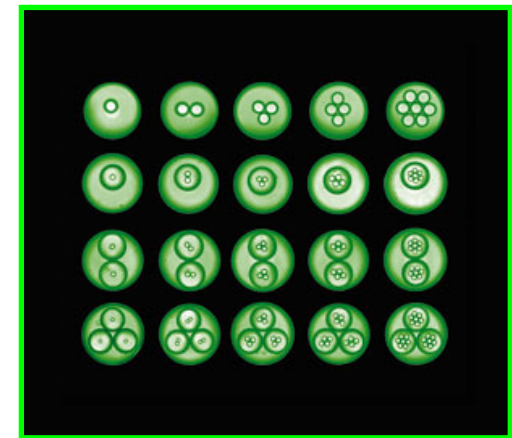
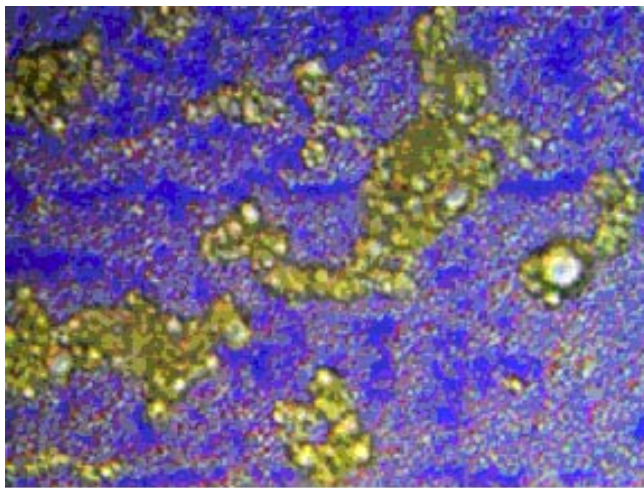
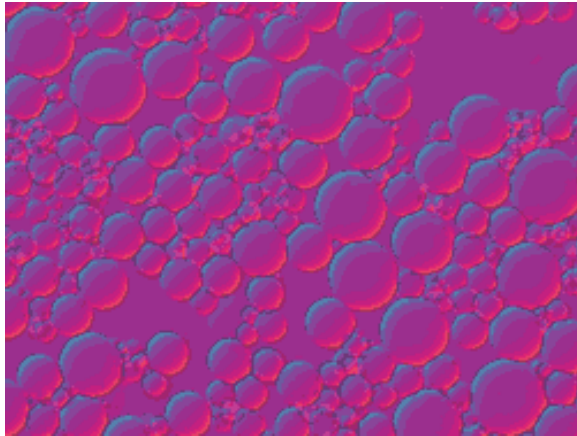


Illustration of multiple emulsions

A microscope image of a flocculated emulsion



Light micrograph of an oil in water emulsion.
Image size 60 x 45 μm
(Image by Mary Parker & Paul Gunning, IFR)

The emulsion type can be recognized:

- By adding some amount of one of the liquids forming the emulsion (its dissolution). For example, if the added water dissolves in the emulsion it is O/W emulsion.
- By using a dye that dissolves only in one of the two liquids forming emulsion (in oil or water).
- By measurements of electrical conductivity, which should be much larger in the case of O/W emulsion.

2. Stability of emulsions

Emulsions are not stable systems, that is after their formation by mechanical force (stirring) the emulsion liquids separate from each other very soon. Therefore to stabilize an emulsion a stabilizing agent has to be added which is called emulsifier.

In the case of oil-in-water emulsion, a surfactant which has a polar head and hydrophobic tail can be used. Then the polar heads will be directed outward the oil droplets to the water phase thus preventing the emulsion from its coalescence.

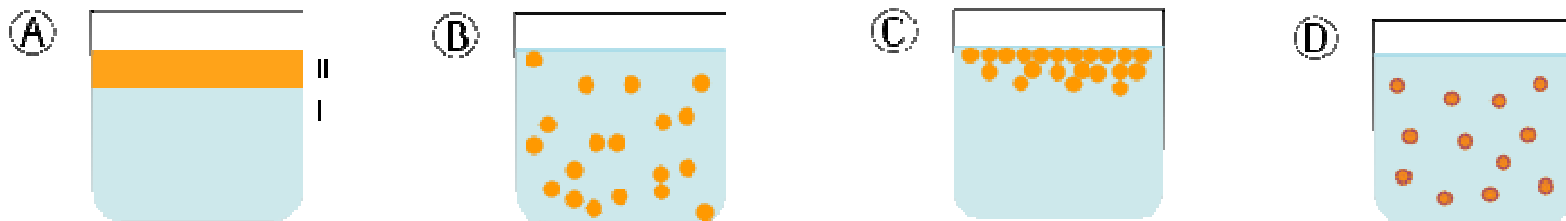


Fig. 1.2. Formation of oil in water emulsion.

