

SELF-ASSEMBLING NANOSYSTEMS

1.1 Mono- and polymolecular layers of surfactants. Thin films

Self-assembling nanosystems relate to the typical colloidal systems. Methods and mechanisms of their formation, peculiarities of the processes, and properties of the systems were studied in the course of colloid chemistry. Generally, they are formed spontaneously by the “bottom-up” approach.

The following systems relate to the spontaneously-forming nanosystems:

- clusters;
- adsorption layers of surface-active agents (surfactants);
- periodic colloidal structures;
- direct and reverse micelles;
- microemulsions.

Clusters are systems of a large number of bonded atoms and molecules. If clusters contain the ions, such bonds might be significant. Under these conditions, the intermolecular (Van der Waals) interactions within the cluster increase and the interfacial boundary between cluster and medium form, i.e., there is a formation of nanoparticles as a dispersed phase of the dispersed system.

Colloidal clusters are formed in solutions and have sizes up to 100 nm. They exist in a liquid phase and they do not coagulate. In relation to the liquid phase, the colloidal clusters can be divided into 2 groups: *lyophilic* (hydrophilic) and *lyophobic* (hydrophobic). Lyophilic clusters are able to adsorb the molecules of the medium on their surface (e.g., water) and form strong solvate layers. Silicon oxides are the typical representatives of hydrophilic particles.

Nanosystems based on surfactants are formed spontaneously. It is known that the surfactant molecules have diphilic (amphiphilic) structure (Fig. 1.1)

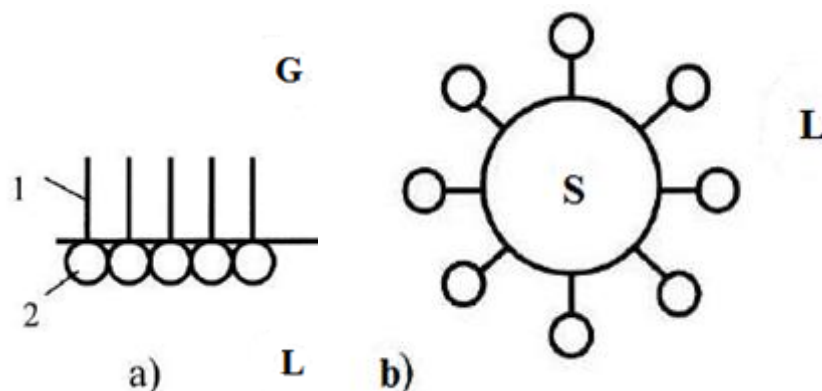
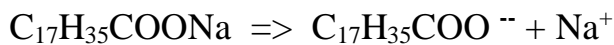


Figure 1.1. Adsorption layers of surfactants at the interface of L/G (a) and on the surface of the particle S/L (b)

The long part of the molecule (1) is a hydrocarbon radical. This radical is non-polar and hydrophobic; it has no affinity to water. The other part of the surfactant molecules, usually the smaller one, contains a hydrophilic polar group (2) which has an affinity to water.

Schematically, the surfactant molecule is depicted as circles (hydrophilic polar group, “hydrophilic head”) and line (hydrophobic non-polar group, “hydrophobic tail”). The groups with significant affinity to water can serve as hydrophilic part of the surfactant molecules: -COOH -OH, -CHO, -NH₂, -SH, -CNS, -SO₂H, -CN, -NO, etc.

The sodium salt of stearic acid is a surfactant, which enters into composition of soap. However, unlike valeric acid, which hardly dissociates in water and does not form ions, sodium stearate dissociates in an aqueous solution, forming a surface-active anion:



the anion $\text{C}_{17}\text{H}_{35}\text{COO}^-$ has a long hydrocarbon radical.

Due to the diphilic structure, surfactant molecules adsorb at the interface of water/air (Fig. 1.1, a). The hydrophilic part of the molecules with affinity to the polar water molecules interact with water and nonpolar hydrophobic part is pushed in a non-polar phase (air).

The maximum adsorption is achieved at a particular concentration of the surfactant solution (Fig. 1.1, a) and nanolayer of surfactant spontaneously forms.

The adsorption of the surfactant on the surface contradicts the laws of diffusion, since the spontaneous process does not proceed from a higher concentration to a lower one, on the contrary, proceeds from a lower concentration (surfactant in solution) to a larger one (surfactant on the surface).

It should be noted that a similar process for the surfactants is determined by the entropy (S). Entropy is one of the thermodynamic functions of the state. It is a characteristic of a spontaneous process.

At the adsorption of surfactants on the surface two processes of entropy change of surfactants and water are observed. In the case of surfactant adsorption, the process goes from disorder (surfactant in water) to order on the surface (Fig. 10.1, a), and entropy decreases, $\Delta S < 0$. The decrease of surfactant concentration in water due to adsorption restores interrupted disorder in water, i.e. the process goes from order to disorder, entropy increases, $\Delta S > 0$, and the second process prevails.

