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The use of objects and methods of colloid chemistry in nanochemistry

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Abstract. Experimental methods and theoretical concepts of colloid chemistry regarding their possible use in nanochemistry and nanotechnology are considered. The main types of disperse systems which can be regarded as nanosystems are distinguished. Some methods for the preparation of colloidal nanosystems are described. Conditions for extrapolation of phenomenological laws of colloid chemistry to nanosize objects are considered. Examples of self-organised colloidal structures are given. The bibliography includes 205 references.

I. Introduction

According to the classification accepted in colloid chemistry, nanosystems are referred to as ultradisperse colloidal systems with the particle sizes ranging from 1 to 100 nm.[1–3] This range of particle sizes corresponds to the maximum degree of dispersion at which a colloidal system still preserves one of its basic properties, *viz*., heterogeneity. According to Rehbinder,[4] the minimum size of the disperse phase particles is about 1 nm (3 – 5 molecular diameters).

In order to establish the relationship between colloid chemistry and nanochemistry, it seems reasonable to recall the main stages in the development of colloid chemistry. After the pioneering studies by M Faraday (1857), who was the first to obtain stable colloidal solutions (sols) of highly dispersed red gold, it was these systems with the particle sizes of 5 – 100 nm that were the focus of attention of numerous physicists and chemists during the second half of the 19th century and the beginning of the 20th century. Experimental and theoretical studies of different properties of colloidal solutions led to the establishment of the main laws of colloid chemistry, *viz*. , the law of Brownian motion and diffusion of colloidal particles (A Einstein), the heterogeneous nature of colloidal solutions (R Zsigmondy), sedimentation – diffusion equilibria of dispersions in the gravitation field (J Perrin) and in a centrifuge (T Svedberg), light scattering (J Rayleigh), coagulation of sols with electrolytes (G Schulze and W Hardy). Studies of properties of colloidal solutions of various substances have led to the establishment of the fundamental principle of the universality of the colloidal state (P Weimarn).[5]

During this period, the leading scientists in the field of colloid chemistry understood well the crucial importance of systematic studies of highly dispersed systems; however, experimental methods of that time did not possess sufficiently high resolution, in particular for the establishment of the structures of ultradisperse particles. Probably it was this circumstance that determined a shift of the peak of studies towards disperse systems with larger particles (foams, emulsions, suspensions, aerosols) and structured systems (gels, coagulation and crystallisation structures).

The appearance of high-resolution methods for the structural studies of substances (NMR, electron and atom-force microscopy, special equipment for measurements of very low surface tensions down to 10^{-3} mJ m^{-2} , computer simulation, photon-correlation spectroscopy and a number of others) in the second half of the 20th century allowed the initiation of systematic studies of the structures and properties of ultradisperse colloidal systems. Over the last 30 – 35 years, considerable progress has been achieved in this field; in particular, radically novel classes of ultradisperse systems † were obtained and studied. A tremendous experience gained in colloid chemistry in the investigations of ultradisperse systems can effectively be used for the solution of a number of basic and applied research problems of nanochemistry, since these systems are nanosystems ‡ in their essence. However, it should be emphasised that one should be very careful in the extrapolation of laws of colloid chemistry and concepts of the structures of disperse particles and thin layers to the nanosize range. The closer the size of a disperse particle (d) to the minimum possible one (*i.e*., to the nanosize), the stronger become the scale effects, *viz*. , the dependence of various properties on the particle size.[7,8] Nonetheless, the methods and concepts of colloid chemistry can also be successfully used in nanochemistry with due respect for appropriate restrictions. This problem is rather com-

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† A spectacular example of ultradisperse systems may be microemulsions, which are thermodynamically stable systems with the disperse phase composed of droplets several nanometers in diameter.[6]

‡ To a certain extent, the problem of what to call the particles with the sizes from 1 to 100 nm is terminological rather than that of meaning: the terms 'nanoparticles' and 'nanosystems' appeared only after the introduction of the SI system of units, *i.e*., much later than the term 'ultradispersity'.

prehensive and includes a large set of theoretical and methodological aspects.

The present review pays major attention to the classification of ultradisperse systems, the methods of their preparation, as well as to the theoretical description of processes occurring in these systems.

II. Ultradisperse systems

In the first place, it is useful to discuss what classes (types) of colloidal systems may be regarded as nanosystems. Let us use the classification which is currently accepted in colloid chemistry and relies on certain important characteristics of disperse systems, such as the sizes of the disperse particles d, their dimensionalities (one-, two-, three-dimensional), concentration of particles v (m^{-3}), the character of interaction between the dispersed phase and the dispersion medium, aggregate states of the dispersed phase and the dispersion medium.[1-3]

As regards their geometrical parameters, nanosystems and ultradisperse systems are virtually equivalent since in the latter the particle size is in the range 1 – 100 nm.

Based on their geometrical characteristics (dimensionalities of disperse particles), colloidal nanosystems may be divided into three groups.

1. Three-dimensional (bulk) nanoparticles in which all the three sizes (d_1, d_2, d_3) are in the nanorange. It should be noted that the bulk particles have rather small radii of curvature. This type includes colloidal solutions (sols), microemulsions, nucleation particles formed upon phase transitions of the first type (crystals, drops, gas vesicles), spherical micelles of surfactants in aqueous and non-aqueous media (direct and reverse micelles).

2. Two-dimensional (thin films and layers) nanoparticles in which only one size (thickness) is in the nanorange, while two others (length and width) may be unlimitedly large. These systems include thin liquid films, adsorption mono- and polylayers at the interface (including the Langmuir – Blodgett films),[9] two-dimensional lamellar micelles of surfactants.[10] Thin liquid films are subdivided into foamy films (between two foam cells), emulsion films (between droplets of direct and reverse emulsions) and wetting films (separating a solid surface and a gas or a liquid). The foamy and emulsion films are referred to as symmetrical films, whereas the wetting films are regarded as non-symmetrical ones. The thickness of symmetrical foamy films stabilised by appropriate surfactants can range from several nanometers (the so-called Newtonian black films)[11-16] to several tens of nanometers.

3. One-dimensional nanoparticles in which the thickness and width are in the nanorange, while the length may be unlimitedly large. The one-dimensional ultradisperse particles include thin fibres, very thin capillaries and pores, cylindrical micelles of surfactants and nanotubes which much resemble them.[17,18] This group also includes the wetting line (or the line of three-phase contact), which separates three phases, *viz*., a solid, a liquid and a gas.[19,20]

The classification of disperse particles based on their dimensionalities is important not only from the formal viewpoint. In conformity with the Ehrenfest principle, the geometry of particles (the dimensionality of space) has a substantial effect on the character of dependences relating physical parameters.[21,22] Thus the power index for the distance in the Newtonian gravitation laws and for the electrostatic Coulomb interaction is -2 for three-dimensional space and -1 for two-dimensional space.[22]

Yet another remarkable parameter confirming the Ehrenfest principle is the different dependence of the heat capacity of solids at constant volume C_V on temperature T in the range of sufficiently low temperatures. Thus Tarasov[23-25] showed experimentally that the law of squares ($C_V \sim T^2$) is fulfilled for the lamellar structures (*e.g*., for graphite and gallium) instead of the Debye law of cubes for isotropic materials whereas the linear dependence ($C_V \sim T$) is observed for the chain structures (of crystals selenium, HF, BiO_3 and $MgSiO_3$). The theory of heat capacity of thin films and thin rods (needles) developed by Lifshitz[26,27] states that at low temperatures the $C_V(T)$ dependences for two- and one-dimensional objects differ substantially from those for three-dimensional crystals.