A. Two immiscible liquids, not yet emulsified.

B. An emulsion of Phase II dispersed in Phase I.

C. The unstable emulsion progressively separates.

D. The surfactant (purple outline around particles) positions itself on the interfaces between Phase II and Phase I, stabilizing the emulsion

(<http://en.wikipedia.org/wiki/emulsion>)

However, it should be stressed that even such stabilized emulsions thermodynamically are not stable systems and they pass slowly to a ripening process and slow coalescence of the oil droplets will occur.

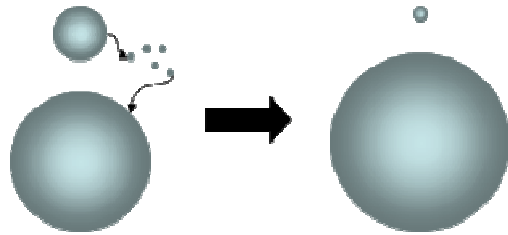
There are three types of instability: **flocculation, creaming, and coalescence**.

Flocculation describes the process by which the dispersed phase comes out of suspension in flakes.

Coalescence is another form of instability, which describes when small droplets combine to form progressively larger ones.

Creaming is the migration of one of the substances to the top (or the bottom, depending on the relative densities of the two phases).

Ostwald ripening is thermodynamically-driven spontaneous process occurs because larger particles are more energetically favored than smaller particles.



Basic schematic of the Ostwald ripening process

This stems from the fact that molecules on the surface of a particle are energetically less stable than the ones in the interior.

HLB - hydrophilicity lipophilicity balance

(From Wikipedia, the free encyclopedia)

Surfactants Classified by HLB Numbers

Surfactants are typically amphiphilic molecules that contain both hydrophilic and lipophilic groups. The hydrophile-lipophile balance (HLB) number is used as a measure of the ratio of these groups. It is a value between 0-60 defining the affinity of a surfactant for water or oil. HLB numbers are calculated for nonionic surfactants, and these surfactants have numbers ranging from 0-20.

HLB numbers >10 have an affinity for water (hydrophilic) and number <10 have an affinity of oil (lipophilic). Ionic surfactants have recently been assigned relative HLB values, allowing the range of numbers to extend to 60.

The term "HLB" was first employed by the lab staff of the Atlas Powder Co. in America.

This means the balance between the oil soluble and water soluble moieties in a surface active molecule, and is expressed as the **Hydrophile-Liphophile Balance**.

A more oil-soluble emulsifier shows a lower HLB and a more water-soluble emulsifier shows the reverse. HLB is a very useful method in selecting an emulsifier, but it still has several limitations to application for every surfactant. The HLB concept is not enough to describe all the characteristics of emulsion.

Calculation of the HLB number from a mixture of surfactants

The HLB number of a mixture composed of x% of surfactants of HLB A and y% of surfactants of HLB B is obtained by the following formula.

$$\text{HLB (A + B)} = (Ax + By) / (x + y)$$

Water Dispersibility by HLB

Type of dispersion	HLB Range
No dispersion	1-4
Poor dispersion	3-6
Milky dispersion after vigorous agitation	6-8
Stable milky dispersion	8-10
Translucent to clear dispersion	10-12
Clear solution	13+

The **Hydrophilic-Lipophilic Balance** of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic, determined by calculating values for the different regions of the molecule, as described by **Griffin in 1949** and **1954**. Other methods have been suggested, notably in **1957** by **Davies**.

Griffin's method for non-ionic surfactants as described in 1954 works as follows:

$$\text{HLB} = 20 * M_h / M$$

where M_h is the molecular mass of the hydrophilic portion of the molecule, and M is the molecular mass of the whole molecule, giving a result on an arbitrary scale of 0 to 20. An HLB value of 0 corresponds to a completely hydrophobic molecule, and a value of 20 would correspond to a molecule made up completely of hydrophilic components.