For this reason, the entropy of the surfactant adsorption process increases and leads to the spontaneous transition of surfactant from solution on the surface. *Adsorption layers of surfactants* at the interface form one-dimensional nanosized structures (Fig. 10.1, a) or *thin films* of surfactants.

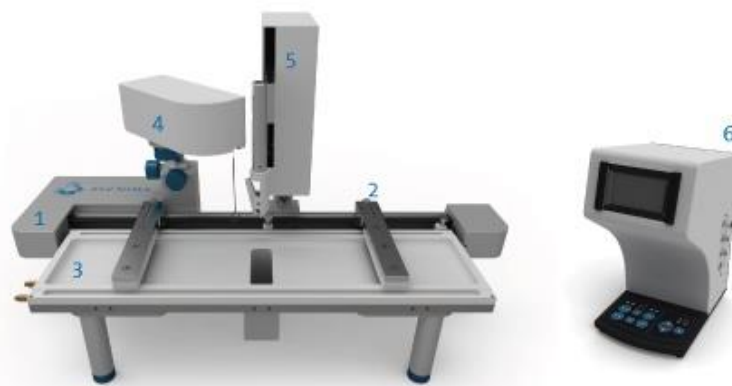
The structural-mechanical barrier preventing the coagulation of nanoparticles is formed due to the adsorption layer of surfactant.

Self-organization is possible by means of the local concentrating of surfactant molecules with the formation of “island” nanoscale structures. Often such structures (in the form of meniscus) occur near the line of three-phase

contact. The essence of the “island” structures is the uneven distribution of the surfactant in the adsorption layer, their high concentration in this layer that causes the formation of singular micelles.

The formation of structures from surfactant molecules can be carried out by the Langmuir - Blodgett technique (Fig. 1.2). The adsorption layers of insoluble surfactants can be transferred from the air-solution interface onto the solid substrate, forming the so-called Langmuir-Blodgett films.

The deposition of adsorption layers takes place on a slide that moves perpendicularly to the air – solution interface containing the adsorption layer. The film transfer usually occurs at a constant and rather high value of the two-dimensional pressure (Fig. 1.2).



1 – Frame, 2 – Barriers, 3– Trough top, 4– Surface pressure sensor, 5– Dipping mechanism (Langmuir-Blodgett option), 6 – Interface unit

Figure 1.2 – The components of Langmuir-Blodgett trough

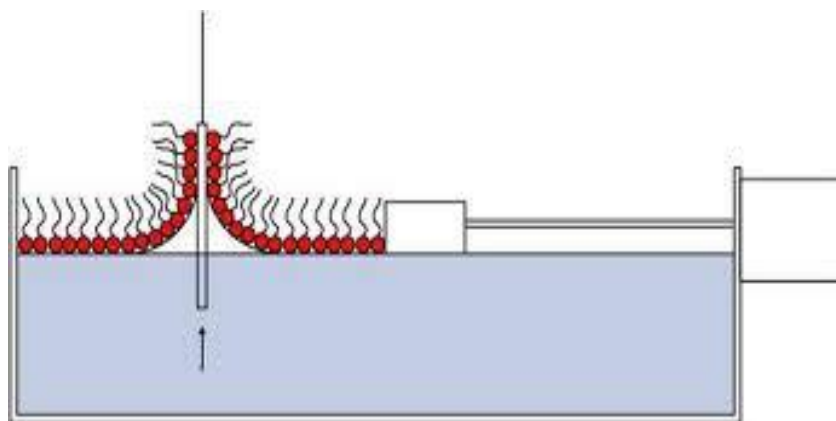


Figure 1.2. The deposition of surfactant adsorption layers on a slide

The method consists of transferring the condensed films from the surface of the liquid to the surface of the slides of metal, glass and other materials. "Direct"

(Fig. 10.3 a, by the hydrophilic part of the surfactant molecules) or "reverse" (Fig. 10.3 b, by hydrophobic part) orientations on solid surface and hydrophilization or hydrophobization of the surface, respectively, depends on the position of the surfactant.

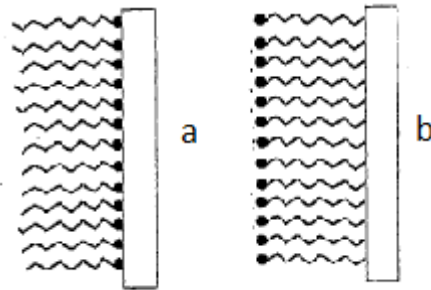
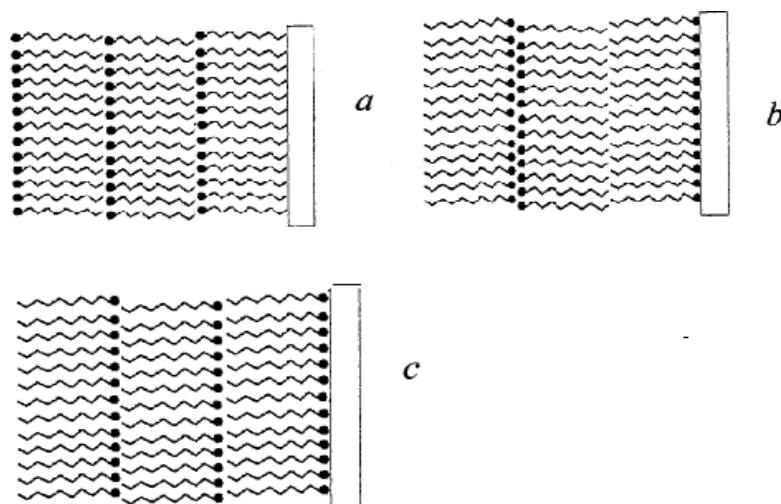