Yet another example concerns the theory of capillarity. Clerot who put forward in 1743 the hypothesis of the existence of molecular forces suggested that they depend on the distance r in the same way as the gravitation forces ($\sim r^{-2}$). However, this hypothesis contradicted the empirical Juren law (1718) describing the upward movement of wetting liquids in capillary tubes. On the contrary, the Laplace hypothesis (1804)[28] of the short-range action of molecular forces ($\sim r^{-1}$) described correctly this phenomenon. It should be noted that the Ehrenfest principle provides the physical substantiation of the Laplace hypothesis. Indeed, the change in the power index from $n = -2$ in the Coulomb law to $n = -1$ in the Laplace hypothesis corresponds, according to Ehrenfest, to the transition from a three-dimensional to a two-dimensional object.

The above-cited regularities reflect changes in a number of physicochemical properties of nanoparticles compared to the corresponding properties of the macrophase. For example, a strong decrease in the melting temperature is observed for nanoparticles of many metals and semiconductors (Ag, Au, Pb, Sn, In, Bi, Ga, CdS).[29,30] It is also known that the strength of filamentous crystals and fibres can be several times higher than that of macroscopic bodies. Nanosize particles possess an enhanced chemical reactivity manifested in the increase in the rates of chemical reactions involving their particles. This property of nanoparticles is used in the preparation of catalysts. It should also be noted that some phases can appear in nanoparticles which are not revealed in macrosystems. A sufficiently detailed description of special properties of nanoparticles can be found in relevant reviews.[31-34]

Thus, the Ehrenfest principle has a fundamental significance. However, it has not yet found uses in colloid chemistry, including the theory of surface phenomena, although its potentialities seem to be very large here, especially for the description of nanosystems.

As has been noted, colloidal systems comprise several phases, at least two, therefore, properties of a system depend on the interaction between these phases. Based on the energy of interaction of the disperse phase and the dispersion medium, dispersion systems are divided into two large classes, *viz*., lyophilic and lyophobic. According to Rehbinder,[4] the formation of stable lyophilic systems results from spontaneous dispersion of a macrophase into particles of colloidal size d. The thermodynamic condition of spontaneous dispersion is described by the expression

$$\sigma d^2 \leqslant \beta k T, \qquad (1)$$

where σ is the surface tension at the disperse phase – dispersion medium interface, β is the coefficient taking into account the particle shape and changes in the entropy of a system due to the involvement of particles in the thermal motion ($\beta = 15-30$), k is the Boltzmann constant and T is temperature. It follows from the condition (1) that the formation of colloidal systems with the particle size of 1 – 100 nm requires a strong decrease in the surface tension, approximately down to $10^{-2}-10^{-3}$ mJ m^{-2}. This type of nanocolloids includes microemulsion systems, critical emulsions and micellar systems.[4,6]

Thus, the range of ultradisperse systems (nanosystems) is very broad and they are very interesting from the scientific viewpoint for reviews, (see, *e.g*., Refs 35, 36).

III. The formation of ultradisperse systems

Numerous methods have been developed in colloid chemistry for the preparation of ultradisperse systems allowing a rather fine control over the sizes of particles, their shapes and structures. The Nobel Prize winner Th Svedberg[37] proposed to divide methods for the preparation of ultradisperse particles into two groups:

dispersion methods (mechanical, thermal, electrical grinding or spraying of a macroscopic phase) and condensation methods (chemical or physical condensation).

It is impossible to consider all these methods in sufficient detail within the frame of this review; therefore, we will discuss only some examples of chemical methods for the preparation of ultradisperse systems. Historically, it was by these methods that the first highly dispersed colloidal solutions were obtained.

1. Preparation of sols

Systematic development of methods for the synthesis and purification of highly dispersed colloidal systems began in the middle of the 19th century when Faraday prepared stable sols of gold (with the particles 2 – 50 nm in size) by reduction of a dilute solution of a gold salt with yellow phosphorus.[38]

$$AuCl_3 + 3H_2O + P \longrightarrow Au + P(OH)_3 + 3HCl\,.$$

Later, Zsigmondy[39] developed methods (which became classical) for the synthesis of monodisperse gold sols with a predetermined degree of dispersion by the reduction of gold(III) compounds with hydrogen peroxide and formaldehyde.

$$2HAuCl_4 + 3H_2O_2 \longrightarrow 2Au + 8HCl + 3O_2\,,$$

$$2HAuCl_4 + 3HCHO + 11KOH \longrightarrow$$

$$\longrightarrow 2Au + 3HCOOK + 8KCl + 8H_2O\,.$$

This process proceeds in two steps. In the first step, nuclei of a new phase are formed and then a slight oversaturation occurs in the sol where no new nuclei are formed and only growth of the existing nuclei takes place. Yellow ($d \sim 20$ nm), red ($d \sim 40$ nm) and blue ($d \sim 100$ nm) sols of gold can be prepared in this way.

The invention of an ultramicroscope (1903) which allowed measurement of ultradisperse particles (down to 3 nm in size) gave a strong impetus to the search for new methods for the preparation of sols and studies of their properties. It is worthwhile to note several basic achievements. Svedberg[40] synthesised highly dispersed sols of alkali metals in organic solvents on strong cooling. Weimarn[41] was the first to establish the conditions under which any substance can be present in the colloidal state: 'Any substance may be obtained in the form of colloidal solution if one succeeds in bringing about the reaction of its formation in a dispersion medium, which dissolves this substance negligibly, at a sufficiently low concentration of reactants.' He prepared sols of several hundred different substances under laboratory conditions.

In the early 1980s, it was found that the solid-phase nanosize particles have special mechanical, optical, electrical and magnetic properties different from the corresponding properties of macrosystems.[34, 42, 43] This fact determined the wide uses of nanoparticles in different fields of science and technologies.

Numerous methods of synthesis of nanoparticles have been developed to date. Analysis of methods for the preparation of nanoparticles of different nature is reviewed in Refs 31, 34 – 46. The present review considers only briefly recent methods for the preparation of sols based on condensation reactions.

Hydrolysis of inorganic salts of metals or metal alkoxides resulting in the formation of sols of oxides and hydroxides of the corresponding metals can serve as an example.[47 – 51] Thus iron hydroxide sol can be prepared by the reaction

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl\,.$$

In this approach to sol preparation, it is important to observe thoroughly the reaction conditions; in particular, it is necessary to control strictly pH and the presence of certain organic compounds in the system. Thus Kandori *et al.*[52] showed that the size of Fe_2O_3 particles resulting from hydrolysis of $FeCl_3$ depends on the concentration of triethanolamine, isopropylamine and piperazine.

The presence of a large excess energy in disperse systems related to the highly developed interface favours the processes of aggregation of colloidal particles (see Section V). To prepare sols of required dispersity, it is necessary to arrest growth of particles in due time. To this end, the surface of particles in the disperse phase is deactivated by formation of a protective layer of surfactants[53 – 55] or by complex formation.[56, 57]

As regards control of the shape and size of nanoparticles, highly promising proved to be the synthesis of nanoparticles in microemulsion systems which will be considered in more detail in Section III.3.

2. The formation of micellar systems

Surfactants, organic substances (synthetic or natural) with limited solubility in water, which can adsorb on the interface thereby reducing the interfacial tension, represent unique aspect of colloid chemistry. These compounds have diphilic structures: a surfactant molecule or ion contains a hydrophobic part and a polar group of some kind. The hydrophobic part is a hydrocarbon radical (C_nH_{2n+1}, C_nH_{2n-1}, $C_nH_{2n+1}C_6H_4$, *etc.*) containing from 8 to 18 carbon atoms. Depending on the nature of the hydrophilic group, the surfactants are divided into cationic (these include primary, secondary and tertiary amines and quaternary ammonium bases), anionic (molecules of these compounds contain carboxy and sulfonic groups and others) and non-ionogenic (these surfactants exist in solution in the form of molecules).[58]

The specificity of the behaviour of surfactants in aqueous solutions is related to peculiarities of the interaction between the water molecules and surfactants. According to numerous studies, at room temperature water is a structured liquid and its structure is similar to that of ice but in contrast to ice, water has only near ordering ($r < 0.8$ nm).[59, 60] Solubilisation of surfactants induces further structuring of water molecules around non-polar hydrocarbon radicals of surfactants, which leads to a decrease in the entropy of the system. As the system tends to the maximum entropy, at a certain concentration called the critical micelle concentration (CMC), the surfactant molecules or ions begin to form spontaneously associates which are called micelles (as proposed by Mac-Ban who discovered them in 1913). The formation of micelles is accompanied by the release of a portion of structured water which is a thermodynamically advantageous process since it leads to an increase in the entropy of the system.

