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THEORETICAL PRINCIPLES OF WATER TREATMENT TECHNOLOGY

Dependence of the Particle Interaction on the Moisture Content of Disperse Systems

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Abstract—The forces of interaction between hydrophilic disperse particles in a humidified dispersion have been analyzed. The minimum volume fraction of water, which is acceptable for the application of DLVO theory formulas in computing the interaction between particles, was determined. It is shown that the formation of thin restricted water layers in gaps between hydrophilic particles gives rise to conditions for the attraction of the latter stipulated by the capillary forces that significantly change the properties of dispersions.

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INTRODUCTION

The interaction of particles in disperse systems essentially depends both on the volume and surface properties of particles themselves and on the disperse medium. The intensity of interparticle interaction changes especially strongly during the transition from the gaseous to aqueous medium. Hence, for example, the calculations performed in paper [1] showed that one of the main forces of interparticle interaction (Van der Waals attraction [2]) could be tens of times weaker in water as compared to that in the air. In addition, the local characteristics of disperse medium near the surface of particles can be distinctly different from the bulk ones that also radically affects the Van der Waals forces. In particular, in the case of hydrophobic particles, the local reduction of water density occurs near their surface or a gaseous interlayer is formed that leads to a significant rise of particle attraction [3]. Conversely, in the case of hydrophilic particles and formation on their surface of a water layer, the attraction of such particles decreases [1]. In addition, if the electrostatic repulsion between the particles in the majority of cases is insignificant in the air that ensures the dominance of Van der Waals forces and, consequently, the aggregation of particles, especially nanoparticles [4], then the electrostatic repulsion in water is often stronger than the attraction forces that results in the stabilization of dispersions [2, 5, 6].

Since dispersions are widely used in water treatment, agriculture, construction, medicine, food, and the other branches of industry, the impact of the moisture content on their stability needs to be investigated that is the purpose of this study.

SURFACE FORCES IN DISPERSE SYSTEMS

The theoretical model of variation of surface forces at the expense of occurrence of the finite size liquid interlayer in the gap between particles presented in this paper was developed on the basis of analysis of main components of DLVO forces: Van der Waals attraction, electrostatic repulsion [1, 2, 5], and also forces of the capillary attraction [2, 5]. This model covers the whole possible interval of moisture content: from a relatively small amount in humid air medium to the maximum possible amount on condition of complete filling of dispersion pores with water.

In the case of hydrophilic disperse particles, water vapors are condensed at pressure values lower than the pressure of saturated vapors over plane surface that results in filling of crevices, pores and gaps between particles with water. As a result of merging of liquid layers formed on particle walls due to vapor adsorption, water interlayers occur in gaps between them. This process contributes to the emergence of the Laplace pressure, i.e., an additional force varying the particle interaction [5].

In studying the general trend of variation of forces, for simplifying the calculations we shall consider a monodisperse system consisting of smooth non-deforming spherical particles. The condensed liquid wets the surface of hydrophilic particles and gradually is accumulated in gaps between them (Fig. 1). Since the wetting angle of surface depends on the degree of hydrophilicity of particle material, the liquid can form strongly or weakly pronounced menisci that determines the value of Laplace pressure and affects the intensity of interaction between particles.

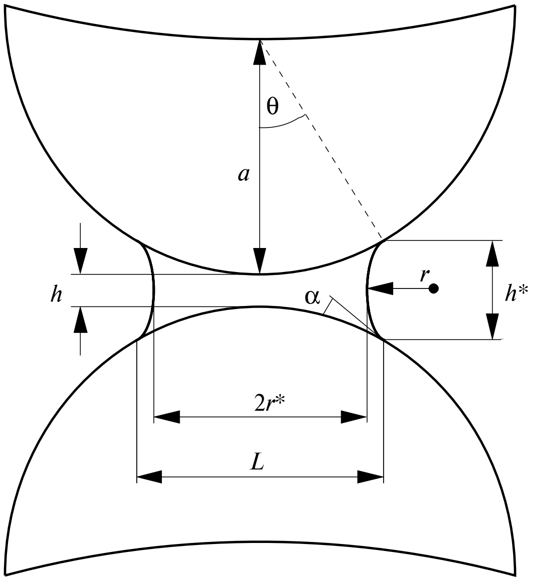


Fig. 1. The schematic representation of a contact of two particles with a gap between them filled with water and formed meniscus of radius *r*. Other designations are presented in text (see below).