Figure 1.3. a) - Hydrophilization and b) - hydrophobization of the surface by Langmuir – Blodgett technique

If the slide is moved by turns in both upward and downward directions, polymolecular films are formed (Fig.1.4).

In these films, the neighboring monolayers alternately come into contact with their hydrocarbon chains and polar groups, as shown in Fig. 1.4, b. If the slide always moves in one direction, the "polar" films (with the uncompensated dipole moment of surfactant molecules in the neighboring monolayers) may be formed. In such layers, the polar groups of one monolayer come in contact with the hydrocarbon chains of the other. If the slide is hydrophobic and moves in a downward direction, the X-type films are formed (Fig. 1.4, a). The deposition on a hydrophilic slide moving in an upward direction results in the formation of Z-type films (Fig. 1.4, c).

The Langmuir-Blodgett technique allows one to form structures with the predetermined molecular arrangement, in which the neighboring monolayers have the desired composition. For example, by using water-insoluble organic acids with a sufficiently long chain length, such as stearic, the composition of deposited layers can be modified by changing the electrolyte content of the substrate solution by introducing polyvalent ions that form insoluble salts with the acids.



a) – X-type, b) – Y-type c) – Z-type films

Figure 1.4. Different types of Langmuir-Blodgett films deposited on a solid surface

The method of the Langmuir - Blodgett is quite widespread for obtaining self-organized nanoparticles at the interfaces. An ordered monolayer of nanoparticles can be formed on vertical surfaces by removing the slide from the colloidal solution and after evaporation of the solvent. Hydrophobic nanoparticles can be formed at the interface air - water and then transferred on a solid substrate.

The use the Langmuir - Blodgett method allows to change the size and shape of nanoparticles from several tens to hundreds nanometers and form various structures of nanosized films.

Ordered structures can be transferred from the surface of the liquid on the solid substrate without noticeable disruption of the crystalline structure of the nanolayer. Various additives are applied to impart strength to the nanolayer. In addition, a layer-by-layer assembly of nanoparticle layers is possible, that allows the creation of the various nanolayer structures.

Among the perspective applications of Langmuir – Blodgett method, one can name their use as monochromators and analyzers of soft long wave X-ray and neutron radiation and for synthesis of light-transmitting, electrically conducting thin films on the surfaces of solids utilized in novel electronic devices.

1.2. Surfactant micelles as self-assembling systems. Types of micelles

Surfactant micelles relate to structured self-assembling nanosystems. They are formed due to the colloidal surfactants.

The hydrophobic part of colloidal surfactants is a hydrocarbon radical C_nH_{2n+1} , C_nH_{2n-1} , $C_nH_{2n+1}C_6H_9$ and others types of radicals, containing from 8 to 18 carbon atoms.

Let us consider the distribution of surfactant molecules in solution in detail (Fig. 1.5).

Part of the surfactant molecules adsorb at the interface of liquid - gas (water - air). There is a dynamic equilibrium between the surfactant molecules on the

adsorption layer of the surface (1) and molecules in solution (2). Part of the surfactant molecules in solution can form micelles (3). There is a balance between colloidal surfactant molecules in solution and molecules within the micelles shown in the Fig. 10.5 by arrows.

The process of micellization of surfactant molecules dissolved in a solvent can be represented as follows:



$$n = \frac{M_n}{M_r}, \quad (1.2)$$

where M_r is the molecular weight of the surfactant molecule, g;

n is the number of surfactant molecules in the micelle (or micellar number),

M_n – micellar weight or weight of micelle, g.

Micelles are aggregates (of spherical form and in the form of plates) consisting of tens of surfactant molecules, in which polar groups contact with water, and hydrophobic radicals are located inside, forming a nonpolar part of the molecule.