The formation of micelles is usually revealed from changes in some physical property of the surfactant solution (*e.g.*, surface tension, electric conductivity, density, viscosity, light scattering, *etc.*) depending on the surfactant concentration. The magnitude of CMC depends on a number of factors: the surfactant nature, the length and degree of branching of a hydrocarbon radical, the presence of an electrolyte or other organic compounds and pH of the solution. However, the basic factor is the ratio between hydrophilic and hydrophobic properties of the surfactant. The longer the hydrocarbon radical and the weaker the polar group the smaller the CMC.§

At concentrations close to CMC, micelles represent nearly spherical formations in which polar groups contact with water, while hydrophobic radicals are directed inwards to form a non-polar nucleus.[4, 61] Molecules or ions constituting micelles are in dynamic equilibrium with the bulk of the solution. This is one of the reasons for the 'roughness' of the outer surface of micelles.[61, 62] The degree of hydration of polar groups, the structure of the hydrate layer, and the structure of the internal nucleus depend on the nature of the surfactant.[63 – 66]

At concentrations higher than CMC, the formation of several types of differently shaped micelles is possible (Fig. 1): spherical, cylindrical, hexagonal packed and lamellar ones. Thus, micelles may be regarded as one-, two- and three-dimensional nanoobjects. Depending on the surfactant nature, the aggregation number (n) can change from tens to several hundreds, the sizes of micelles will be changing accordingly.[67]

§ Modern concepts of the thermodynamics of surfactant solutions and micellisation processes are considered in sufficient detail in Rusanov's monograph.[61]

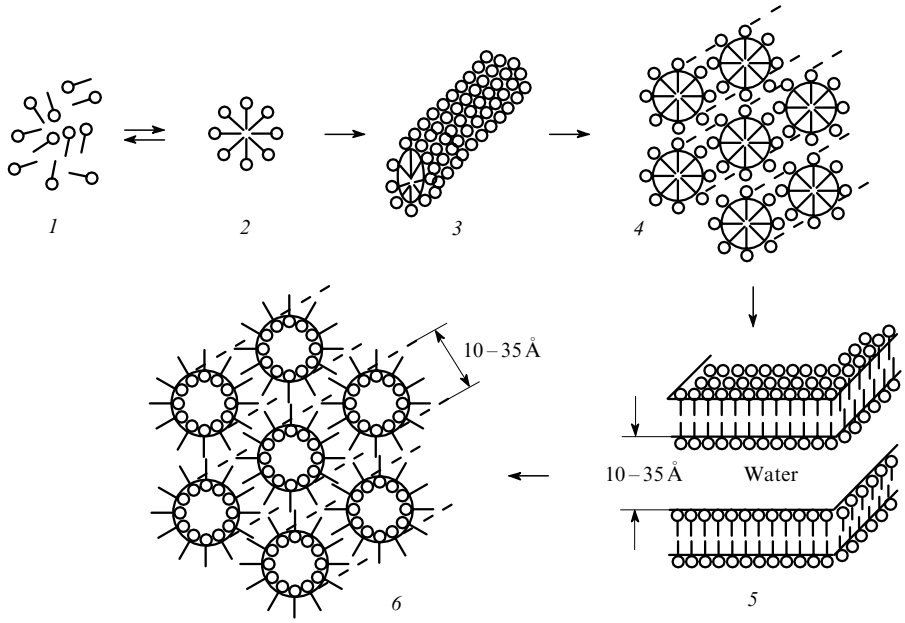


Figure 1. Structures arising in solutions of surfactants: (*1*) monomers; (*2*) micelle; (*3*) cylindrical micelle; (*4*) cylindrical micelles as packed hexagons; (*5*) lamellar micelle; (*6*) water droplets packed as hexagons in the reverse micellar system.

Water-insoluble surfactant molecules with a long hydrocarbon radical and a weakly polar group can be dissolved in non-polar liquid phases. In this case, at a definite surfactant concentration the formation of micelles is also observed and is determined by specific interactions between the polar groups of the surfactant.[68–71] These are called reverse micelles. The shapes of the reverse micelles are not necessarily the same, this depends on the surfactant concentration.

There are two approaches to the description of micelle formation. According to the first approach (the quasi-chemical model), the micellate formation is considered from the standpoint of the mass action law. The second approach interprets the appearance of micelles as the formation of a new phase.

One of the most important properties of the micellar systems is their ability to solubilise, *viz*. , to increase considerably the solubilities of hydrocarbons in aqueous micellar solutions, or, respectively, of polar liquids in the reverse micellar systems.[72–74] Solubilisation results in the appearance of thermodynamically stable equilibrium isotropic systems, which are called microemulsions (these systems will be considered in more detail in the next section). Due to numerous factors which influence solubilisation (the nature of contacting phases and surfactants, the presence of electrolytes, temperature), the maximum solubilities of substances in surfactant micelles can vary within very broad limits. It should be noted that upon solubilisation the properties of compounds change largely and can also result in changes in the rates of chemical reactions occurring in these systems. This phenomenon known as the micellar catalysis finds wide uses in chemistry, biology, medicine and various technological processes. For example, the increase in the reactivities of compounds is widely used in the processes of emulsional polymerisation[75–77] and enzymatic catalysis.[78–80]

3. Formation of microemulsions

Microemulsions are thermodynamically stable isotropic dispersions of two non-miscible liquids. Upon mixing these liquids, the droplets of one of them stabilised by the interfacial film of a surfactant and a co-surfactant (a low-molecular-mass alcohol) are distributed in the other liquid. The term 'microemulsion' was proposed by Schulman[81] who was the first to obtain such systems upon addition of surfactants to a macroemulsion. Microemulsions are regarded as lyophilic disperse systems and may be obtained either by spontaneous dispersion of two non-miscible liquids as a result of a strong decrease in the interface tension or in the process of solubilisation, as noted above. The thermodynamic stabilities of microemulsion systems are determined by low interface tension which, according to the literature data, may be 10^{-5} mJ m^{-2} for ionic surfactants and 10^{-4} mJ m^{-2} for non-ionogenic surfactants.[82] Depending on which phase is dispersed and which is continuous, the microemulsions can be direct [oil in water (o/w)] or reverse [water in oil (w/o)].¶ In both cases the dispersed phase consists of droplets whose size does not exceed 100 nm.

Microemulsions are, as a rule, multicomponent systems comprising different structures (bilayer, cylindrical or spherical micelles).[83–85] In the process of micelle formation, optically anisotropic micellar phases, for example, lamellar smectic and hexagonal phases consisting of rod-shaped aggregates of infinite lengths, are formed in addition to the liquid isotropic micellar phases, *i.e*., microemulsions possess internal microstructures which are currently studied by different methods.[86–88] In the case where the contents of water and oil in the system are comparable, bicontinuous systems can be formed.[89, 90]

The properties of microemulsions are largely determined by the sizes and shapes of the dispersed phase particles as well as by rheological properties of interface adsorption layers formed by surfactants. Since the microemulsions are highly mobile and posses large interfaces, they can serve as versatile media for numerous chemical syntheses, including the preparation of solid nanoparticles.

