

On Coagulation of Polydisperse Metal Nanocolloids and Conditions for Applicability of the Muller–Smoluchowski Theory

S. V. Karpov^{a, b} and P. N. Semina^a

^a Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia

^b Siberian Federal University, ul. Kirenskogo 26, Krasnoyarsk, 660028 Russia

e-mail: karpov@iph.krasn.ru

Received June 24, 2011

Abstract—The regularities of the coagulation of metal nanocolloids with different degrees of polydispersity are studied by the Brownian dynamics method. The results of the numerical calculations of coagulation kinetics are compared with the conclusions of the Muller–Smoluchowski theory. It is revealed that these data deviate from the predictions of the theory upon a decrease in the viscosity of dispersion medium, an increase in the thickness of layers adsorbed on particles, and the combination of these factors. It is demonstrated that no acceleration of the colloid coagulation with a rise in the degree of polydispersity, which is predicted by the theory, takes place under these conditions.

DOI: 10.1134/S1061933X12030040

1. INTRODUCTION AND FORMULATION OF THE PROBLEM

Production of nanocolloids with desired properties, which are resistant to the coagulation of disperse phase particles, is one of the topical problems of practical significance. This, in particular, concerns the technologies for the production of drugs based on metal hydrosols with long-term shelf life, development of ultradisperse material-based chemical catalysts stable to aggregation, nanocolloid-based nonlinear optical limiters of laser radiation intensity for protection of fiber-optics communication lines, etc.

The inverse problem relevant to reducing the aggregation stability of colloids is of practical significance as well (e.g., upon the development of technological processes for purification of liquids from suspended substances or separation of dispersed phases with desired compositions from liquids).

The fast coagulation of unstabilized colloidal systems, when each collision of particles upon thermal motion results in their aggregation, was described by Smoluchowski as applied to an initially monodisperse system composed of spherical particles [1–5]. One of the conclusions of this theory is the known expression for coagulation half-time $t_{1/2}$, which corresponds to the moment at which the total number of particles in a system (including particle aggregates) halves:

$$t_{1/2} = 3\eta/8k_B T v_0, \quad (1)$$

where v_0 is the initial concentration of particles in a disperse system, η is the viscosity of a dispersion medium, T is temperature, and k_B is Boltzmann's constant. This expression was obtained assuming that the Brownian diffusion coefficient D of particles is

related to their radius R via the equation $D = k_B T / (6\pi\eta R)$.

The coagulation half-time is related to the rate constant of fast coagulation K_{fast} as follows:

$$t_{1/2} = 1/K_{\text{fast}} v_0. \quad (2)$$

In the Smoluchowski theory modified by Muller as applied to fast coagulation of polydisperse sols, it is stated that the coagulation rate of polydisperse systems is higher than that of monodisperse ones [5].

The formula for the rate constant of fast coagulation of a polydisperse sol $K_{\text{fast_nm}}$ (reflecting the fact of coalescence of aggregates or individual particles with sizes R_n and R_m and total size R_{nm}) appears in the Muller theory as:

$$K_{\text{fast_nm}} = \frac{2k_B T}{3\eta} R_{nm} \left(\frac{1}{R_n} + \frac{1}{R_m} \right) = \frac{2k_B T (R_m + R_n)^2}{3\eta R_m R_n}. \quad (3)$$

At $R_n = R_m$, Eq. (3) yields a constant corresponding to a monodisperse system. The dependence of parameter $K_{\text{fast_nm}}$ on the ratio between the sizes of coagulating particles R_m/R_n is shown in Fig. 1.

In the case of the so-called slow coagulation of partly stabilized colloidal systems [1, 2], according to the Fuchs theory, the rate constant can be described by the following simplified expression:

$$K_{\text{slow}} = 4\pi D_{nm} R_{nm} P \exp[-\Delta U / (k_B T)]. \quad (4)$$

Here, $R_{nm} = R_m + R_n$, $D_{nm} = D_m + D_n$ is the sum of the diffusion coefficients of colliding particles; and $P \leq 1$ is the steric factor, which, in particular, takes into

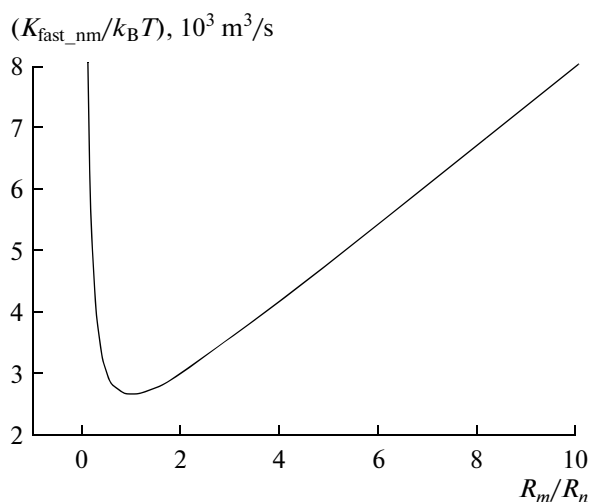


Fig. 1. The rate constant of fast coagulation $K_{\text{fast_nm}}/k_{\text{B}}T$ of a polydisperse ensemble of particles as a function of their size ratio (R_m/R_n). The viscosity and temperature of the interparticle medium are $\eta = 10^{-3}$ Pa s and $T = 300$ K, respectively.

account the spatial arrangement of particles upon a collision; and ΔU is the energy barrier. The energy barrier may be generated by repulsive interactions of polymer adsorption layers (ALs) or electrical double layers of electrostatically stabilized colloidal particles.

Since the rate constant of fast coagulation is $K_{\text{fast}} = 4\pi D_{nm} R_{nm}$, the following equation is valid for the factor of coagulation deceleration:

$$W = \frac{K_{\text{fast}}}{K_{\text{slow}}} = \frac{1}{P} \exp[\Delta U/(k_{\text{B}}T)]. \quad (5)$$

As was mentioned above, the presence of ALs on disperse phase particles is one of the reasons for decelerating coagulation of a colloidal system. In particular, ALs inhibit coagulation in the secondary potential minimum. This deceleration is caused by the fact that the depth of the secondary potential minimum decreases with increasing AL thickness, which allows the particles with high kinetic energy to leave the potential well at a certain viscosity of the dispersion medium (Fig. 2).