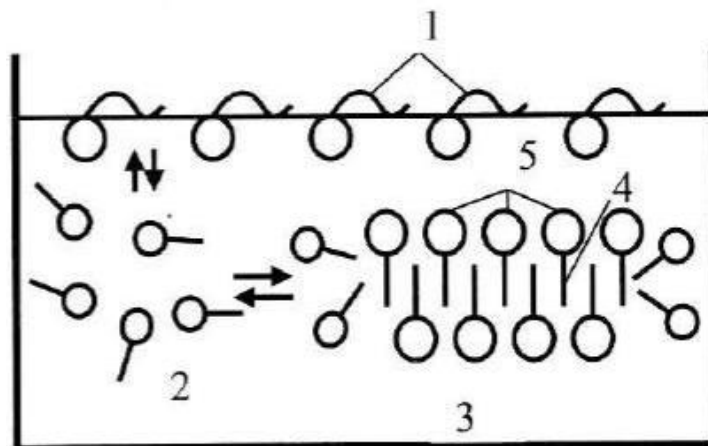


Figure 1.5. The position of colloidal surfactants: 1 - on the surface; 2 and 3 – as true and colloidal solutions; 4 - hydrocarbon nonpolar part; 5 - hydrophilic polar groups

The state of surfactants in solution depends on their concentration. True solutions are formed at low concentrations (10^{-4} - 10^{-2} M). Above a particular concentration (or more precisely above a very narrow concentration range) called a critical micellization concentration (CMC), micelles are formed, and are in thermodynamic equilibrium with surfactant molecules in solution.

Micelle formation is a thermodynamic favourable process and ΔG of micellization is negative due to the contribution of entropy. Thus, micelles relate to *lyophilic systems*.

The lyophilic processes form spontaneously. It is known that the processes can occur spontaneously, if they are accompanied by $\Delta G < 0$. Consequently, lyophilic systems are characterized by a very low value of interfacial tension between dispersed phase and dispersion medium. The critical value of interfacial tension, at which the spontaneous dispersion proceeds and the thermodynamic stability is provided, can be calculated according to the Shchukin-Rehbinder equation:

$$\sigma_{cr} = \gamma \frac{k_B T}{d^2}, \quad (1.3)$$

where σ_{cr} is an interfacial tension, J/m²;
 k_B – Boltzmann constant, 1.38×10^{-23} J/K;
 T – temperature, K;
 d – average size of particle, m.

The systems with interfacial tension $\sigma \leq \sigma_{cr}$ relate to lyophilic systems. The value of critical interfacial tension depending on particle size is in the range of 1 mJ/m² –

10^{-4} mJ/m². The bigger size of particles is, the less is the value of critical interfacial tension. However, lyophilic systems are highly dispersed systems subjected to the Brownian motion.

Micellization causes the change of physicochemical properties of surfactant solution (Fig. 10.6). The study of the physicochemical properties of surfactant solutions allows to determine the CMC value.

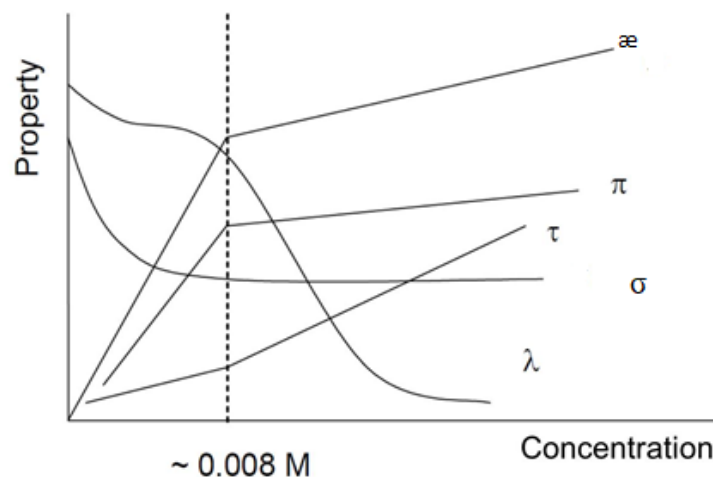


Figure 1.6. The change in some physical chemical properties of sodium dodecylsulphate (SDS) as a function of SDS concentration. æ – specific electroconductivity, π – osmotic pressure, τ – turbidity, σ – surface tension, λ – equivalent electroconductivity of SDS solution

The dependence of the CMC value on number of CH₂-groups is calculated according to the formula:

$$\lg \text{CMC} = A - Bn, \quad (1.4)$$

where A and B are constants for this particular type of surfactant (A depends on the nature and the number of hydrophilic groups, temperature), B characterizes the energy of the dissolving per one CH₂ group, ($B \approx \lg 2$), n is the number of carbon atoms in a hydrocarbon chain.

(1.4) is used for water solutions of surfactants. For nonpolar media the following equation is applied:

$$\lg \text{CMC} = A + Bn \quad (1.5)$$

The CMC value in some particular solvent is a characteristic of the surfactant but depends on several other factors, because micellization is influenced by thermal and electrostatic forces. Therefore, the CMC values depend on many factors like the carbon chain (tail) length, chain branching, number of C=C bonds, various types of additives, temperature and pressure. The CMC value decreases with the increase of the hydrocarbon chain-length. An addition of strong electrolyte to an ionic surfactant tends to decrease the CMC because it reduces the repulsion between the charged groups at the surface of the micelle by the screening action of the added ions. Therefore, the CMC is lowered.