4. The formation of solid particles in microemulsions

In a microemulsion system, the dispersed phase particles continuously collide, coalesce and degrade again, which leads to a continuous exchange of their contents. Collision of droplets depends on their diffusion in the oil phase (for the reverse microemulsion system), whereas the process of exchange is determined by the interaction of adsorption layers of surfactants and the flexibility of the interface (the latter circumstance is crucial for carrying out chemical reactions in such systems).[91, 92]

Reverse microemulsion systems are often used for the preparation of solid nanoparticles. To this end, two identical microemulsion systems (w/o) containing in their aqueous phases

¶ The term 'oil' means a non-polar organic liquid.

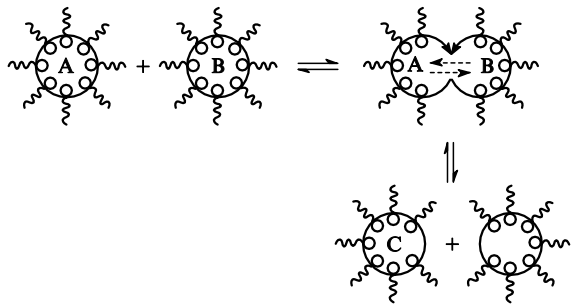


Figure 2. Scheme of a reaction occurring in the reverse microemulsion system.

compounds A and B which form a poorly soluble product C in the chemical reaction are mixed. The new compound C is formed in droplets as a result of coalescence (Fig. 2). The sizes of the new phase particles will be restricted by the size of droplets of the polar phase.

Metal nanoparticles can also be obtained by adding a reducing agent (*e.g.*, hydrazine) to a microemulsion containing a metal salt or by bubbling a gas (*e.g.*, H_2 or CO) through this emulsion. It was in this way (reduction of a metal salt by hydrazine) that monodispersed metal particles of Pt, Pd, Rh and Ir were obtained with a particle sizes of 3–5 nm.[93] An analogous method was applied for the synthesis of bimetallic particles of platinum and palladium.[94]

At present, precipitation reactions in microemulsion systems are widely used for the synthesis of metal nanoparticles,[95–97] semiconductors,[98–102] barium, calcium and strontium carbonates and sulfates,[103–107] monodispersed SiO_2 particles[108–110] and high-temperature ceramics.[111–113]

Despite the fact that the mechanism of formation of nanoparticles has not yet been ultimately established, it is possible to identify a number of factors which influence this reaction. These are primarily the ratio of the aqueous phase to the surfactant ($W = [H_2O]/[\text{surfactant}]$) in the system, the structure and properties of the solubilised aqueous phase, the dynamic behaviour of microemulsions and the mean concentration of reagents in the aqueous phase. The sizes of droplets in the disperse phase are also influenced by the nature of the surfactants which stabilise the microemulsion system. However, in all cases the sizes of nanoparticles formed in the reaction are governed by the sizes of droplets of the initial microemulsion. For instance, Petit and Pileni[99] showed that the sizes of CdS nanoparticles increase virtually linearly as the ratio W increases. On the other hand, the sizes of particles obtained in the reverse microemulsion system stabilised by sodium di(ethylhexyl) sulfosuccinate (Aerosol OT) proved to be smaller than those in the system stabilised by the nonionogenic surfactant Triton X-100 [polyethylene glycol ($n = 10$) *p*-iso-octylphenyl ether].

Microemulsion systems are also used for conducting hydrolysis. Hydrolysis of tetraethoxysilane in the reverse micellar system stabilised by Aerosol OT can serve as an example.[114]

$$Si(OEt)_4 + 2\,H_2O \longrightarrow SiO_2 + 4\,EtOH\,.$$

It should also be noted that microemulsion systems are used for the preparation of organic compounds, which is important for the creation of new medicinal forms.[115]

Most of studies in this field relate to the synthesis of spherical nanoparticles. On the other hand, the preparation of asymmetrical particles (filaments, discs, ellipsoids) and a rigorous control of their shapes is also of high scientific and practical interest. Syntheses carried out in the microemulsion systems allowed the preparation of $BaCO_3$ nanofibres[116] and asymmetrical nanoparticles of various compounds with unusual magnetic properties.[117–119]

Highly interesting is the synthesis of nanocomposites consisting of particles of one material (the particle size is 50–100 nm) coated with a thin layer of another meterial.[120, 121]

5. Preparation of mono- and polymolecular layers

Surfactants can form monomolecular films on various interfaces: water–air, solid–liquid and liquid–liquid. Such films may be regarded as two-dimensional nanosystems. The surfactant monolayers on the water–air interface were studied by Langmuir who developed an experimental method for the studies of these films (the Langmuir balances).[122] For this work Langmuir was awarded the Nobel Prize in 1932. Monomolecular films on the surface of liquids may be in the gaseous, liquid and solid states. These states are characterised by different energies of interaction of the surfactant molecules.

Under definite conditions (pH, temperature), the water–air interface is the site of spontaneous formation of highly ordered structures, in which the surfactant molecules (or ions) are arranged in such a way that the polar group is in solution, while the hydrocarbon radical is oriented into the air at a small angle to the interface. The processes of self-organisation in a film are determined by the diphilicity of the surfactant molecules and may be analysed from the viewpoint of interaction of the polar group with the water substrate and interaction of the hydrocarbon radicals with each other.[122–126]

Chemical reactions occurring in monomolecular films are of considerable interest. By varying the surface pressure it is possible to control the orientation of molecules in the surface layer and influence thereby specifically the occurrence of these reactions. Thus the Langmuir–Blodgett films are used for the preparation of solid nanoparticles of different nature directly in the process of chemical reaction or photochemical reduction of metal salts.[127–130] Similar processes also occur in biological systems.[131]

The films deposited onto the solid surface can form both mono- and polylayers. For example, if a glass plate positioned vertically is drawn from water through a monolayer of barium stearate on its surface, this plate becomes coated with a surfactant layer in which the hydrocarbon radicals are oriented outwards. The result is that the surface of this plate becomes hydrophobic. It can then be covered with the next layer. Hydrophilic or hydrophobic surfaces may be obtained by successive deposition of layers.[132] The films composed of layers of the same orientation are called the X-films, whereas those with the oppositely oriented layers are called the Y-films. In this way, it is possible to obtain polylayer coatings with thicknesses in the range of nanometers.

IV. The structures and forms of ultradisperse particles

The questions concerning the mechanisms of formation and the structures of nanosize particles are regarded as the most important and essential for colloid chemistry. Indeed, ultradisperse particles are some kind of 'elementary particles' of colloid chemistry. The transition from a simple qualitative definition of the concept of disperse particles to the determination of their quantitative parameters and relationships requires detailed elucidation of the structures of ultradisperse particles in different colloidal systems, such as sols, micellar solutions, microemulsions, gels, *etc*.

