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Some peculiarities in stability of nanodispersions[♣]

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The stability of some classes of dispersion systems, extensively studied in modern material sciences and nanotechnology, is discussed in terms of the classical colloid chemistry laws. Some limitations of the technologies resulting from the specificity of the nanodispersed systems, utilized in nowadays applications, are pointed out.

1. INTRODUCTION

The surface and colloid science has been expanding recently as a result of new areas of development [1-3]. At the same time, these classical fundamental disciplines have turned into the applied sciences, namely the material science and nanotechnology. Their main concern are the dispersions with tailored properties designed for target applications. One of the most important properties is the system stability which guaranties the repeatability of experiments and long-time usefulness of the new materials or formulations. The stability of the products of nanotechnology can be discussed on the basis of fundamental laws governing the behaviour of dispersion systems.

Let us at first consider properties of colloidal suspension as a representative of the group of colloid systems. These properties include the colloidal stability of the suspension. The colloidal stability is a specific term different from the general sense of the term – thermodynamic stability. Its concept concerns both – the kinetic and thermodynamic stability. The micellar system is thermodynamically stable despite the fact that micelles can exchange the surfactant molecules with the bulk and that their aggregation number may

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[♣] Dedicated to Professor Emil Chibowski on his 65th birthday.

fluctuate. Almost all colloidal suspensions are thermodynamically unstable but, at the same time, they can be classified as kinetically stable, since they may last many months or even years, as their destabilization requires the overcoming of the free energy barrier.

Another aspect of the colloidal stability deals with the scale of the possible destabilization processes. One can observe the destabilization as the micro-scale aggregation often detected only spectroscopically and the macro-scale destabilization – the sedimentation or creaming processes, leading to the sediment formation or to the phase separation.

The main scope of the paper is to discuss the stability of two classes of dispersions: the suspensions built of microparticles of the size in the range 50 – 500 nm and nanoparticles – objects of diameters of 5 – 50 nm, in the categories of basic laws and theories governing the colloid system properties. The latter category includes micelles, globular proteins and, as an example of the colloidal suspensions, gold nanoparticles of diameters of the order of 10 nm, widely used in many nanotechnology applications.

2. SEDIMENTATION

The susceptibility of the dispersion system to destabilisation through sedimentation possibly followed by phase separation can be discussed in terms of the hypsometric equation. Below this equation is written in the form permitting calculation of the probability p of finding a particle at a height z above the bottom of the vessel:

$$p = \frac{1/\xi}{1 - \exp\left(-\frac{z_{\mathrm{H}}}{\xi} \right)} \exp\left(-\frac{z}{\xi} \right) \tag{1}$$

where z_{H} is the height of the column of the suspension and

$$\xi = \frac{3kT}{4\pi g \rho a^3} \tag{2}$$

k – is the Boltzmann constant, T – temperature, g – acceleration of gravity, ρ – the difference in density between the particle and the dispersion medium, a – the particle radius.

The profiles of numerical density of particles of different diameters along the height of the vessel are presented in Figure 1. The profile obtained for the radius *a*=20 nm indicates the particle tendency to accumulation near the bottom, that is to precipitate. The probability of finding a particle of the radius *a*=5 nm is almost independent of the height. Thus, such a suspension makes an almost stable system showing behaviour similar to that of the real solution.

3. AGGREGATION

The aggregation stability of a colloidal suspension is determined by the London attractive force and by electrostatic repulsion force. The suspension does not undergo a notable coagulation if a superposition of these two types of interactions produces a potential energy barrier of a height greater than the thermal energy of the particle motion or if the depth of the energy minimum reached as a result of the particles approaching each other is small relative to the kinetic energy of particles.