For these systems, one can use the following formula:

$$\lg \text{CMC} = A' - B'n - k \lg c \quad (1.6)$$

where A' and B' have the same meaning as A and B constant, k is the constant, c is the concentration of counter-ions of indifferent electrolyte.

Micellization is opposed by thermal agitation and CMC's would thus be expected to increase with the increase of the temperature. This is usually, but not always, in the case of nonionic surfactants CMC value decreases due to the dehydration of oxyethylated groups under the influence of temperature.

Determination of the CMC is important in order to understand the self-organizing behaviors of surfactants in solution.

When surfactant concentration is above CMC, the excess of surfactant forms micelles. Direct and reverse micelles can form. In direct micelles (Fig. 38) the hydrophilic part of the surfactant molecules faces the dispersion medium (water), then in reverse micelles - the hydrophobic part.

At significant content of surfactants, the spherical, cylindrical, lamellar types of micelles can form up to complex structure as liquid crystals and gels (Fig. 1.7). The change of forms of micelles is referred to as polymorphism.

The formation of micelles is a spontaneous process. Several types of micelles with sizes up to tens of nanometers are possible.

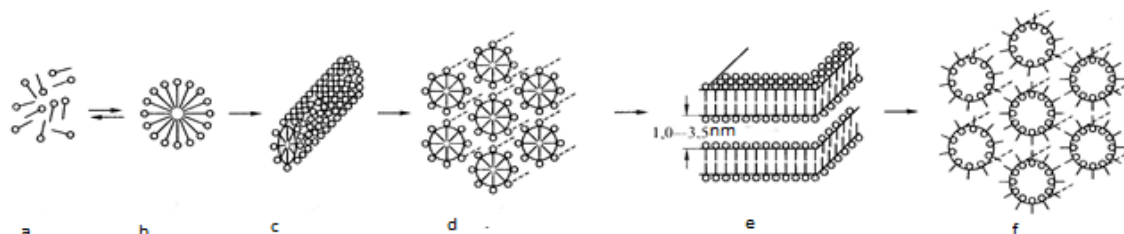


Figure 1.7. Polymorphism of surfactant micelles. *a* – molecules of surfactants in true solution; *b* – direct spherical micelle; *c* – direct cylindric micelle; *ϵ* – hexagonal location of direct spherical micelle; *z* – lamellar micelles; *δ* – hexagonal location of reverse cylindric micelles

Micellar solutions of surfactants can be regarded as a model of easily reproducible system to study the nanosized particles and the structure of the electrical double layer.

Micelles have a perfect spherical shape and their radius equals to the units of nanometers. They are characterized by a relatively narrow distribution.

For the interface of micelle - dispersion medium the classical theory of EDL (electrical double layer) is fair. This micellar solution is represented in the form of uniform spherical particles dispersed in a liquid containing ions. Surface-active ions forming the core of the micelle represent the inner part of EDL.

Micelles promote the synthesis of clusters that under certain terms can form a nanodisperse system.

For example, to obtain Ag_2S nanoparticles, it is necessary to use two types of reverse micelles, comprising Na_2S and Ag. Coalescence (flowing of drops) occurs as a result of collision of the micelles and the exchange of incident components (Na_2S and Ag) takes place, leading to the formation of Ag_2S .

To release the nanoparticles from the micelles, the solution is destroyed by thiols, then subject to heat in benzene, filter and evaporate. This is the way to get monodisperse nanoclusters with sizes up to 10 nm. These clusters form ordered nanostructures (the colloidal crystals) by planting on substrate. By this method, two-dimensional and three-dimensional colloidal crystals are obtained: metallic clusters of Ag, Co, Au, and an oxide of metal clusters.

The formation of micelles is possible in the oil phase; it is determined by the interaction of polar groups of surfactants in the cores of reverse micelles or by the interaction of non-polar groups of surfactants with nonpolar solvents.

1.3. Microemulsions as self-assembling systems. Differences between emulsions and microemulsions

Microemulsions are related to self-assembling systems, they can form spontaneously.

Microemulsions are fine disperse systems of the type L/L, i.e. they consist of two immiscible liquids.

Macroemulsions are coarse disperse systems in which one liquid phase is water (W) and the another one represents the water-insoluble liquid, called an oil (O) (liquid fat, mineral oil, etc). Depending on the composition of the dispersed phase and the dispersion medium, they can be direct or reverse emulsion.

Direct emulsion of oil-in-water (o/w) type is a dispersion of oil droplet in water, dispersed phase in direct emulsion is an oil (Fig. 11.1, a). Reverse emulsion of water-in-oil type (w/o) is the dispersion of water in oil, they are water drops distributed in the oil medium (Fig. 1.8, b).