The early concept of the structures of solid ultradisperse particles was based on the suggestion that their structures are analogous to that of the macrophase of the same substance. However, further studies of the process of nucleation and growth of a new phase showed that depending on crystallisation conditions (the degree of oversaturation or overcooling, the presence of admixtures and a number of other factors), both amorphous and crystalline ultradisperse particles can be formed from solutions.[133, 134] Back in 1910, Weimarn[5] found that the shapes of $BaSO_4$ particles formed by crystallisation from solution depended on the degree of its oversaturation. Thus he obtained highly dispersed sols, flocculent structures, well faceted microcrystals

and needle-shaped crystals. The temperature of the synthesis of nanoparticles also plays an important role. For example, nanoparticles of titanium dioxide obtained by the sol–gel method are rod-shaped at low temperature and have the form of bipyramidal crystals at high temperature.[135] Yet another confirmation of the diversity of forms of nanoparticles is the formation of dendrites upon crystallisation from solutions and melts.[136]

The diversity of forms is due to the fact that the processes of new phase formation (the self-organisation processes) occur under essentially non-equilibrium conditions, and the extent of structural perfection depends on how far the crystallisation conditions deviate from the equilibrium conditions. For example, in the synthesis of diamond from a dense gas phase and plasma, a more perfect structure is formed under more non-equilibrium conditions.[137]

Surfactants present in solution can strongly influence the crystallisation process. Depending on the nature and concentration of the surfactants, they can change the rate of nucleation and growth of nuclei of the new phase, the shape of crystals and distribution of nanoparticles with respect to the size.[138–141] All these effects are related to the selective adsorption of surfactant molecules or ions on different facets of the crystals formed and consequently to the retardation of growth of some facets compared to others.[142] In addition, the nature of the surfactant also influences the polymorphism of the compounds formed. For example, Füredi-Milhofer *et al.*[143] showed that crystallisation of calcium oxalate in solutions of octaethylene glycol monohexadecyl ether results in the formation of calcium oxalate monohydrate, whereas in solutions of sodium dodecyl sulfate, dihydrate is formed.

An important feature of the crystallisation processes leading to the formation of nanoparticles is that their shapes cannot be described by the methods of usual geometry. These systems are described using the fractal geometry, since in the case of strong deviations from equilibrium and consequently high values of the driving force of the crystallisation process the instability of the interface leads, as a rule, to the formation of fractal structures.[144]

Of interest are the studies reported by Melikhov *et al.*[145, 146] who showed that highly dispersed primary single crystals are formed first in the mutual crystallisation of ammonium halides and cesium iodide from highly oversaturated vapour. Owing to highly developed interface, the disperse system formed possesses a large energy excess and for this reason it is the site of the occurrence of aggregation processes, which are accompanied by the concrescence of the initial single crystalline particles of approximately the same size. This aggregation results in the formation of pseudo-single crystals.

The processes of formation of ultradisperse systems in the case of metal crystallisation are much more complex and diverse. In the essence, investigation of these processes laid the foundation for a new direction known as the chemistry of clusters.[147–149] Cluster particles occupy the intermediate position between mononuclear compounds and disperse particles. The metal particles with $d < 30$ nm can be obtained by the methods of gas-phase nucleation, cryogenic synthesis and reactions in polymeric matrices and reverse microemulsion systems.[150–153]

It should be noted in conclusion that until now there is no sufficiently comprehensive quantitative theory of nucleation and growth of colloidal particles.

V. The application of theoretical concepts of colloid chemistry in nanochemistry

The concepts of colloid chemistry may also be used for the description of nanosystems (ultradisperse colloids). However, this involves rather complex methodological problems. These are due to the intermediate position occupied by the ultradisperse particles between molecules (atoms, ions) and macroscopic bodies (phases).

Both chemical and physical approaches are used for the theoretical description of colloidal systems. This is related to the boundary position of colloid chemistry between chemistry and physics, which exerts a strong effect on its methodology.[154] For example, the chemical approach prevails in studies of the highly dispersed state (including surface layers). Chemical methods are applied for the calculation of the electronic structure of nanoparticles (clusters) and its effect on their catalytic properties,[149] surface forces and Hamaker constants,[155, 156] as well as for the determination of the constants of adsorption equilibrium using the mass action law.[61] Based on the analogy of a bimolecular reaction and an elementary act of coagulation, the theory of rapid coagulation of sols under the action of electrolytes was developed (M Smolukhovsky, 1916). The theory of electrokinetic phenomena (electrophoresis and electroosmosis) is based on the concepts of electrochemistry on the structure of the double electrical layer and electrocapillary effects.

At the same time, the concepts of molecular physics, chemical thermodynamics and mechanics of continuous media are widely used for the description of relatively large particles and colloidal systems formed by them.

Of particular conceptual interest are the colloidal systems where the progress in the studies has been achieved upon the parallel use of chemical and physical theories, models and methods. A spectacular example of this approach is the investigation of the formation of direct and reverse micelles in solutions of surfactants.

The modern theory of micelle formation has been developed based on two complementary models, *viz.*, the quasi-chemical model (the formation of a micelle resulting from the reversible aggregation reaction) and the model of a phase transition of the second type.[61] Such a conceptual dualism is rather characteristic of the methodology of colloid chemistry. Combination of macroscopic and molecular properties in a single object (colloidal particle, surface layer) was duly appreciated long ago by both chemists and physicists. Thus studies of the capillary and surface phenomena have made it possible to derive first quantitative estimates of the sizes of molecules (B Franklin, T Young) and have led to the discovery of forces of molecular attraction (A Clairaut, P Laplace). Studies of the temperature dependence of the capillary rise of organic liquids made it possible to establish their critical temperatures (D Mendeleev). The Boltzmann constant was calculated from the temperature coefficients of surface tension of pure substances.

Yet another example of the combination of physical and chemical approaches to studies of colloidal systems is the discovery of the effect of adsorption-induced decrease in strength (the Rehbinder effect).[157] The modern theory of this effect borrows a number of notions and concepts from the physics of solids and mechanics (dislocation, the concept of tensions in the uppermost part of a fissure, the Griffith theory for the calculation of the critical sizes of nuclei of a crack and others). On the other hand, studies of molecular mechanisms of the Rehbinder effect involve inevitably chemical processes and factors, since the decrease in the strength and plasticity of metals, ionic crystals and other solids was caused by the adsorption of the corresponding compounds in the predestruction zone.[157]

Phenomenological laws of colloid chemistry established on the basis of molecular physics, thermodynamics and mechanics of continuous media have a fundamental character. However, their direct extrapolation to the ultradisperse field is not, as a rule, sufficiently accurate. This is due to the fact that many properties of substances in the ultradisperse field are substantially dependent on the particle size (d), and changes in properties may be caused by different reasons. For instance, in the range of $d < 1$ μm an increase in the strength of crystals is observed as their diameter d decreases. To an order of magnitude, this 'threshold' corresponds to the mean distance between dislocations in non-deformed crystals.[158]

Colloidal systems are characterised by a very large specific surface Ω of the dispersed phase

$$\Omega \approx \frac{K}{d\rho},$$

where K is a dimensionless coefficient (for the spherical and cubic particles, $K = 6$), ρ is the disperse phase density. Other most important parameters which characterise colloidal systems are the specific free surface energy σ (surface tension), the surface entropy η and the specific adsorption Γ. For the systems with the moderate degree of dispersion, the surface tension σ is determined only by chemical compositions (the nature) of the dispersed phase and dispersion medium. However, for the nanosystems one has to take into account the dependence of the surface tension on the sizes of dispersed particles.

Because of special importance of the surface tension, let us consider this aspect in more detail. Two approaches are widely used for the analysis of the scale (dimensional) dependence of the surface tension. One of them relates the surface tension to the surface curvature and is used, *e.g.*, for the description of surface properties of droplets, gas bubbles and nuclei of the new phase particles. Tolman [159] proposed the following equation for the description of this relationship:

$$\sigma_r\left(1 + 2\frac{\delta}{r}\right) = \sigma_0, \quad (2)$$

where σ_r is the surface tension corresponding to the curvature radius r, σ_0 is the surface tension for a flat surface, δ is the thickness of the surface layer of a substance characterised (according to Gibbs) by excess thermodynamic functions. According to a number of estimates, $\delta \approx 1$ nm; therefore, for the nanosize particles and gas bubbles a substantial change (increase) in the surface tension is observed. For this reason, the corresponding corrections considering the dependence $\sigma = f(r)$ should be made in all fundamental laws of colloid chemistry, *viz.*, the Laplace law of capillary pressure, the Young law of contact angles of wetting, the Kelvin law of the saturated vapour pressure over a curved surface and others. The dimensional factor plays a rather substantial role in the formation of nucleation particles during phase transitions. Indeed, the classical thermodynamic relations which determine the critical size of the nucleus of a new phase include the surface tension for the surface of small curvature, though it is in the nucleation particle that the surface curvature is the largest.