Let us find the conditions that make it possible to utilize the simplest formulas for DLVO forces. Since we are interested in dense dispersions, i.e. at small distances the Van der Waals force for solid gaseous $F_A^G(h)$ and aqueous $F_A^W(h)$ media can be presented in the view [1, 2, 5]:

$$F_A^G(h) = -\frac{aA_P^G}{12h^2} \text{ and } F_A^W(h) = -\frac{aA_P^W}{12h^2}, \quad (1)$$

where *a* is the radius of particles, *h* is the shortest distance between their surfaces, A_P^G is the Hamaker constant for particles in air medium equal to the Hamaker constant for vacuum A_p, and A_P^W is the Hamaker constant for particles in aqueous medium.

Taking into account that $A_P^W = \left(\sqrt{A_P^G} - \sqrt{A_W}\right)^2$ [2], we can find the ratio of interaction forces of two particles in air and aqueous media:

$$F_A^G(h)/F_A^W(h) = A_P^G/\left(\sqrt{A_P^G} - \sqrt{A_W}\right)^2, \quad (2)$$

where A_W is the Hamaker constant for water in air medium.

The closer are values of the Hamaker constant for particle and water, the larger is the difference between forces in the air and aqueous media. Since $A_W = 4.38 \times 10^{-20}$ J, we can find, for example, that the attraction of polystyrene or polyurethane particles ($A^G_p \sim 10 \times 10^{-20}$ J) in water is ~8.7 times less than their attraction in air; for barium titanate ($A^G_p \sim 20 \times 10^{-20}$ J) and gold ($A^G_p \sim 40 \times 10^{-20}$ J) this figure of weakening amounts to 3.5 and 2.2 times, respectively. For such an appreciable weakening of the Van der Waals force, the complete replacement of the air with aqueous medium is not compulsory. It is sufficient to fill the gap between particles with water that is possible owing to the moisture condensation from the air, by the capillary sucking in of liquid into gaps between hydrophilic particles or retaining in gaps of water flowing through the coarse dispersion system. The applicability of the above formulas is limited by such humidity of dispersion and, correspondingly, such size of water interlayer that make it possible to cover the whole region of possible interaction. The analysis of numerical data obtained in paper [1] enables us to conclude that at medium values of the Hamaker constant typical of many natural disperse particles ($A_p \sim (5–10) \times 10^{-20}$ J) the strongest change of the Van der Waals forces occurs at distances of the order of $X_{cr} = 50–100$ nm.

Let us determine now the humidity of the system, for which condition $h^* = X_{cr} = 50$, 100 and 200 nm (see Fig. 1) is satisfied, where h^* is the distance between particles in the region of meniscus. The volume fraction of water ϕ_{cr} for close packed dispersion can be obtained with due regard for the volume of interlayer of liquid between surfaces of two identical particles V_W, the number of contacts of each particle with its neighbors, and the volume of dispersion per one particle of the specified radius a. In a particular case of the cubic packing of spherical particles and thin gap between them ($h \to 0$), the formula for the volume fraction of water assumes a simple form:

$$\phi_{cr} \approx \frac{\pi X_{cr}^2 (3a - X_{cr})}{32a^3}. \tag{3}$$

In order to simplify the derivation of formula (3), it was assumed that the volume of interlayer of liquid between surfaces of two spherical particles could be approximately calculated on the basis of geometrical characteristics of such system by replacing the menisci limiting the liquid interlayer in gap with cylindrical surface of radius $L/2$ (see dashed lines in Fig. 1). As can be seen from formula (3) and the table, the volume ratio of water and solid phase in dispersion sharply increases with an increase of X_{cr} and reduction of a.