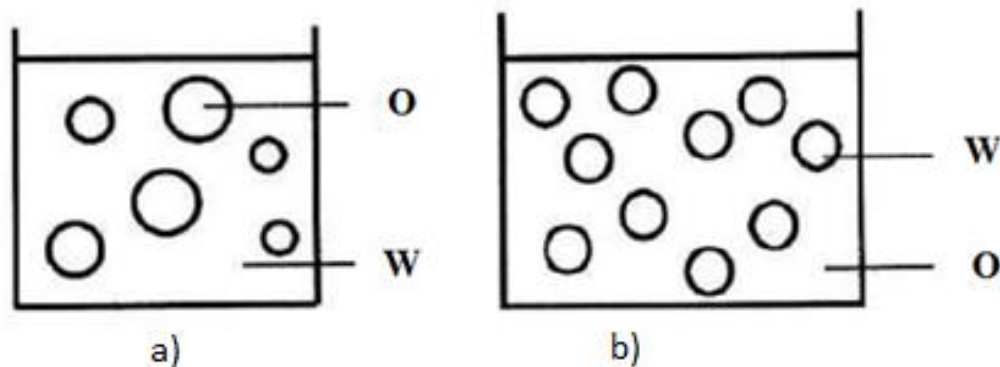


Figure 1.8. Oil-in-water (a) and water-in-oil (b) emulsions.

Microemulsions should not be regarded as emulsions with very small droplet sizes; microemulsions and ordinary coarse disperse emulsions are fundamentally different.

Whereas emulsions are inherently unstable systems in which the droplets eventually undergo coalescence, microemulsions are thermodynamically stable with a very high degree of dynamics with regard to the internal structure (Table 1.1, Fig. 1.9). As a thermodynamically stable phase on surfactant self-assemblies, it has much in common with other surfactant phases, micellar solutions and liquid crystalline phases.

Microemulsions can be prepared by controlled addition of lower alkanols (butanol, pentanol and hexanol) to ordinary milky emulsions to produce transparent solutions comprising dispersions of either water-in-oil (w/o) or oil-in-water (o/w) in nanometer or colloidal dispersions (~ 100 nm).

The lower alkanols are called cosurfactants, they lower the interfacial tension between oil and water sufficiently low for almost spontaneous formation of the said microheterogeneous systems.

Table 1.1. Characteristic differences between emulsions and microemulsions

Emulsion	Microemulsion
<ul style="list-style-type: none"> - Unstable, eventually separated to two liquid phases - Relatively large droplets (1-10 μm) - Relatively static system - Moderately large internal surface, moderate amount of surfactant needed - Small oil/water curvature 	<ul style="list-style-type: none"> - Thermodynamically stable - Small droplets ($\sim 10 \text{ nm} - 200 \text{ nm}$) - Highly dynamic system - High internal surface, high amount of surfactant needed - The oil/water interfacial film can be highly curved

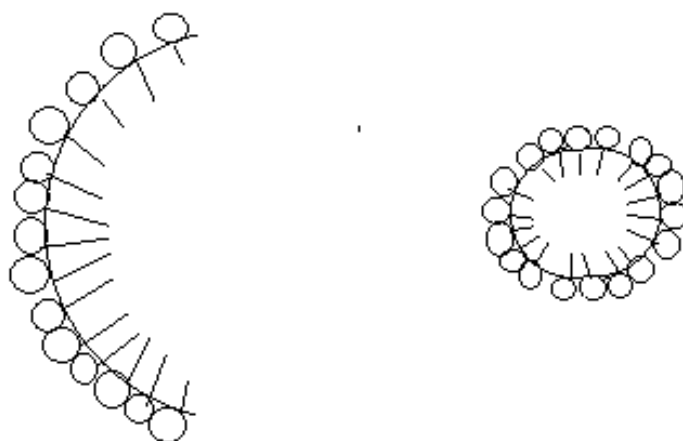


Figure 1.9. The scheme illustrating the size of emulsion and microemulsion droplet and oil/water interfacial film curvature

The miscibility of oil, water and amphiphile (surfactant plus cosurfactant) depends on the overall composition, which is system-specific.

A well-known classification of microemulsions is that of Winsor, who identified the four general types of phase equilibria (Fig. 1.10):

- Type I: the surfactant is preferentially soluble in water and oil-in-water (o/w) microemulsions form (Winsor I). The surfactant-rich water phase coexists with the oil phase, where surfactant is only present as monomers at small concentration.

- Type II: the surfactant is mainly in the oil phase and water-in-oil (w/o) microemulsions form. The surfactant-rich oil phase coexists with the surfactant-poor aqueous phase (Winsor II).

- Type III: a three-phase system, where a surfactant-rich middle-phase coexists with both excess water and oil surfactant-poor phases (Winsor III or middle-phase bicontinuous microemulsion).

- Type IV: a single-phase (isotropic) micellar solution that forms upon addition of a sufficient quantity of amphiphile (surfactant plus alcohol).