In addition to the thickness of a polymer AL, its elasticity modulus is an important factor influencing the coagulation rate of disperse phase particles. An increase in the elasticity modulus of an AL enhances energy barrier ΔU , which is related to the elastic repulsion of particles, and strongly decelerates the coagulation.

The coagulation in the secondary potential minimum can also be decelerated in the case of electrostatically stabilized colloids. The deceleration is also associated with aggregate disintegration; in this case, only a small fraction of particles are, as a rule, capable of overcoming the energy barrier and coagulating in the primary minimum. In such systems, slow coagulation

in the secondary minimum takes place only for submicron particles, whereas the coagulation of nanosized particles is possible only in the primary minimum [6, 7].

One of the reasons for the deceleration of the aggregation is the low viscosity of a dispersion medium. At a weak viscous friction, particle coagulation is impossible even at a very deep secondary potential minimum ($10k_{\text{B}}T$ and deeper) (Fig. 2c). Under these conditions, particles possessing appreciably high energy are almost elastically reflected from the potential barrier (Fig. 2c) and the viscous dissipation does not have time to reduce their energy to a level that would ensure their capture in the secondary minimum.

It should be emphasized that, on the other hand, as can be seen from Eq. (1), an increase in the viscosity is, per se, an additional factor of coagulation deceleration due to a reduction in the particle mobility. However, this kind of deceleration is only observed when the viscosity increases to the value at which the efficient dissipation of the energy of colliding particles begins to cause coagulation in the secondary minimum.

The concepts of accelerated coagulation of polydisperse colloidal systems (compared to monodisperse ones) are rather common [1–5] and considered to be applicable to interpreting the regularities of coagulation of an arbitrary disperse system regardless of its specific parameters. However, these concepts may be erroneous, since they do not allow for the coagulation conditions and the properties of a disperse system. Additional comparative studies are required to assess the validity of these concepts.

The Brownian dynamics method is an efficient approach to studying coagulation kinetics. This method enables one to most realistically simulate particle motion under the conditions of dissipative and stochastic forces and allow for different types of interparticle pair interactions, which result in the formation and partial disintegration of aggregates. The development of computer engineering has made the Brownian dynamics method an efficient tool for studying the processes of structure formation in colloidal systems with viscous dispersion medium and enabled one to resolve problems that were previously unsolvable.

This study was aimed at verifying the thesis postulated in the Muller–Smoluchowski theory concerning accelerated coagulation of colloidal systems with high degrees of polydispersity, determining the boundaries of applicability of this theory, and ascertaining the reasons for the deviations from it. The formulated problem was solved using the Brownian dynamics method.

2. METHOD

Simulation of particle coagulation using the Brownian dynamics method is one of its conventional

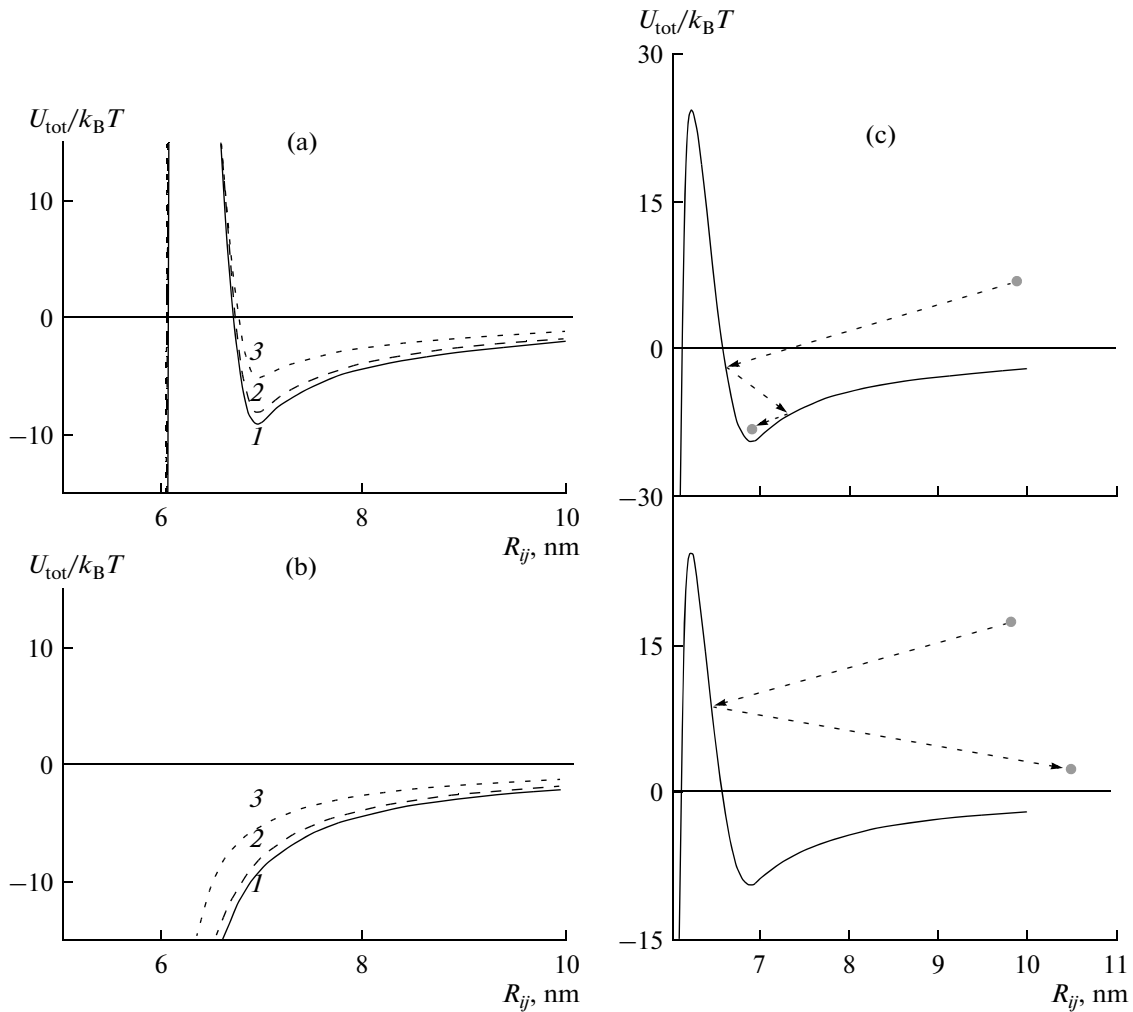


Fig. 2. The pair interaction potentials for particles with radii (1) $R_i = 3$ and $R_j = 3$, (2) $R_i = 2$ and $R_j = 4$, and (3) $R_i = 1$ and $R_j = 5$ nm: AL thicknesses are (a) $h_i = h_j = 0.5$ and (b) $h_i = h_j = 0.1$ nm. Imitation of the particle (c) capture in the potential well and (d) escape from it when it is reflected from the barrier at a high initial kinetic energy.