The HLB value can be used to predict the surfactant properties of a molecule:

- 0 to 3 an ~~anti-foaming~~ agent
- 4 to 6 a ~~W/O (water in oil)~~ emulsifier
- 7 to 9 a ~~wetting~~ agent
- 8 to 18 an ~~O/W (oil in water)~~ emulsifier
- 13 to 15 ~~typical of detergents~~
- 10 to 18 a ~~solubiliser~~ or hydrotrope.

Davies' method is based on calculating a value based on the chemical groups of the molecule. The advantage of this method is that it takes into account the effect of strongly and less strongly hydrophilic groups. The method works as follows:

$$\text{HLB} = 7 + m \times H_h - n \times H_l$$

with:

m - Number of hydrophilic groups in the molecule

H_h - Value of the hydrophilic groups

n - Number of lipophilic groups in the molecule

H_l - Value of the lipophilic groups

Examples of matching HLB values to application needs

	HLB's
mixing unlike oils together	1 to 3
making water-in-oil emulsions	4 to 6
wetting powders into oils	7 to 9
making self emulsifying oils	7 to 10
making oil-in-water emulsions	8 to 16
making detergent solutions	13 to 15
for solubilizing oils (micro-emulsifying) into water	13 to 18

HLB numbers of functional groups

Hydrophilic groups	HLB	Lipophilic groups	HLB
-SO ₄ Na	38.7	-CH-	} -0.475
-COOK	21.1	-CH ₂ -	
-COONa	19.1	-CH ₃ -	
-sulfonic group (-SO ₃ H)	11.0	-CH=	
quaternary ammonium (≡N) ⁺	9.4	-(CH ₂ - CH ₂ - CH ₂ -O-)	-0.15
ester (sorbitan ring)	6.8		
ester (free)	2.4		
-COOH	2.1		
-OH (free)	1.9		
-O-	1.3		
-OH (sorbitan ring)	0.5		

Example: calculation of HLB number for 1-hexadecanol (cety alcohol) C₁₆H₃₃OH

$$HLB = 7 + m \times H_h - n \times H_l = 7 + 1.9 + 16(-0.475) = 1.3$$

It should be kept in mind that HLB numbers are not additive in some systems or compounds.

Nevertheless HLB numbers helped to systemize and optimize the emulsion systems.

MICROEMULSIONS

Microemulsions are clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salt(s) and/or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons and olefins. In contrast to ordinary emulsions, microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions. The two basic types of microemulsions are direct (oil dispersed in water, o/w) and reversed (water dispersed in oil, w/o).

The **term microemulsion** was first used by Jack H. Shulman, a professor of chemistry at Columbia University, in 1959. Alternative names for these systems are often used, such as **transparent emulsion, swollen micelle, micellar solution, and solubilized oil**. More confusingly still, the term microemulsion can refer to the single isotropic phase that is a mixture of oil, water and surfactant, or to one that is in equilibrium with coexisting predominantly oil and/or aqueous phases, or even to other non-isotropic phases.

In ternary systems such as microemulsions, where two immiscible phases (water and 'oil') are present with a surfactant, the surfactant molecules may form a monolayer at the interface between the oil and water, with the hydrophobic tails of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the aqueous phase.

MINIEMULSION

A [mini-emulsion](#) is a [special case of emulsion](#). A mini-emulsion is obtained by shearing a mixture comprising two immiscible liquid phases, one surfactant and one co-surfactant (typical examples are hexadecane or cetyl alcohol).

The shearing proceeds usually via ultrasonication of the mixture or with a high-pressure homogenizer, which are high-shearing processes. In an ideal mini-emulsion system, coalescence and Ostwald ripening are suppressed thanks to the presence of the surfactant and co-surfactant, respectively.

Stable droplets are then obtained, which have typically a size between 50 and 500 nm. The mini-emulsion process is therefore particularly adapted for the generation of nanomaterials. There is a fundamental difference between traditional emulsion polymerisation and a mini-emulsion polymerisation. Particle formation in the former is a mixture of micellar and homogenous nucleation, particles formed via mini-emulsion however are mainly formed by droplet nucleation.

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