Let us clarify this statement with the following example. The critical size of the new phase nucleus r_c in the homogeneous formation resulting from the phase transition of the first type is determined in the Gibbs theory by the equation

$$r_c = \frac{2\sigma T_m}{Q_m \Delta T}, \quad (3)$$

where T_m and Q_m are the temperature and heat of phase transition and ΔT is the deviation of temperature from T_m. Thus, rather considerable overcoolings ΔT are required for the crystallisation of very small droplets of liquid metals, starting approximately from 5 nm. For instance, the values of ΔT for mercury, tin, copper and platinum were found to be 77, 118, 236 and 370 °C, respectively.[160] The simplest rationale is the increase in the surface tension as the curvature radius decreases [Eqn (2)], which leads to the corresponding increase in the overcooling ΔT (at a fixed value of the droplet size r_c).

A different approach to the description of special properties of ultradispersed objects (thin liquid films) is used in the concept of disjoining pressure Π introduced by Deryagin.[19] The disjoining pressure is the difference between the pressure P_H inside the film of thickness H and the pressure in the bulk phase P_0 of the same substance at the same values of temperature and chemical potentials as in the thin film.

$$\Pi = P_H - P_0. \quad (4)$$

The most important feature of thin films is that their thickness H is commensurable with the surface layer thickness δ. The overlapping of the surface layers of two contacting phases (for $H < \delta$) makes an additional contribution to the free energy of the film.

The concept of disjoining pressure has been developed in sufficient detail and is widely used nowadays for the description of many phenomena. Thus the concept of disjoining pressure forms the basis of the theory of stability of colloidal solutions [the Deryagin – Landau – Verwey – Overbeck theory (DLVO)].[161–163]

Certain problems also arise in the description of wetting of solids with nanosize droplets. In these cases, the equilibrium contact angle of wetting Θ_r depends on the linear tension $\varkappa$. The corresponding equation is

$$\cos\Theta_r = \cos\Theta_0 - \frac{\varkappa}{\sigma r}, \quad (5)$$

where Θ_0 is the equilibrium angle of a droplet at a large curvature radius ($\geqslant 0.1$ mm) and r is the radius of the droplet base.

This relation, which is analogous to the Laplace law of capillary pressure $P_r = 2\sigma/r$, was obtained for the first time and confirmed experimentally in measurements of forces on the wetting line in the plane of a bubble base on a solid support.[164] The contact angle Θ_r for a droplet or a bubble with a small radius r is determined from the conditions of mechanical equilibrium on the three-phase contact line (TPL).[165, 166]

The direct confirmation of the dependence of Θ_r on the linear tension was obtained for microdroplets of organic liquids on asbestos filaments.[167] According to different estimates, the magnitude of linear tension is $\sim 10^{-7}$ mN.[166] Therefore, this can make a noticeable contribution to the magnitude of contact angles (for liquids with the surface tension $\sigma \approx 50-100$ mN m^{-1}) only in the case of nanosize droplets ($r \sim 10^{-9}$ m).

The influence of linear tension becomes rather substantial in the heterogeneous formation of the new phase nuclei, *e.g.*, upon vapour condensation on wetted solid substrates. Thermodynamic analysis [166] provides the following equation for the work of a nucleus (droplet) formation as a spherical segment

$$A = \frac{PV}{2} + \frac{\varkappa l}{2}, \quad (6)$$

where P is the capillary pressure, V is the droplet volume, l is the length of the TPL. Relation (6) may be regarded as a generalised equation with the aid of which one can calculate the work of formation of the new phase nucleus in the nanosize range (it is for this purpose that the linear tension $\varkappa$ is introduced). In the case of a spherical droplet $\varkappa = 0$, and relation (6) is transformed into the equation which describes the work of homogeneous formation of the new phase nuclei (A_0).

In order to calculate the work of heterogeneous formation of the new phase nucleus A_h, use is made of the well known Volmer equation [168]

$$A_h = A_0(2 - 3\cos\Theta_0 + \cos^3\Theta_0). \quad (7)$$

Finally, for $V = 0$ equation (6) describes the work of formation of a two-dimensional nucleus ($A = \varkappa l/2$).

The above-cited examples of extrapolation of some laws of colloid chemistry to nanodispersed objects should be regarded only as a first approximation. The basic reason for the limited action of these laws, even with the consideration of the mentioned corrections, consists in peculiarities of the structure of nanosystems (see Section III). The complexity and non-triviality of the problems arising in this extrapolation will be explained by the example of two nanoobjects which are widely distributed in technological and natural processes: the surface layer of a liquid and LTC.

At the interface of a pure liquid and a gas phase the surface layer (SL) has a very small thickness (δ) which is of the order of several molecular layers (far from the critical temperature), *i.e.*, it represents formally a two-dimensional nanoparticle with two

macroscopic sizes (length and width) and one nanosize (thickness). Such a definition follows from the classical Young – Laplace theory; it is also confirmed by calculations based on macroscopic theories. The Gibbs theory considers the SL of a substance as an independent phase, the thermodynamic parameters of which differ from analogous parameters of the bulk phase of the same substance. Evidently, it is for this reason that the structure of SL of a liquid will differ from the structure in the bulk.

Until recently, the SL structure could not be studied in detail because of the absence of adequate experimental methods. Only in the last 5 – 7 years has the improved method of small-angle scattering made it possible to obtain reliable information about the SL structure of different liquids (mercury, gallium, alkanes starting from $C_{16}H_{34}$ and some others). It was found for all the compounds studied that their SL represents a two-dimensional quasi-crystalline structure at temperatures several degrees higher than the melting temperature T_m. The thickness of SL is estimated to be 1 – 2 molecular (atomic) diameters. It was established that the parameters of a two-dimensional crystal differ from the parameters of the lattice of a 'bulk' crystal of the same substance.[169, 170]

These experimental data confirm the recent network model of the surface layer of a liquid,[171 – 173] according to which it contains nanoparticles of the solid phase. They form a structure ('network') which determines the appearance of the surface tension of a liquid. The model predicts rather simple correlations between the surface tension and the heat of melting, which are in good agreement with experimental data for liquid metals and liquefied inert gases.

These results seem to be of principal significance. It follows from them that the surface nanolayer of a pure liquid has in fact an aggregation state different from the state in the bulk. This confirms one of the initial postulates about the thermodynamics of the surface Gibbs phenomena which states that the SL is an independent phase.[171, 174]

On this basis, the process of SL formation may be regarded as the phase transition liquid – two-dimensional solid.[162] In the framework of this model, the surface tension σ_m is proportional to the heat of melting Q_m near the melting temperature T_m. It thus follows that

$$\sigma_m = Q_m \rho_s \delta = Q_{sf}\,, \tag{8}$$

where ρ_s is the solid phase density and Q_{sf} is the heat of SL melting per surface unit. In the first approximation, the thickness of the SL (δ) is equal to a (a is a parameter of the crystal lattice of a given compound). Figure 3 shows that the dependence $\sigma_m = f(Q_m)$ is very well respected for many liquid metals and liquefied inert gases. The thickness of the SL for liquid alkali metals, other melts and liquefied gases corresponds to four, two and one monolayers, respectively.