applications [6–9]. This method allows one to monitor the process and vary any parameters of a system, namely, the sizes and materials of particles, thicknesses and elastic properties of adsorption layers, viscosities and temperatures of dispersion medium, etc. The use of realistic models of interparticle pair interaction makes it possible to reproduce the conditions of both fast and slow coagulation with allowance for disintegration of the aggregates being formed.

Metal sols with a liquid dispersion medium (disperse phase consisting of nanosized silver nanoparticles) were selected as the object of the study performed within the framework of the Brownian dynamics model (see [7]). The simulation was carried out in a cubic cell, the sizes of which were larger than the average particle diameter by two to three orders of magnitude. At the initial moment, N nanoparticles were randomly and uniformly distributed in the cubic cell. The collisions of the particles with cell walls were considered to be elastic.

The equations of motion were solved for all the particles at each iteration step:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \quad m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i, \quad (6)$$

where \mathbf{r}_i , \mathbf{v}_i , m_i , and $\mathbf{F}_i = (\mathbf{F}_p)_i + (\mathbf{F}_{np})_i$ are the coordinate, velocity, mass, and the resultant of potential $(\mathbf{F}_p)_i = -\text{grad}(U_{\text{tot}})_i$ and nonpotential $(\mathbf{F}_{np})_i$ forces acting on an i th particle, respectively, and $(U_{\text{tot}})_i$ is the total energy of the interaction of the i th particle with other particles or external fields. The nonpotential forces comprise dissipative forces (in particular, viscous friction force \mathbf{F}_f) and stochastic hydrodynamic force \mathbf{F}_c . The Nordsieck-Gear fifth-order predictor–corrector method was used to solve the motion equations in this study. The resultant of the forces was calculated at each moment t based on the total energy $(U_{\text{tot}})_i$ of pair interaction between the i th particle and all other particles in the cell. The total interparticle

interaction energy comprised the Van der Waals and elastic interactions.

The interparticle pair interactions in the Brownian dynamics model were thoroughly described in [7]. Let us briefly discuss them.

The Van der Waals attraction is described in terms of the Hamaker–de Boer approximation (see, e.g., [10]), according to which the energy of the dissipative interaction between two spherical particles formed from the same material with radii R_i and R_j is described as

$$U_v = -\frac{A_H}{6} \left(\frac{2R_i R_j}{h^2 + 2R_i h + 2R_j h} + \frac{2R_i R_j}{h^2 + 2R_i h + 2R_j h + 2R_i R_j} + \ln \frac{h^2 + 2R_i h + 2R_j h}{h^2 + 2R_i h + 2R_j h + 2R_i R_j} \right). \quad (7)$$

Here, $h = R_{ij} - (R_i + R_j)$ is the interparticle gap, R_{ij} is the distance between the particle centers, and A_H is the effective Hamaker constant (its value for silver hydro-sol particles is $A_H \approx 50k_B T$ [11] at $T = 300$ K). For contacting particles, gap h is equal to the total thickness of the deformed ALs of the particles; the initial thickness of an AL is considered to be independent of the particle radius.

The potential energy of the elastic interaction between two spherical particles with polymer ALs (this energy is caused by AL deformation in the region of the contact) can be described by the following expression [7, 12]:

$$U_e = \frac{4}{15} (h_i + h_j - h)^{5/2} \times \left[\frac{(R_i + h_i)(R_j + h_j)}{(R_i + h_i) + (R_j + h_j)} \right]^{1/2} \left(\frac{E_e}{1 - \sigma_e^2} \right), \quad (8)$$

where h_i and h_j are the thicknesses of undeformed adsorption layers of the i th and j th particles, respectively; E_e is the effective elasticity modulus of polymer adsorption layers (it is assumed to be the same for all of the particles); and σ_e is the Poisson coefficient. Since $\sigma_e \approx 0.15$ and $\sigma_e^2 \ll 1$, this parameter will be ignored below.

In this study, we confine ourselves to discussing coagulation of colloidal particles stabilized with polymer AL alone.

Realization of the Brownian motion implies the fluctuation interaction of particles with environments, which causes random changes in the trajectories of particle motion and must compensate for the action of dissipative forces and maintain the mobility of the dispersed phase. In this model, stochastic hydrodynamic force $F_s(t)$ was characterized by the Gaussian distribution of amplitude and described by a δ -correlated ran-

dom process. During each time step Δt , a spherical particle undergoes the action of the stochastic hydrodynamic force. Prior to each integration step, the projections of random force $F_{s,i}$ ($i = x, y, z$) onto the coordinate axes are selected from the Gaussian distribution with the zero average value and the following deviation:

$$\langle F_{s,i} \rangle = \frac{12\pi\eta R_i k_B T}{\Delta t}. \quad (9)$$

The viscous friction force, which is the main factor of kinetic energy dissipation, is determined by the Stokes formula for spherical particles of radius R_i as follows:

$$F_f = 6\pi\eta R_i \mathbf{v}, \quad (10)$$

where η is the dynamic viscosity of the dispersion medium and \mathbf{v} is the particle velocity.

The presence of the stochastic and dissipative forces in the Brownian dynamics model results in a probabilistic character of nanoparticle aggregation and partial disintegration of subaggregates being formed, which reproduces the conditions that are taken into account in the Fuchs theory of slow coagulation.