The critical volume fraction of water ϕ_{cr} at different values of X_{cr}

X_{cr}, nm	a, μm			
	5	10	50	100
50	1.0×10^{-5}	2.5×10^{-6}	1.0×10^{-7}	2.5×10^{-8}
100	3.9×10^{-5}	1.0×10^{-5}	3.9×10^{-7}	1.0×10^{-7}
200	1.5×10^{-4}	3.8×10^{-5}	$1.5 \times \cdot 10^{-6}$	3.9×10^{-7}

It should be noted that the replacement of menisci with direct lines results in the increased values of ϕ_{cr} obtained by calculations, i.e., actually, the values of ϕ_{cr} are somewhat smaller than those specified in the table. Thus, even at $X_{cr} = 200$ nm and $a = 5$ μm, for which the maximum value of ϕ_{cr} was obtained, significant changes of the Van der Waals interaction forces calculated by formula (2) correspond to the humidity of dispersions < 0.015%. It should be emphasized once more that we discuss the formation of water interlayers in gaps between particles. If we assume that the water corresponding to ϕ_{cr} is uniformly distributed over the entire surface of particles, the very thin layers of water will be obtained that weakly affect the interaction of particles. In particular, the distribution of 0.015% of moisture over the surface of particles with radius of 5 μm in the case of their dense packing results in a layer having thickness of ~ 1 nm that according to paper [1] leads to relatively small changes of the Van der Waals interaction forces.

The applicability of the formula for electrostatic repulsion between particles in the case of the presence of interlayer of liquid between them is determined by the length of double electric layer (Debye-Huckel radius $\kappa^{-1} \sim 1/\sqrt{C_0}$) that decreases with the rise of concentrations of salts dissolved in water C_0. Usually, in natural water we have $\kappa^{-1} < X_{cr}$ (see table) that also makes it possible to use simple formula [1, 2]:

$$F_e^W(h) = \frac{a\varepsilon\kappa\psi^2}{2}\exp(-\kappa h), \tag{4}$$

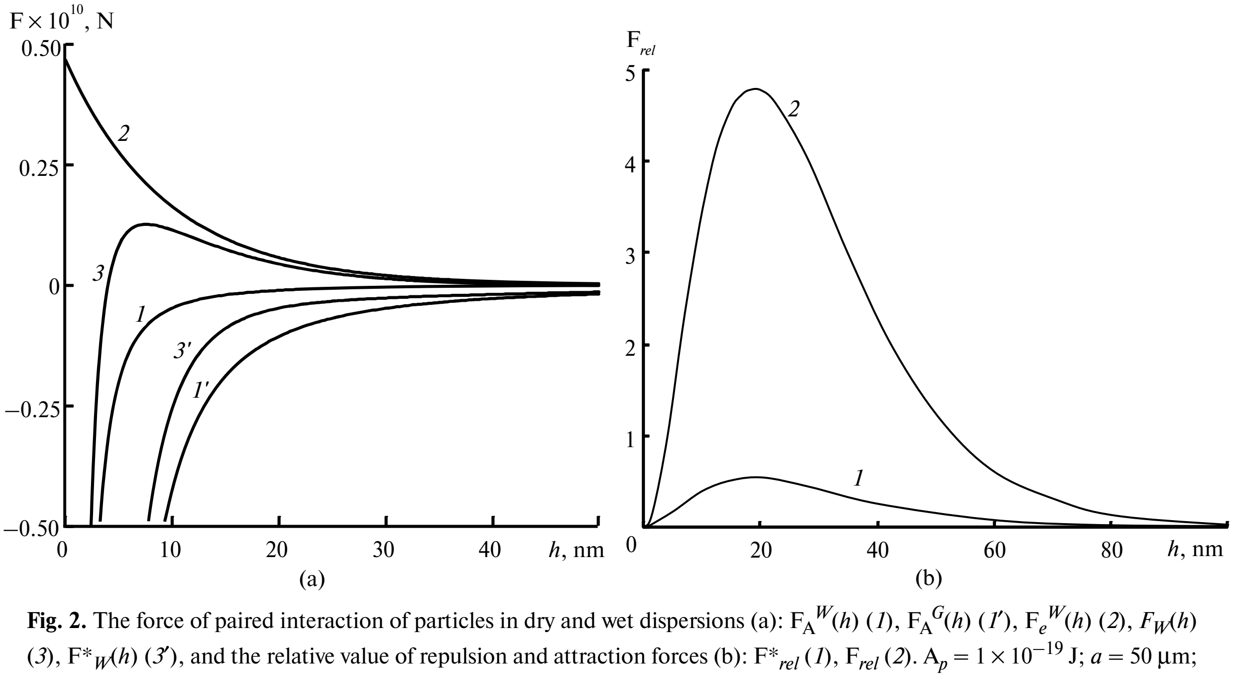
where ε is the dielectric permittivity of dispersion medium, ψ is the surface potential of particles.