The model of the solid SL makes it also possible to calculate the temperature coefficient of surface tension $-d\sigma/dT$ from the entropy of melting $\Delta S = Q_m/T_m$. Calculations of the coefficients of surface tension for many liquid metals give a rather close correspondence to experimental data.[171, 172]

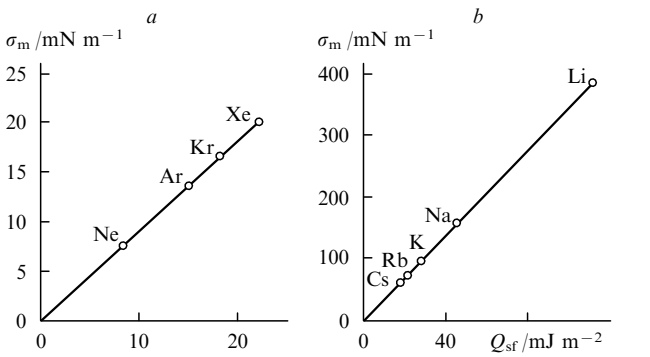


Figure 3. Correlation of the surface tension σ_m near the melting point with heat of melting Q_{sf}: (*a*) liquefied inert gases, (*b*) alkali metals.

Let us consider yet another example of the insufficiency of introduction of additional thermodynamic parameters (the disjoining pressure Π, the linear tension $\varkappa$) for the development of a comprehensive theory of colloidal nanosystems. In three-phase systems, the most important nanoobject is the three-phase contact line. This appears upon wetting, capillary flow, adhesion of liquids, spreading of drops over the surface of solids, condensation of vapours on supports and other phenomena. In these processes, the TPL is the front boundary of the liquid meniscus. Besides the term 'three-phase contact line' (TPL), the term 'wetting line' is used in a number of cases. As noted above, the linear tension describes special properties of TPL. Various theoretical models which consider the influence of the linear tension $\varkappa$ on the contact angles Θ [see Eqn (5)] include in the implicit form the suggestion that the wetting line is a regular circumference, *i.e.*, it has the same curvature $1/r$ along the entire length. An analogous assumption is also used, *e.g.*, in the theoretical description of spontaneous spreading of a drop of wetting liquid over a solid or liquid surface,[7, 175, 176] flows in capillaries and porous media,[177, 178] *etc*.

However, precision studies of the contour of drops of various liquids on solid supports (electron microscopy, laser interferometry) led to the conclusion about a totally different form of the wetting line. In the nanoscale, it represents an irregular alternation of protrusions and depressions, which are respectively ahead of or behind the mean position of the 'round' wetting line, *i.e.*, it is composed of small sites of positive and negative curvature.

This result is rather important for the development of a microscopic theory of wetting. In the first place, it shows that the movement of the wetting line upon the drop spreading should not be regarded as a smooth expansion of the wetted area within the limits of the entire contour (this assumption is used in the hydrodynamic theory of spreading).[15, 176] A different mechanism of motion appears to be more probable, *viz.*, the fluctuational formation of leading meniscuses in the radial direction and subsequent tangential flow of a liquid under the action of the capillary pressure created. This mechanism of the wetting line dislocation requires a much lower activation energy than that based on the simultaneous spreading of a drop over the entire perimeter. Such a movement of TPL has much in common with the sliding of edge dislocations in crystals;[137] therefore, one can effectively use the corresponding models (formation of kinks, their expansion, *etc*) for its description. At the same time, good prospects are open for the use of methods of fractal geometry for the description of these objects.

VI. Self-organised colloidal structures

A fundamental property of dispersed systems is their capacity for a gradual evolution. This evolution is associated with the nature of the colloidal (dispersed) state and primarily with the thermodynamic non-equilibrium of most colloidal systems. The excess of free energy, which is determined by the presence of a highly developed interface separating the dispersed phase and dispersion medium, stimulates different processes (physical, physicochemical) leading to a decrease in the Helmholtz free energy F.

Without consideration of the chemical component, the variation of the Helmholtz free energy dF at a constant temperature is

$$dF = -T dS + d(\sigma\Omega)\,, \tag{9}$$

where Ω is the interface magnitude.

The thermodynamic condition of evolution $dF < 0$ may be created in energy- and entropy-based ways. The former is characterised by changes in the second member of Eqn (9). This may be attained by decreasing the interface separating the dispersed phase and dispersion medium ($\sigma d\Omega < 0$) and by decreasing the inter-

facial free surface energy (the surface tension) ($\Omega d\sigma < 0$). Upon the decrease in the interface, an increase in the mean sizes of particles d takes place, *i.e.*, the distribution of particles over their sizes, which is fixed directly at the moment of their formation, is shifted with time towards the larger particles. The mechanisms of this process may be completely different: coalescence of droplets in emulsions and of gas bubbles in foams upon their direct contact, isothermal distillation of the disperse phase particles in conformity with the Kelvin law, the Ostwald ripening of solid particles. As a result of these processes, the solid particles can become so large that they loose their sedimentational stability. Ultimately, these processes can lead to the partition of a dispersed system into two macrophases.[179]

The decrease in the specific free surface energy $d\sigma < 0$ also occurs upon the interaction of the dispersed particles through the dispersion medium film, as well as upon the loss of aggregation stability by the system in the process of coalescence. The theory of sol stability (the DLVO theory)[163] considers in the first approximation the interaction of colloidal particles as the sum of dispersion (attraction) and electrostatic (repulsion) interactions which take place upon overlapping of the ionic atmospheres due to the approach of sol particles to each other. In the case where the radius of the dispersed particles is much larger than the thickness of ionic atmosphere, the energy of interaction of colloidal particles $U(h)$ may be expressed as

$$U(h) = \frac{Bc_0kT\gamma^2}{\varkappa}\exp(-\varkappa H) - \frac{A^*}{12\pi H^2}\,, \qquad (10)$$

where B is a numerical coefficient, c_0 is the electrolyte concentration in the system, $\gamma = \tanh(ze\phi_0/4kT)$ (z is the valence of the counterion and ϕ_0 is the thermodynamic potential of the solid surface), $\varkappa$ is the magnitude of the reciprocal thickness of ionic atmosphere in the Debye–Hückel theory, $\varkappa = (\varepsilon\varepsilon_0 kT/2z^2e^2c_0)^{-1/2}$ (ε is the dielectric constant of the medium, ε_0 is the dielectric constant equal to 8.85×10^{-12} F m^{-1}), H is the thickness of the dispersion medium film between particles, A^* is the Hamaker complex constant characterising the interaction of contacting phases.

It follows from the DLVO theory that if the energy barrier related to the electrostatic repulsion of particles (E_{el}) is substantially higher than the energy of thermal motion (*i.e.*, $E_{el} \gg kT$), then the system is stable to aggregation, and no enlargement of particles occurs.

If $E_{el} \ll kT$, then each collision will lead to the formation of an aggregate, and the rate of formation of aggregates will be limited by the rate of their diffusion in the dispersion medium. This process is called rapid coagulation (M Smolukhovsky, 1916). The parameter which characterises the process of rapid coagulation is the coagulation period (τ), *viz.*, the time during which the concentration of particles v_0 decreases by a factor of two. According to the Smolukhovsky theory,

$$\tau = \frac{3\eta}{8kTv_0}\,, \qquad (11)$$

where η is the viscosity of the dispersion medium. For the rapid coagulation, the value of τ does not usually exceed a few seconds.

Upon a decrease in the electrolyte concentration, the efficiency of collisions decreases and only a portion of them leads to the formation of aggregates. This is the case of the so-called slow coagulation (N Fuchs, 1934). In conformity with the Fuchs theory, the decrease in the rate of aggregate formation is associated with the presence of a barrier in the dependence of potential energy on the distance between the centres of particles.[180] The theoretically predicted dependences of the coagulation rate on concentration, as well as the ratio of rates as a function of the coagulating ion charge are in a satisfactory correlation with experimental results.