3. RESULTS AND DISCUSSION

The kinetics of coagulation of monodisperse and bimodal ensembles composed of $N = 100$ nanoparticles with a density equal to that of silver were comparatively studied. The radius of the particles of the monodisperse ensemble was 3 nm; the radii of the particles in the bimodal ensembles were equal to 2 and 4 or 1 and 5 nm. The thickness of polymer ALs on the particles was selected to be $h = 0.1$ nm (to implement the regime of fast barrierless coagulation, Fig. 2b) and $h = 0.5$ nm (to investigate slow coagulation in the secondary potential minimum, Fig. 2a). The viscosity values of the dispersion medium were taken equal to $\eta = 10^{-3}$ Pa s, which corresponds to a hydrosol at $T = 300$ K, and $\eta = 10^{-4}$ Pa s, which is close to the viscosity of dispersion medium of certain types of organosols.

Coagulation half-times $t_{1/2}$ for the ensembles of silver nanoparticles were calculated at these parameter values, and their dependences on the initial particle concentrations were plotted (Figs. 3–6).

One of the goals of the study was to ascertain the conditions at which the Muller–Smoluchowski theory and the Brownian dynamics method yield consistent results. For this purpose, the regime of fast coagulation of a colloidal system had to be realized. The necessary conditions for this realization are the minimum thickness of the adsorption layers on the particles (0.1 nm) and a relatively high viscosity of the dispersion medium ($\eta = 10^{-3}$ Pa s), which ensures the efficient dissipation of the kinetic energy of colliding particles.

In order to investigate the coagulation kinetics, the ratio between the aggregation half-time values

obtained for a monodisperse sol using the Muller–Smoluchowski theory ($t_{1/2,MS}(v_0)$) and the Brownian dynamics method ($t_{1/2,BD}(v_0)$), $t_{1/2,MS}(v_0)/t_{1/2,BD}(v_0)$, was calculated in a wide range of initial particle concentrations from 1.08×10^{22} to $1.63 \times 10^{24} \text{ m}^{-3}$ (Fig. 3a). It was demonstrated that, at concentrations lower than 10^{24} m^{-3} , the ratio $t_{1/2,MS}(v_0)/t_{1/2,BD}(v_0)$ tends to unity and reaches a value of 1.836 at $v_0 = 1.08 \times 10^{22} \text{ m}^{-3}$. A decrease in the $t_{1/2,MS}(v_0)/t_{1/2,BD}(v_0)$ ratio with a reduction in the concentration is caused by a decline in the average energy of the Van der Waals interparticle attraction due to an increase in the interparticle distances.

However, at very low concentrations, the computation time increases abruptly (by an order of magnitude and above), because approaching particles have large interparticle distances to overcome during chaotic Brownian drift. Therefore, in the subsequent calculations, we confined ourselves to the concentration range of the disperse phase particles $v_0 = 1.08 \times 10^{24} - 1.63 \times 10^{24} \text{ m}^{-3}$. Within this concentration range, the coagulation half-time calculated using the Brownian dynamics method differs twofold for the monodisperse sol and by an order of magnitude for the bimodal sols. An increase in the particle concentration made it possible to considerably reduce the computation time due to a decrease in the average interparticle distance. As a result, larger amounts of computations could be performed and the basic statistical regularities of the coagulation kinetics could be determined.

It should be noted that the Muller–Smoluchowski theory does not allow for changes in the effective interparticle interaction with concentration. Therefore, a significant deviation of times $t_{1/2,BD}(v_0)$ from the theoretically predicted ones $t_{1/2,MS}(v_0)$ is observed upon increasing particle concentrations. Concentration dependences of $t_{1/2,MS}(v_0)/t_{1/2,BD}(v_0)$ are strongly oscillating due to the stochastic character of the Brownian dynamics process. After averaging over ten values, the relative error for each value of the concentration dependence of $t_{1/2,MS}(v_0)/t_{1/2,BD}(v_0)$ is equal to 15–20%.

Thus, Figs. 3a and 3b illustrate the concentration dependences of $t_{1/2,MS}(v_0)/t_{1/2,BD}(v_0)$ for the monodisperse ensemble composed of $N = 100$ silver nanoparticles at the viscosities of the dispersion medium $\eta = 10^{-3}$ and 10^{-4} Pa s , respectively. Figures 3c–3f show the same dependences for the bimodal ensembles. Figures 3a, 3c, and 3e demonstrate the general tendency toward a rise in the $t_{1/2,MS}(v_0)/t_{1/2,BD}(v_0)$ ratio with increasing concentration under the conditions of the high coagulation efficiency of interparticle collisions.

However, at a lower viscosity and, hence, weaker dissipation of particle kinetic energy ($\eta = 10^{-4} \text{ Pa s}$; see Figs. 3b, 3d, and 3f), the $t_{1/2,MS}(v_0)/t_{1/2,BD}(v_0)$ ratio decreases because of more frequent disintegrations of subaggregates being formed as compared with these dependences at $\eta = 10^{-3} \text{ Pa s}$ (Figs. 3a, 3c, 3e). More-

over, as can be seen from Fig. 2a, the potential well for a particle pair with radii $R_i = R_j = 3 \text{ nm}$ is deeper than that for pairs with $R_i = 2$ and $R_j = 4$ or $R_i = 1$ and $R_j = 5 \text{ nm}$. This fact is responsible for the greater number of subaggregate disintegrations in the case of bimodal ensembles.

The comparative kinetics of aggregation of monodisperse and bimodal colloids at different viscosities of the dispersion medium and AL thicknesses on nanoparticles is shown in Fig. 4. This figure clearly shows the deviation of the aggregation half-times analytically calculated for polydisperse colloids (curves 3) from those obtained using the Brownian dynamics method at increasing influence of the factors of coagulation deceleration. These factors are determined by the thickness of AL (curves 1, 2) and the viscosity of a dispersion medium.