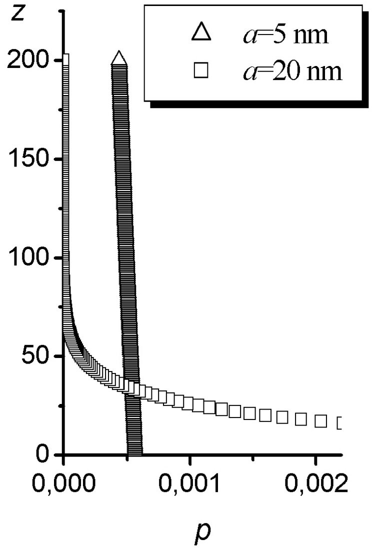

Fig. 1. Numerical density of particles versus the height over the bottom of the vessel (sedimentation equilibrium state, ρ=1gcm^{-3}, the radius of particles given in the figure).

The height of the potential energy barrier and the depth of the minimum can be estimated within the DLVO theory. Considering the interactions between relatively large spherical particles (for electrostatic interactions it means that $\kappa d < a$, where κ is the reciprocal Debye length, d – the particle-particle distance and a the particle radius), their energy can be expressed by the equations:

$$V_{\mathrm{L}} = -\frac{Ha}{12d} \tag{3}$$

and

$$V_{\mathrm{E}} = \frac{8k^2T^2\varepsilon a}{e^2z^2}\exp(-\kappa d)\left(\frac{\exp\left(\frac{z\Psi}{2kT}\right)-1}{\exp\left(\frac{z\Psi}{2kT}\right)+1}\right)^2 \tag{4}$$

where ε is the permittivity of the dispersion medium; z is the valence of the electrolyte ions and Ψ – the Stern potential.

The energy of the interparticle interactions versus the distance between them is illustrated in Figure 2.

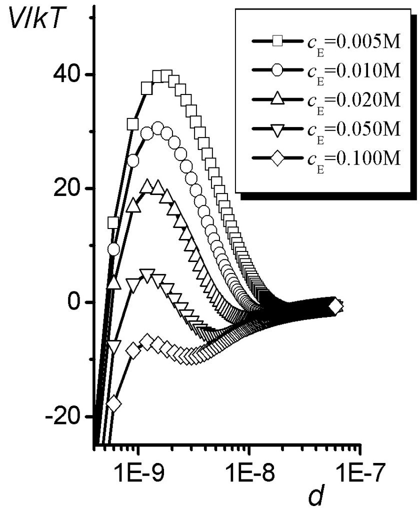

Fig. 2. The energy of interactions between two spherical particles of the radii 500 nm (Ψ=50 mV, H=10^{-19} J, T=293 K).

As follows from the figure, to be able to aggregate the particles must overcome an energy maximum of the height dependent on the type of particles and the dispersion medium (determined by the Stern potential constant and the Hamaker). For the particular system the shape of the curves depends on temperature and concentration of the electrolyte in the dispersion medium. For appropriately chosen parameters the maximum on the curve is accompanied by two minima: a deep one corresponding to a close approach of the particles and a shallow one corresponding to a greater distance between the particles. The system of such a profile of interactions shows specific properties. The approach of particles to a distance corresponding to the first minimum leads to a practically irreversible coagulation: the process of deaggregation is kinetically inhibited as it would require an overcoming of the potential barrier. In addition, the particles in contact may undergo irreversible coalescence. The final product of coagulation at the distances corresponding to the first minimum is an aggregate of compact structure. The process can be stopped by adsorption of polymer molecules on the surface of micro-particles, which leads to the so-called steric polymer stabilisation.

The approach of particles to a distance corresponding to the second minimum leads to another flocculation process. This process is reversible and leads to formation of a loosely bound aggregates in which the surfaces of the particles are not in direct contact. This type of aggregation plays an important role in structure formation and stability control of concentrated foams and emulsions.

When the particles size is decreased from microparticles to nanoparticles the qualitative changes take place in the equations (3) and (4) [4-9]:

$$V_{\mathrm{L}} = -\frac{H}{6}\left(\frac{2a^2}{d^2-4a^2} + \frac{2a^2}{d^2} + \ln\left(\frac{d^2-4a^2}{d^2}\right)\right) \tag{5}$$

$$V_{\mathrm{E}} = \frac{\Psi^2\varepsilon}{d}\exp(-\kappa(d-2a))\frac{1+\alpha}{1+\frac{\exp(-\kappa(d-2a))(1-\exp(-2\kappa a))(1+\alpha)}{2\kappa d}} \tag{6}$$

where α is a complicated function of κa and κd [9].