The coagulation of sols yields aggregates, the fractal dimensionality of which depends on the coagulation type. For the aggregates formed under the conditions of slow coagulation, the fractal dimensionality proves to be higher[181–183] than for the aggregates formed under the conditions of rapid coagulation, which points to a higher degree of their organisation.

Analysis of Eqn (10) showed that at sufficiently large values of H a minimum can be observed on the curve of the dependence of interaction energy of particles on the distance. The interaction of particles at large distances, the so-called far interaction, leads to the formation of ensembles possessing the phase stability. Such ordered formations are called periodic colloidal structures.[184]

A spectacular example of the periodic structures are the Schiller layers, *viz.*, the structures formed in sols of iron hydroxides, vanadium oxides and some others whose particles have the anisometric forms. At low sol concentration, the particles form horizontal layers upon sedimentation separated from each other by several hundred nanometers.[185] The increase in the sol concentration leads to the spindle-like aggregates which are called tactoids. In this case, the dispersed particles are arranged nearly in parallel to the spindle axis, while the distance between them is decreased to tens of nanometers. The dispersed particles can also be oriented near a solid support.[135, 186]

The periodic colloidal structures include also the Liesegang layers and rings,[187] which were apparently the first examples of the self-organised structures studied. Let us consider these objects in more detail.

The Liesegang rings (1896) can be prepared in the following way. A drop of 15% solution of $AgNO_3$ is placed on a film of the gelatine gel which has been pre-impregnated with 0.4% potassium dichromate solution. The silver salt diffuses gradually into the gel. This results in the precipitation of silver dichromate. The precipitate does not form a continuous zone around the drop but is in the form of concentric rings separated by transparent clear areas.

Usually, the Liesegang rings appear when a concentrated salt solution diffuses through a gel which contains another electrolyte at a lower concentration. The chemical reaction results in the formation of a salt of a poorly soluble compound which is precipitated in some periodic way.[187–190] The precipitate can form not only the concentrated rings but also segments and radial formations.[191, 192] It should be noted that despite the long time which has passed since the discovery of Liesegang rings, a sufficiently complete theory of their formation has not been developed until now. It should be mentioned that this phenomenon is of a considerable interest not only for colloid chemistry but also for other sciences, *e.g.*, biophysics. Indeed, the Liesegang rings are similar to ring structures which result from the autowave processes occurring in unidimensional systems (thin layers).[193] In such 'distributed' systems, the periodic wave structures appear due to diffusion undisturbed by convective fluxes, *i.e.*, owing to the distribution of concentration waves. The same conditions are necessary for the formation of Liesegang rings. In the case of the reaction under discussion, one of the possible reasons for the appearance of Liesegang rings may be formation of colloidal particles of silver dichromate which coagulate because of the excess of one of the reagents.

The processes of self-organisation are observed in the disperse systems under external impacts as well. Thus it was shown in a number of studies[194–198] that the aggregation of initial particles with the formation of ordered structures is possible in the shear flow of suspensions.

The above-cited examples refer to the ordered colloidal nanosystems with relatively large sizes of particles.

Let us consider now another extreme case, *viz.*, the self-organised nanosystems in which the size of dispersed particles is only slightly larger than the molecular size. These systems include, *e.g.*, aqueous solutions of surfactants. The possible cases of self-organisation of the surfactant molecules are shown in Fig. 4; they include adsorption layers of surfactants at the interface, as well as direct and reverse micelles.

Indeed, the close-to-saturation layers of surfactants at the interfaces water–air, water–oil and polar solid surface–surfactant solution can have a rather high degree of ordering at which all

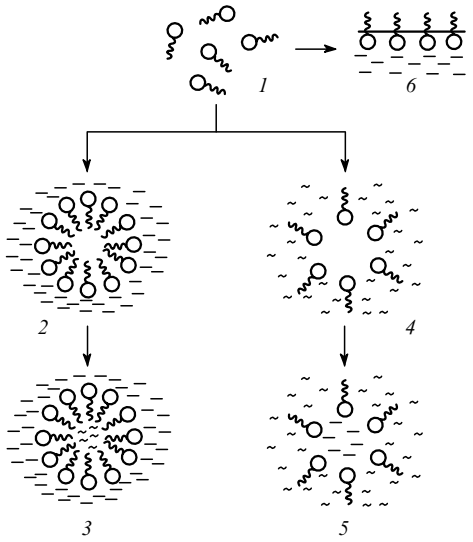


Figure 4. A scheme of the formation of organised structures in solutions of surfactants: (*1*) surfactant solution; (*2*) direct micelle in aqueous solution; (*3*) solubilisation of a non-polar liquid by the direct micelle; (*4*) reverse micelle in a non-polar liquid; (*5*) solubilisation of the polar phase by the reverse micelle; (*6*) adsorption layer of the surfactant at the aqueous solution – air interface.

the surfactant molecules (ions) are oriented perpendicular to the interface in a way ensuring the contact of the polar groups of the surfactant with the polar phase. It should be specially noted that the formation of self-organised biologically active structures on the water surface plays an extremely important role in biological evolution. Numerous data and calculations show that the surfaces of oceans (seas) are the most favourable regions for the appearance of Protozoa.[193]

Another class of self-organised colloidal nanostructures of minimum size includes the direct and reverse spherical micelles of surfactants. The ordering of micelles is characterised by the same orientation of the surfactant molecules (ions) in the radial direction from the centre of the micelle to its outer surface, on which the functional groups similar in their nature to the dispersion medium (water or an organic liquid) are positioned. The self-organised nanostructures of this type also include lamellar and cylindrical micelles, bilayers of surfactants and vesicles.

The factors favouring the formation of self-organised structures of surfactants depend to a considerable extent on the nature of the liquid phase or the nature of the solid substrate (when considering the processes of adsorption of surfactants from solutions on solid surfaces). In aqueous solutions of surfactants, the processes of self-organisation are determined by the general increase in the entropy of the system $dS > 0$ which is the sum of changes in the entropy of the dispersed phase dS_d and in the entropy of the dispersion medium dS_m. In this case, the local decrease in the entropy of the surfactant molecules in the processes of adsorption on the interface aqueous solution – air and micelle formation is compensated by the increase in the entropy of the water molecules so that the total change in the entropy of the system $dS > 0$.[61, 199–202]

On the contrary, the appearance of micelles in the oil phase, as well as the adsorption of surfactants at the interface water – oil or on a polar solid surface are determined by changes in the enthalpy of the system due to the interaction of the polar groups of surfactants with each other in the nuclei of reverse micelles or because of the interaction of the polar groups of surfactants with a polar solid surface or a polar solvent.[203, 204]

It should be noted that the processes of self-organisation of surfactant ions can also be observed in gels.[205]

Thus, the most important feature of the evolutionary processes in colloidal systems consists in that they often lead to the appearance of ordered structures of different scale (nano-, meso-, and micro-macrostructures). These structures may be two-dimensional and three-dimensional, while their size can change from several nanometers to hundreds of nanometers. Such structures are rather widely distributed. They are of a considerable applied and scientific interest, being convenient models of a number of biophysical and biochemical systems.

VII. Conclusion

The nanoparticles considered in colloid chemistry are the ultradisperse particles. Among the ultradisperse systems a special place is occupied by the systems in which particles have a specific colloidal nature: they include micellar systems, microemulsions, adsorption layers of surfactants at the interface and the Langmuir – Blodgett layers.

The methods for the preparation and studies of ultradispersed systems developed in colloid chemistry may be used rather efficiently in nanochemistry and nanotechnology. In many cases, the methods of colloid chemistry make it possible to regulate rigorously the sizes, shapes, compositions of ultradispersed particles and properties of the structures formed by them. The theoretical concepts of colloid chemistry concerning the surface phenomena, stability and evolution of disperse systems combined with the models used for studies of the thermodynamics of irreversible processes and synergism may also be applied successfully to the nanodisperse systems.

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