At a high viscosity of a dispersion medium and a small thickness of an AL, which provide a high efficiency of particle coalescence upon collisions (Figs. 4a, 4c, 4e, curves 1), a correlation with identical dependences obtained using the Muller–Smoluchowski theory (curves 3) takes place. Namely, the aggregation half-time decreases with increasing particle concentration. However, an increase in the polydispersity is accompanied by oppositely directed tendencies in the kinetic dependences corresponding to curves 2 and 3 in Figs. 4a, 4c, and 4e at increased AL thicknesses. The coagulation decelerates with a rise in the degree of polydispersity that can be seen from the mutual arrangement of curves 2 and 3 corresponding to particle coagulation in the presence of a potential barrier (2) and to the Muller–Smoluchowski theory (3).

Even more obvious deviation of the data of the analytical Brownian dynamics theory takes place when the viscosity of the dispersion medium is reduced by an order of magnitude (Figs. 4b, 4d, 4f). For AL thickness $h_i = 0.1 \text{ nm}$ (curve 1) and particle sizes $R_i = 1$ and $R_j = 5 \text{ nm}$, the coagulation half-times shown in Fig. 4f are considerably longer than those corresponding to the monodisperse sol and the bimodal sol with particle sizes $R_i = 2$ and $R_j = 4 \text{ nm}$ (Figs. 4b, 4d). At AL thickness $h_i = 0.5 \text{ nm}$ and increased polydispersity of the sols, the coagulation time is even longer than that predicted by the analytical theory (see the mutual arrangement of curves 2 and 3 in Fig. 4f) in addition to decelerated coagulation.

This behavior of the coagulation half-time can be explained by a smaller depth of the potential well for a particle pair with sizes $R_i = 1$ and $R_j = 5 \text{ nm}$, as compared to particle pairs with radii $R_i = 2$ and $R_j = 4$ or $R_i = R_j = 3 \text{ nm}$ (Fig. 2a), which is responsible for the decelerated coagulation of highly polydisperse particles.

Figure 5 shows the dependences obtained for the monodisperse and bimodal colloids at a small AL thickness and two viscosities of the dispersion medium

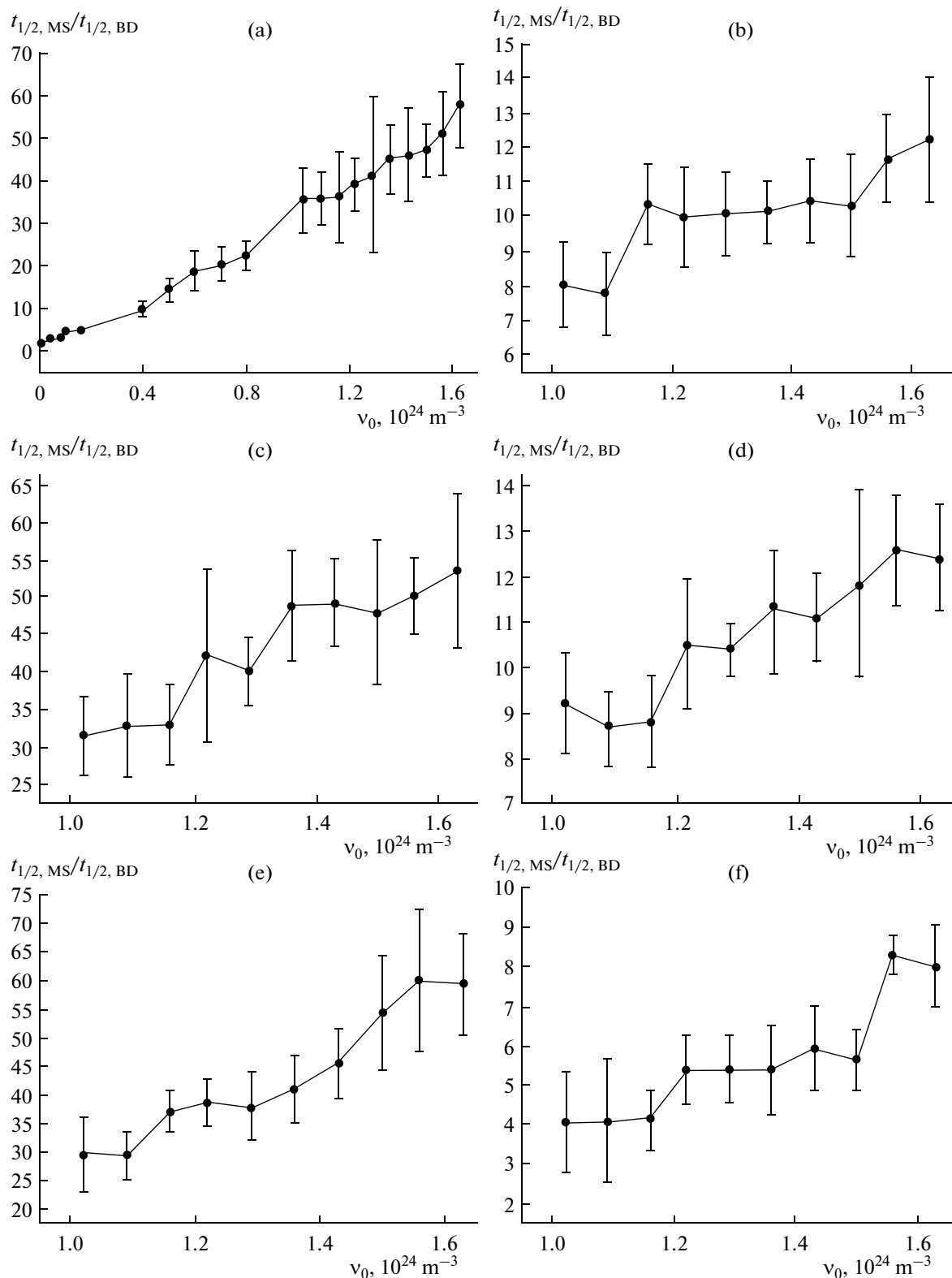


Fig. 3. The ratios between the coagulation half-time $t_{1/2, MS}$ corresponding to the Muller–Smoluchowski theory and that calculated in terms of the Brownian dynamics model $t_{1/2, BD}$ as functions of the concentration of silver particles v_0 for (a, b) a monodisperse ensemble with $R_i = 3$ nm and bimodal particle ensembles with (c, d) $R_i = 2$ and $R_i = 4$ and (e, f) $R_i = 1$ and $R_i = 5$ nm. AL thickness is $h_i = 0.1$ nm, viscosities of the dispersion medium are $\eta =$ (a, c, e) 10^{-3} and (b, d, f) 10^{-4} Pa s, and elasticity modulus of polymer AL is $E_e = 3 \times 10^9$ N/m.