The change in the character of the curves seems obvious when taking into regard that the energy of London interactions for large sphere surfaces is inversely proportional to the distance between them (see (3)) while for individual molecules it is proportional to d^{-6}. The change in the scale of the objects modifies also the electrostatic interactions which for nanoparticles become similar to those between ions in the form described by the Debye-Hückel theory of electrolytes. For nanoparticles the curves illustrating the superposition of London and electrostatic interactions are shown in Figure 3.

A comparison of Figures 2 and 3 reveals the first serious difference in the properties of micro- and nanoparticles. Irrespective of the parameters of Eqs. (5) and (6), for nanoparticles the second minimum does not occur, so their flocculation leading to formation of loosely bound aggregations is not possible. Moreover, the first minimum in the potential energy curves for nanoparticles is shallower – its character is determined by a superposition of London and Born forces. This fact implies two important conclusions.

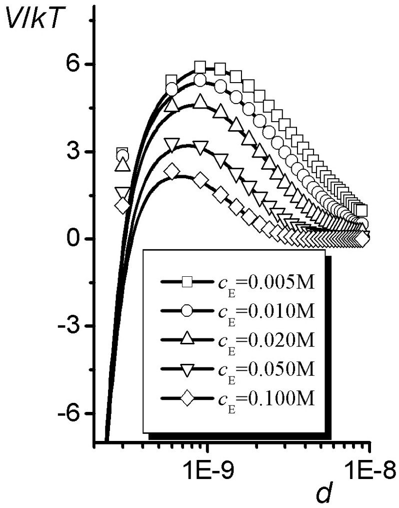

Fig. 3. The energy of interactions between two spherical particles of the radii of 5 nm (Ψ=50 mV, $H=10^{-19}$ J, T=293 K).

The first is that the screening of the energy minimum is possible by adsorption of molecules of the sizes much smaller than the average size of polymer molecules, e.g. a gold hydrosol can be stabilised by adsorption of n-octanthiol. The second is that the appearance probability of such fluctuations that would be able to move the particles out of the energy minimum is much greater. The relaxation times t_R of the process of decay of a dimer composed of two particles can be found from the Chandrasekhar equation [10]:

$$t_R = \frac{6\pi\eta a^2}{kT}\exp\left(-\frac{V_{min}}{kT}\right) \tag{7}$$

where η is the viscosity of the dispersion medium and Ψ_{min} is the depth of the potential well.

The relaxation times of the aggregates formed by particles of different size are given in Table 1.

Tab. 1. The relaxation times of aggregates built of two particles of different size for different depths of the energy minimum.

a/μm	$V_{\min}/kT$=–1	$V_{\min}/kT$=–10
0.001	11 s	1.0 days
0.1	1.3 days	29 years

A comparison of the relaxation times shows that if the energy minimum is not too deep (~kT) then, because of short lifetime of the aggregates, the aggregates and free particles can be at equilibrium and no decrease of dispersion degree will proceed.

Another problem related to the stability of systems containing micro- and nanoparticles is the efficiency of electrostatic repulsion [11]. It should be realised that the energy of electrostatic interactions calculated from the Coulomb law is a function of the density of surface charge σ and the particle radius:

$$V_{\mathrm{E}} = \frac{q^2}{4\pi\varepsilon\, d} = \frac{a^2\sigma^2}{\varepsilon d} \tag{8}$$

As follows, at the constant surface charge, the electric charge of a particle is scaled as a^2, so rapidly decreases with decreasing radius of the particle, which leads to the situation in which the electrostatic repulsion energy becomes comparable with the energy of thermal motion. In such a system coagulation of particles can occur if the London forces between them are great enough. For instance for silica molecules for which the density of ionogenic groups is 8/nm^2, at natural pH and the ionic strength corresponding to $1/\kappa$=0.28 nm, the density of ionic groups on the particle surface is close to 0.002/nm^2, which means that on average there is less than one elementary charge (0.6e) [12, 13] per one particle of 10 nm in diameter. Therefore, in the system studied there is no effective electrostatic interaction between the particles.