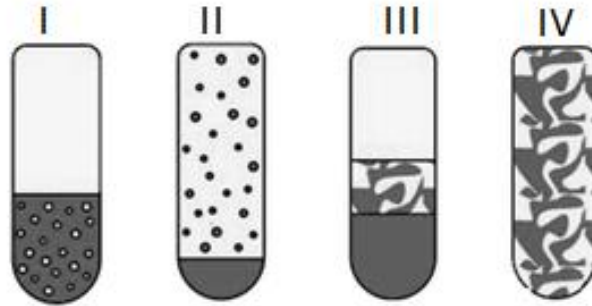


Figure 1.10. Schematic illustration of the four Winsor systems (light: organic phase, dark: aqueous phase). From left to right: I – (o/w) microemulsion system, II – (w/o) microemulsion system, III – three phase microemulsion system (bicontinuous middle phase), and IV – one phase microemulsion (or bicontinuous system)

Microemulsions were not really recognized until the work of Hoar and Schulman in 1943, who reported a spontaneous emulsion of water and oil on an addition of a strong surface-active agent. There has been a lot of debate on the word “microemulsion” to describe such systems. They are termed a “micellar emulsion” or “swollen micelles” or “nanoemulsions”.

Microemulsions were probably discovered well before the studies of Schulmann: Australian housewives have used water/eucalyptus oil/soap flake/white spirit mixtures to wash wool since the beginning of last century, and the first commercial microemulsions were probably the liquid waxes discovered by Rodawald in 1928. An interest in microemulsions really stepped up in the late 1970's and early 1980's, when it was recognized that such systems could improve oil recovery and when oil prices reached levels where tertiary recovery methods became profit earning.

Nowadays, by the means of microemulsion it is possible to extract oil from wells, to produce the regeneration and to improve the quality of lubricants, to use pesticides and other biological substances effectively, to improve the properties of cosmetic products, etc.

1.4. Application of microemulsions at template synthesis

Recently, microemulsion, particularly of water-in-oil type (w/o) has become of interest as a medium for fabrication of nanoparticles. Fine dispersed water droplets represent ideal microreactors (templates) for the synthesis of nanoparticles due to the sizes of drops, which control the sizes of grown nanoparticles. Microemulsions are used to produce the monodisperse nanoparticles.

Thus, the synthesis of nanoparticles of Pt, Pd, Rh, Ir was carried out by the reduction of corresponding salts in water droplets.

Microemulsions are widely used to obtain a variety of nanoparticles, as well as individual metals and their compounds. The preparation of silver, gold, platinum, cobalt and iron nanoparticles has started in 1990-s by means of

microemulsion. Nanoparticles are formed as a result of the reduction of the appropriate metal salts with sodium borohydride or hydrazine or due to the ion exchange reactions provided by mixing the microemulsions.

Functional surfactant bis(2-ethylhexyl) sulfosuccinate of copper $\text{Cu}(\text{AOT})_2$ are used at nanoparticle fabrication. This surfactant plays a dual role: it serves as a stabilizer of water droplets and, on the other hand, it is a source of copper ions in microemulsion droplets.

For the preparation of nanoparticles the w/o microemulsion stabilized by $\text{Cu}(\text{AOT})_2$ and $\text{Na}(\text{AOT})$ in isooctane was mixed with a microemulsion of droplets of sodium borohydride solution stabilized with $\text{Na}(\text{AOT})$. After mixing the microemulsions, the exchange of substances between droplets and the reduction of copper occurs. Due to the size limitation provided by microemulsion drops, nanosized copper particles are formed (Fig. 1.11).

Microemulsions are differed by the size and shape of droplets. The change in the size, structure and shape of the nanodrops can be quantitatively estimated using the following relation:

$$W = \frac{[H_2O]}{[\text{surfactant}]}, \quad (1.7)$$

where $[H_2O]$ and $[\text{surfactant}]$ are the fractions of water and surfactant, correspondingly. The value $W < 4$ means that the microemulsion contains only spherical droplets, the size of which is proportional to W . Further increase of water content ($4 < W < 5,5$) leads to a change in the form of microdrops: they are of spheroidal shape. Accordingly, at the reduction of copper the nanoparticles of spherical shape with diameters of 8.2 nm and 12 nm and nanoparticles of cylinder form with a diameter of 12 nm and a length of 18.5 nm are formed. When the relative water content is in the range of $5.5 < W < 11$, the microemulsion has a structure of bi-continuous phase and spherical nanoparticles with diameters of 6.7 and 9.5 nm and nanorods with a length of 22.6 nm and a diameter of 9.5 nm are formed.

The subsequent increase of water content ($W > 11$) leads to the transformation of the microemulsion structure in which only the rods with a length from 300 to 1500 nm and a diameter of 10 to 30 nm are formed.