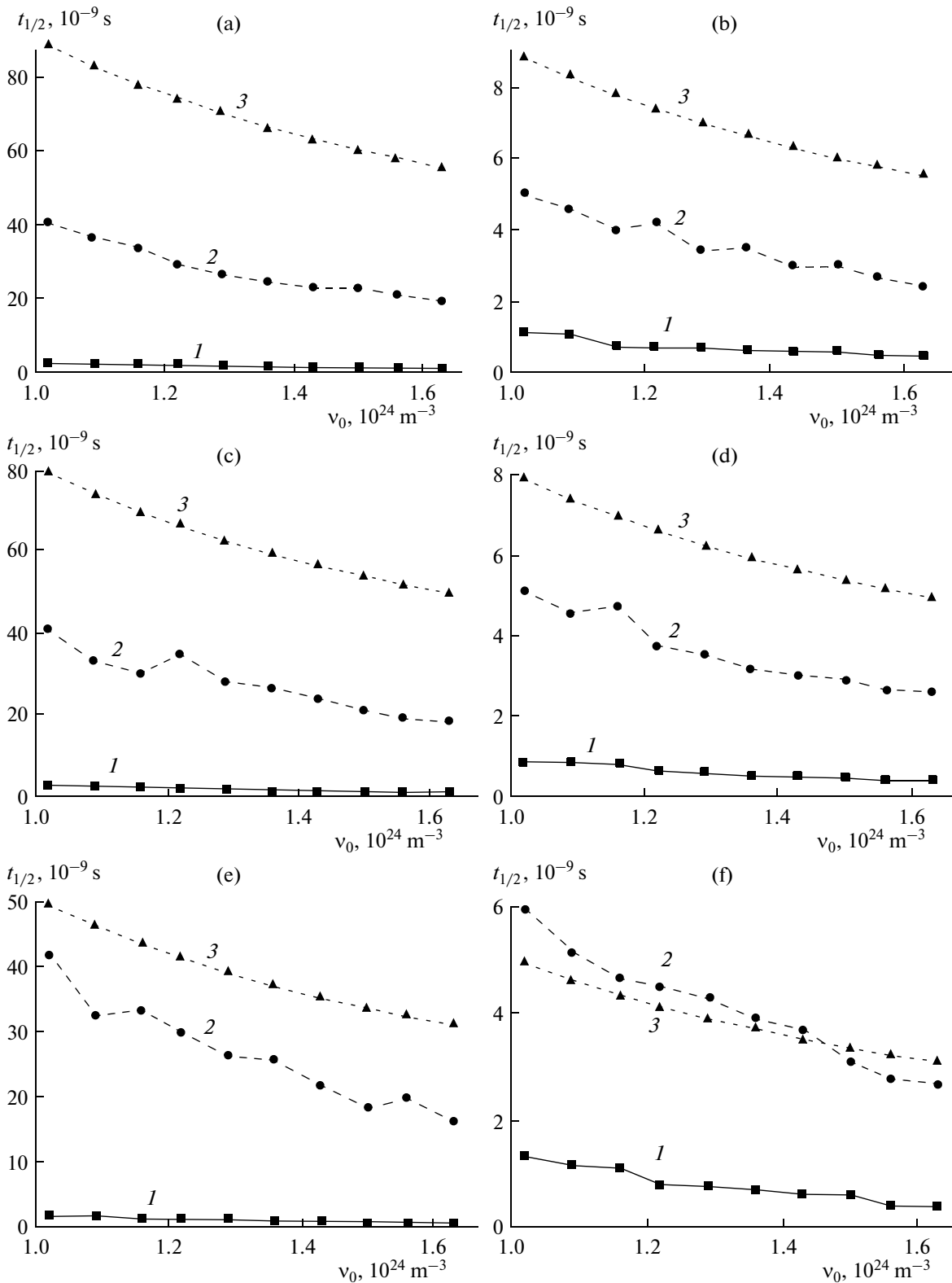


Fig. 4. Aggregation half-times $t_{1/2}$ calculated by the Brownian dynamics method as functions of disperse phase particle concentration v_0 for (a, b) a monodisperse ensemble with $R_i = 3$ nm and bimodal ensembles with (c, d) $R_i = 2$ and $R_j = 4$ and (e, f) $R_i = 1$ and $R_j = 5$ nm at AL thicknesses $h_i = (1)$ 0.1 and (2) 0.5 nm. Curves 3 are calculated according to the Muller–Smoluchowski theory. Viscosities of the dispersion medium are $\eta = (a, c, e)$ 10^{-3} and (b, d, f) $\eta = 10^{-4}$ Pa s; elasticity modulus of the polymer AL is $E_e = 3 \times 10^9$ N/m.