4. DISSOLUTION INSTABILITY – OSTWALD RIPENING

The pressure difference ΔP, between the two sides of the curved interface is determined by the Laplace law

$$\Delta P = \gamma\Im \tag{9}$$

where $\Im$ is the mean curvature of the interface and γ is the interfacial tension. In analogy, the ratio of the solubility of the hardly soluble substance S in the vicinity of the surface of a microcrystallite or a cluster of microcrystallites to its solubility near the flat surface S0, is described by the Kelvin equation:

$$\ln\left(\frac{S}{S_0}\right)=\frac{V\gamma\mathfrak{H}}{RT} \tag{10}$$

where V is the molar volume and R is the gas constant. As follows from eq. (9) and (10), the equilibrium vapour pressure over the convex surface of the drop of liquid and the solubility of hardly soluble salt near the curved surface of the particle strongly increase with increasing mean curvature of the surface of the object studied.

Analysis of the above equations implies that in the polydisperse system containing solid or liquid micro- and nanoparticles, the lower size objects will undergo gradual evaporation or dissolution accompanied by an increasing size of objects of greater size. This process will be particularly fast for the smallest size particles. It means that the aerosols composed of fine drops of liquid, foam containing fine gas bubbles and colloidal suspensions containing fine particles are unstable systems in which phase separation will occur if the particle composites are capable of relatively fast diffusion in the dispersion medium. In the most colloidal suspension containing salts or oxides, the phase separation occurs as the solubilities of these compounds are relatively great. Therefore, it is impossible to get stable suspensions of nanoparticles of e.g. AgCl, $CaCO_3$ or TiO_2 . This fact has stimulated the interest in such systems as suspensions of gold particles, thermodynamically stable micellar solutions and even in such exotic – from the point of view of the chemistry of colloids – systems as suspensions of dendrimers [11], fullerenes (in which atoms are bound by covalent bonds) or liposomes.

5. STABILITY MODIFICATIONS INDUCED BY POLYMERS

Introduction of a polymer into a dispersion medium of a colloidal suspension may lead to a polymer flocculation or steric stabilisation of particles. The effect caused by polymer introduced depends on the degree of coverage of the particle surface; at the insufficient coverage the flocculation caused by simultaneous adsorption of polymer molecule onto two or more particles is observed, while on saturation with polymer a protective layer is formed. Thus, the effect is a function of the polymer concentration and the number and size of particles. Although the phenomena discussed are quantitatively dependent on the size of particles, a transition from micro- to nanoparticles can be accompanied by unexpected qualitative deviations from the theoretical extrapolation.

Adsorption of a single macromolecule on the surface of two microparticles leads to the bridge flocculation, i.e. to the system's destabilisation. The aggregates of the size greater than that of the initial particles are characterised by a lower diffusion coefficient and a greater weight, which shifts the sedimentation equilibrium towards precipitation of sediment, see Eq. (1). Introduction of a polymer with long chains into the suspension of nanoparticles may lead to formation of aggregates made of a single macromolecule and a few nanoparticles, as shown in Figure 4. The loose aggregate formed is characterised by a diffusion coefficient of a value intermediate between that of the compact aggregate of the same number of particles and that of the single free particle [14, 15]. Hence, the loose aggregate may show a small tendency to sedimentation and the suspension containing such aggregates may stay stable. Consequently, the effect of a linear polymer of high molecular weight on the stability of suspension of micro- and nanoparticles may be quite different.