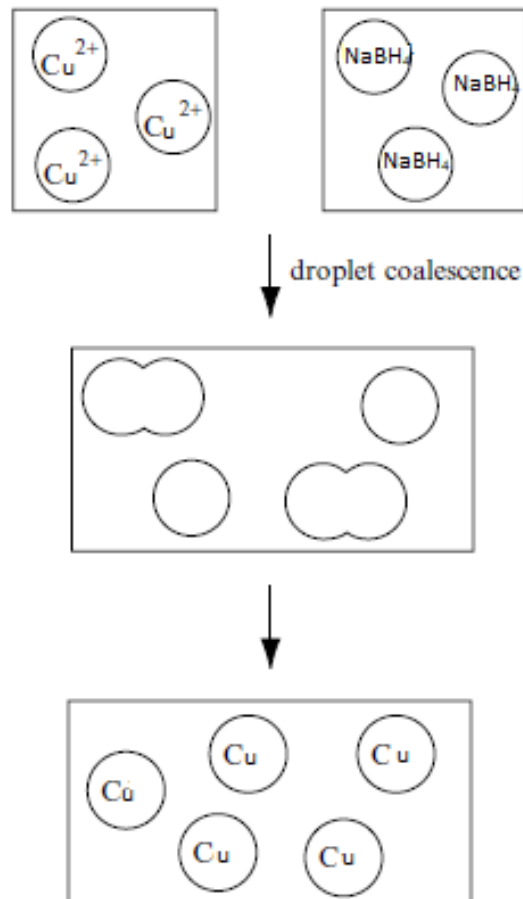


Figure 1.11. Fabrication of copper nanoparticles by means of template synthesis based on microemulsion

According to the data of electronic microscopy, the nanoparticles synthesized in microemulsion (including long rods noted above) are characterized by the defect-free surface that indicates the high quality of nanoparticles obtained by the means of microemulsions.

1.5. Periodic colloidal structures

A periodic spatial structure can form as a result of chemical reactions. According to the DLVO theory, they are characterized as systems forming in the second potential minimum of the dependence of total energy on distance or at the predominance of attraction energy.

They can be considered nanoparticles or nanostructures. A similar process occurs at the formation of the so-called rings of Liesegang. They are formed due to the formation and precipitation of solid nanosized particles in the medium of gel (Fig. 1.12).

They are formed due to the mutual diffusion of the two reagents. The rings of Liesegang are formed in the medium of agar, gelatine, polyacrylamide and other gels as a precipitate of nanoparticle of halides and chromates of heavy metals. The process of nanoparticles formation is associated with crystallization:

first, due to the supersaturation, and then as a result of diffusion and achievement of the re-saturation limit.

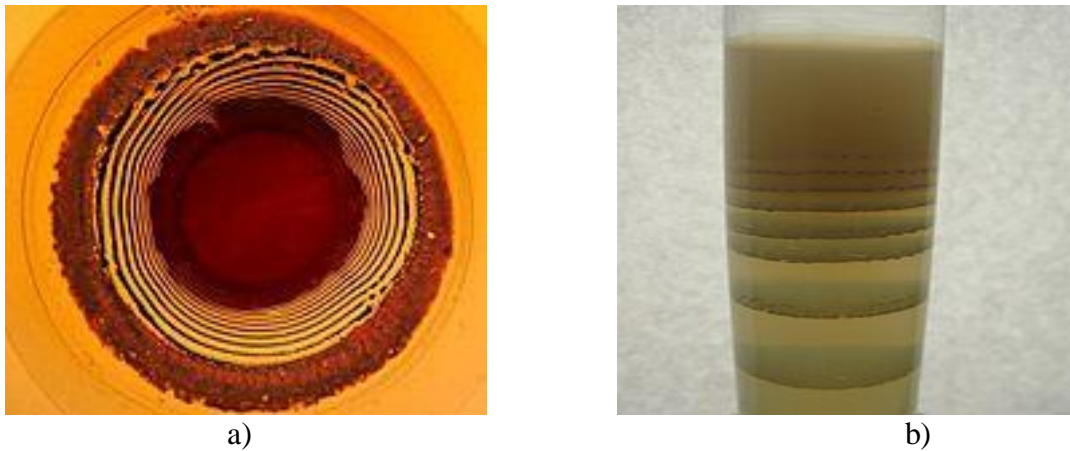


Figure 1.12. a) Liesegang rings - Silver-chromate precipitate pattern in a layer of gelatine, b) Liesegang rings of Magnesium hydroxide in Agar gel. Made by diffusing Ammonium hydroxide into an Agar gel containing Magnesium chloride.

Thus, a major feature of evolutionary processes in colloidal systems is that they often lead to the emergence of ordered structures of various sizes in a nanoscale. These structures can be both two-dimensional and three-dimensional particles, and their size can vary from few nanometers to hundreds of nanometers. Such structures are fairly common. They are of applied and research interest, including that they are convenient models of a number of biophysical and biochemical systems.

Revision questions:

1. Give examples of self-assembling colloidal systems?
2. What are colloidal clusters? Give examples.
3. What self-assembling structures based on surfactants do you know?
4. Explain the amphiphilic structure of surfactants.
5. How does the entropy of surfactant adsorption process change?
6. Describe the Langmuir – Blodgett technique?
7. Describe the structure of Langmuir – Blodgett films.