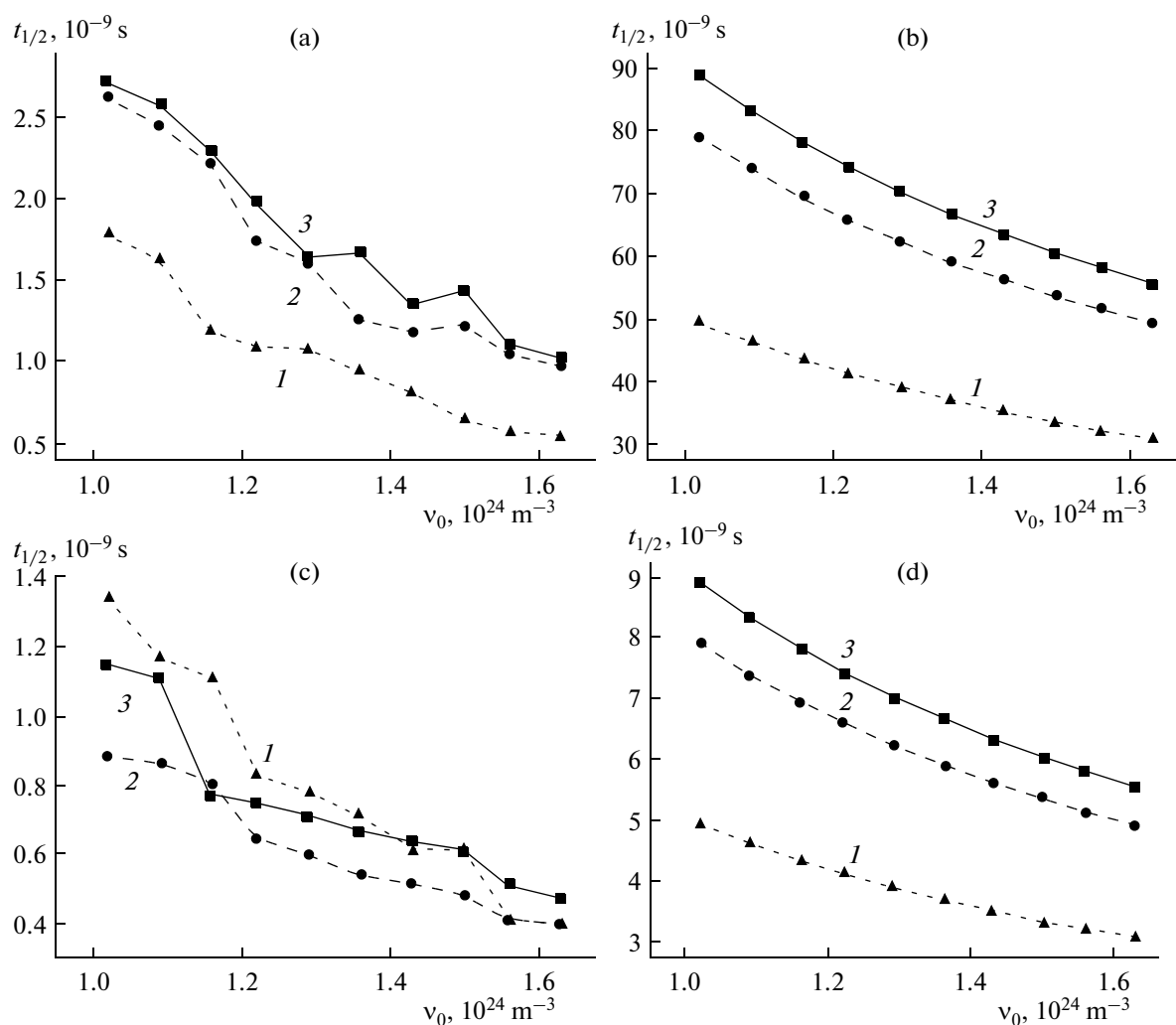


Fig. 5. Dependences of aggregation half-time $t_{1/2}$ on particle concentration calculated using (a, c) the Brownian dynamics method for the smaller AL thickness $h_i = 0.1$ nm and (b, d) those calculated according to the Muller–Smoluchowski theory for bimodal ensembles with (1) $R_i = 1$ and $R_j = 5$ and (2) $R_i = 2$ and $R_j = 4$ nm, as well as (3) a monodisperse ensemble with $R_i = 3$ nm. Viscosity of the dispersion medium is $\eta =$ (a, b) 10^{-3} and (c, d) 10^{-4} Pa s; elasticity modulus of the polymer AL is $E_c = 3 \times 10^9$ N/m.

using the Brownian dynamics method and the Muller–Smoluchowski theory.

At preset concentrations of disperse phase particles, the Van der Waals attraction accelerates the coagulation of the monodisperse and bimodal sols as compared to the predictions of the Muller–Smoluchowski theory. However, the violation of the “conventional” relation between the coagulation times of the monodisperse and bimodal sols is easy to establish at interparticle medium viscosity $\eta = 10^{-3}$ Pa s. This is evident from the mutual arrangement of curves 2 and 3 in Fig. 5a, where the average aggregation half-times of the monodisperse ($R_i = 3$ nm) and bimodal ($R_i = 2$, $R_j = 4$ nm) sols at some particle concentrations almost coincide with one another and appear to be longer

than those corresponding to the ensemble with the higher polydispersity.

An even stronger pronounced deviation from the Muller–Smoluchowski theory takes place when the medium viscosity is decreased by an order of magnitude (see the mutual arrangement of curves 1–3 in Fig. 5c). In this situation, the bimodal colloid with the higher degree of polydispersity ($R_i = 1$ and $R_j = 5$ nm) coagulates slower than not only the bimodal sol with the smaller difference between the modes ($R_i = 2$ and $R_j = 4$ nm), but even than the monodisperse colloid ($R_i = 3$ nm). This behavior of coagulation half-times can be accounted for by the smaller depth of the potential minimum for particles with greatly different sizes (Fig. 2b).