The steric repulsion between the particles coated with polymer layer originates from two effects, generally induced by the compression of the polymer layer on approaching of the particles. The first is a decrease in the conformation entropy of the chains and the second is an increase in the osmotic pressure of the solvent between the concentrated solution of the polymer segments in the area of collisions and the diluted solution in the bulk. The quantitative solution of the problem has been proposed in the theory of Evans-Napper (EN) [16] and Hesselink-Vrij-Overbeek (HVO) [17].

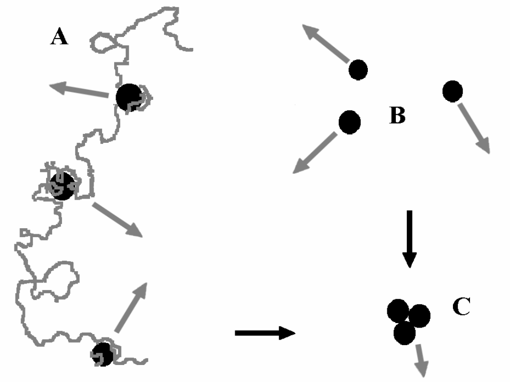

Fig. 4. A schematic presentation of the loosely bound aggregate made by nanoparticles linked by a log polymer chain. (A). A decrease in the polymer chain length (in analogy to coagulation of free particles (B)), leads to formation of compact aggregates undergoing sedimentation (C). Grey arrows illustrate the possible vectors of Brownian movements.

Usually the Deriaguin procedure is used to derive the relation for the energy of interaction between the particles of curved surfaces, irrespectively of the type of the interactions. In this procedure, the energy of interactions between the rings into which the particle surfaces can be divided is integrated, as illustrated in Figure 5. The preliminary energy of interactions is assumed to be the same as for flat planes. The procedure is fully justified when the functions integrated are continuous. Relatively large number of macromolecules adsorbed on the surface of micro-particles makes a layer that in a good approximation may be treated as continuous.

The number of macromolecules per a nanoparticle is much lower. A great curvature of the surface may lead to the appearance of voids between the neighbouring chains, into which the macromolecules adsorbed on other nanoparticles may penetrate causing unexpected flocculation due to the bridging mechanism. Therefore, the application of the Derjaguin procedure for determination of the energy of steric interactions of nanoparticles may lead to errors following from the granular structure of the polymer layer.

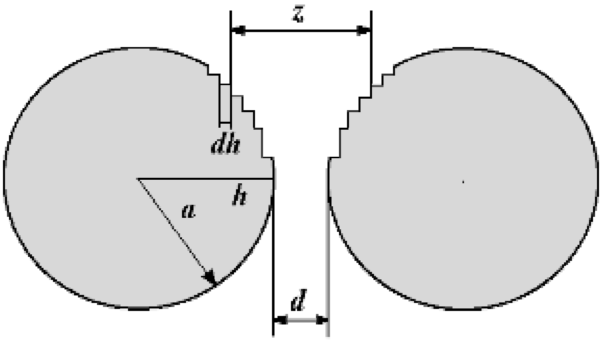

Fig. 5. Illustration of the Deriaguin procedure.

6. CONCLUSIONS

The paper presents a discussion of a few problems related to the stability of suspensions containing micro- and nanoparticles. It has been shown that extrapolation of the properties of the dispersion systems depending on the particles size onto the systems containing nanoparticles may lead to erroneous results or to conclusions in contrast to intuition-based expectations. Therefore, even the well-known and accepted theories such as DLVO, HVO and EN cannot be expected to bring correct results when applied directly to the systems containing nanoparticles. Instead of the tools typical of the colloid science, analysis of the nanoparticle suspension stability often is more appropriate to be based on study of intermolecular interactions including hydrogen bonds, and if the particles are endowed with electrical charge – the Debye-Hückel theory.

Specific requirements of the advanced material technology and nanotechnology on the one hand indicate nanoparticle dispersions as the basic components of advanced systems but on the other hand, eliminate a considerable group of such dispersions because of their instabilities.

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