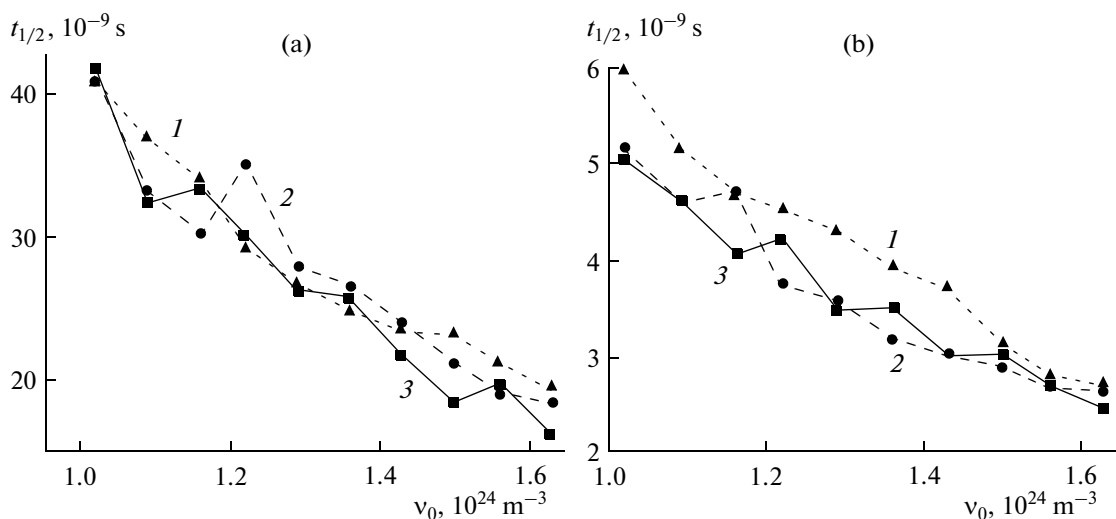


Fig. 6. Dependences of aggregation half-time $t_{1/2}$ on particle concentration calculated using the Brownian dynamics method at the larger AL thickness ($h_i = 0.5$ nm) for bimodal ensembles with (1) $R_i = 1$ and $R_j = 5$ and (2) $R_i = 2$ and $R_j = 4$ nm, as well as (3) a monodisperse ensemble with $R_i = 3$ nm. Viscosities of the dispersion medium are $\eta =$ (a) 10^{-3} and (b) 10^{-4} Pa s; elasticity modulus of the polymer AL is $E_e = 3 \times 10^9$ N/m.

Finally, for coagulation in the presence of the potential barrier (at a large thickness of AL), the kinetic dependences calculated using the Brownian dynamics method exhibit complete violation of the “conventional” relation between the aggregation half-times of the monodisperse and bimodal colloids.

Figures 6a and 6b show the concentration dependences plotted for the average coagulation half-times under conditions of the maximum influence of the factors of its deceleration, i.e., at an AL thickness of 0.5 nm, which ensures the appearance of the secondary potential maximum and the energy barrier in the pair interaction, and different viscosities of the dispersion medium. Under these conditions, an increase in AL thickness, which causes a reduction in the depth of the secondary potential minimum (Fig. 2a), facilitates the disintegration of aggregates being formed. In combination with an insufficient energy dissipation, which takes place at low viscosities of the dispersion medium, this fact additionally violates the coagulation regularities corresponding to the Muller–Smoluchowski theory.

CONCLUSIONS

The results obtained and the tendencies revealed in the work lead us to state the following.

Slow coagulation of polydisperse nanocolloids accompanied by partial disintegration of subaggregates being formed cannot be described by the Muller–Smoluchowski theory. The theory is inapplicable under the following conditions: the existence of a thick adsorption layer on particle surfaces, a high

elasticity modulus of the layer, a large height of the potential barrier, and a low viscosity of a dispersion medium.

A combination of these factors or a strong effect of one of them does not allow one to use the Muller–Smoluchowski theory to substantiate the accelerated coagulation of polydisperse colloids observed in a particular experiment.

Sporadic experimental data, which indicate that the coagulation of polydisperse metal sols is accelerated as compared to that of monodisperse systems (see, e.g., [13, 14]), and the results of studying the coagulation of polydisperse metal sols [5], enable one to conclude that there are certain mechanisms (that have not been taken into account in the Brownian dynamics method) that facilitate the acceleration of the aggregation of polydisperse particles.

We suppose that one of these mechanisms may be related to the electron tunneling effect, which induces mutual heteropolar charging of particles with different sizes at the moments of collisions. As a result, a dynamic increase in particle attraction energy may take place due to additional electrostatic interaction between the particles, as well an increase in the depth of the potential minimum and a rise in the coagulation efficiency of interparticle collisions. A thorough analysis of the tunneling mechanism of coagulation acceleration was made in [15].

ACKNOWLEDGMENTS

Authors are thankful to G.A. Chiganova and A.P. Gavriluk for discussions and helpful comments.

Studies were carried out with the support of grants: the Presidium of RAS № 29 and № 31, OFN RAS III.9.5, IP SB RAS № 43, IP SB RAS (and SFU) № 101.

REFERENCES

1. Voyutskii, S.S., *Kurs kolloidnoi khimii* (Course of Colloid Chemistry), Moscow: Khimiya, 1975.
2. Frolov, Yu.G., *Kurs kolloidnoi khimii. Poverkhnostnye yavleniya i dispersnye sistemy* (Course of Colloid Chemistry. Surface Phenomena and Disperse Systems), Moscow: Khimiya, 1989.
3. Fridrikhsberg, D.A., *Kurs kolloidnoi khimii* (Course of Colloid Chemistry), Leningrad: Khimiya, 1984.
4. Shchukin, E.D., Pertsov, A.V., and Amelina, E.A., *Kolloidnaya khimiya* (Colloid Chemistry), Moscow: Mosk. Gos. Univ., 1984.
5. Myuller, G., *Teoriya koagulyatsii polidispersnykh sistem. Koagulyatsiya kolloidov* (Theory of Polydisperse System Coagulation. Colloids Coagulation), Moscow: Glavn. Red. Khim. Lit., 1936.
6. Ansell, G.C. and Dickinson, E., *Chem. Phys. Lett.*, 1985, vol. 122, p. 594.
7. Karpov, S.V., Isaev, I.L., Gavriilyuk, A.P., Gerasimov, V.S., and Grachev, A.S., *Kolloidn. Zh.*, 2009, vol. 71, p. 314.
8. Hutter, M., *Phys. Chem. Chem. Phys.*, 1999, vol. 1, p. 4429.
9. Mishchuk, N.A., *Kolloidn. Zh.*, 2005, vol. 67, p. 381.
10. Sonntag, H. and Strenge, K., *Koagulation und Stabilitat Disperser Systeme*, Berlin: Deutscher Verlag der Wissenschaften, 1970.
11. Derjaguin, B.V., *Teoriya ustoychivosti kolloidov i tonkikh plenok* (The Theory of Stability of Colloids and Thin Films), Moscow: Nauka, 1986.
12. Landau, L.D. and Lifshits, E.M., *Teoriya uprugosti* (Elasticity Theory), Moscow: Nauka, 1987.
13. Khachatryan, A.A. and Lunina, M.A., *Kolloidn. Zh.*, 1985, vol. 47, p. 562.
14. Lunina, M.A., Romina, N.N., and Korenev, A.D., *Kolloidn. Zh.*, 1989, vol. 51, p. 774.
15. Karpov, S.V., Semina, P.N., Gavriilyuk A.P., *Kolloidn. Zh.* 2012, vol. 74, no. 3, p. 329.