The efficiency of the influence of water interlayer on the variation of stability of disperse system at the expense of the DLVO forces, i.e., the sum of the Van der Waals attraction forces and electrostatic repulsion, can be determined by comparing the force of particle interaction in dry $F_A = F_A{}^G(h)$ and wet $F_W = F_A{}^W(h) +$

$F_e^W(h)$ dispersions (Fig. 2a). As the water interlayer between particles is formed, the attraction force decreases (curves *1, 1′*), while its summation with the force of electrostatic repulsion (curve *2*) results in the appearance of a maximum (curve *3*) characterizing the degree of particle repulsion and ensuring the dispersion stability. For clarifying the role of Van der Waals forces, the specified figure also presents curve *3′* obtained on assumption that the electrostatic repulsion occurs after the emergence of water interlayer, while the Van der Waals attraction forces do not change, i.e., $F^*_W = F_A^G(h) + F_e^W(h)$. In this case, the maximum is not present and the particles are attracted over the entire interval of distances, i.e., they are found in aggregated state. Thus, as can be seen from comparing curves *3* and *3′*, the transition of dispersion into disaggregated state can be effected both by the emergence of electrostatic repulsion and by the reduction of Van der Waals forces.

The relationships $F_{rel} = |F_e^W(h)/F_A^W(h)|$ and $F^*_{rel} = |F_e^W(h)/F_A^G(h)|$ are presented in Fig. 2b for better pictorial view of occurring changes. If condition $F^*_{rel} < 1$ (curve *1*) is satisfied at the parameters selected for calculation and at all distances between particles, then the attraction prevails (curve *2*) at $h < 4$ nm and $h >$ 53 nm, while the repulsion is dominant at intermediate values of h (4 nm $< h <$ 53 nm). The presence of two domains satisfying condition $F_{rel} \leq 1$ corresponds to the so-called primary and secondary minimums [2, 6]. Unfortunately, the primary minimum is very deep, and the particles in gaseous medium are found just in this minimum. Therefore, the automatic transition to disaggregated state is not possible in the case of wetting the dispersion. Such transition involves the need of fulfillment of additional conditions.

The first condition can be provided by the proper disperse system, if adsorption layers or irregularities ensuring the steric forces of repulsion are found on the surface of particles [7, 8]. The range of action of such forces usually amounts to several nanometers, therefore it cannot affect the aggregation in air, where the intense Van der Waals attraction is active at much larger distances (see Fig. 1a, curve *1′*). At the same time, in the case of dispersion wetting, the short-range steric repulsion can prevent the closing-in of particles in a more narrow primary minimum (see Fig. 2a, curve *1′*); hence, except the shallow and usually not very important secondary minimum, particles will always be in the region of repulsion. Thus, in the case of wetting the disperse system, a specific combination of electrostatic and steric repulsion and Van der Waals attraction can ensure the disaggregation of particles.



(a) (b)

Fig. 2. The force of paired interaction of particles in dry and wet dispersions (a): $F_A^W(h)$ (*1*), $F_A^G(h)$ (*1′*), $F_e^W(h)$ (*2*), $F_W(h)$ (*3*), $F^*_W(h)$ (*3′*), and the relative value of repulsion and attraction forces (b): F^*_{rel} (*1*), F_{rel} (*2*). $A_p = 1 \times 10^{-19}$ J; $a = 50$ μm; $\psi = 5$ mV; $C_0 = 0.001$ mol/dm^3; $\kappa^{-1} \approx 10$ nm.

In case of insufficiently complete covering of the primary minimum, the external short-term mechanical action shifting particles in relation to one another can play an important part, because it results in particles getting into the region of repulsion. In particular, it is just the reason for using the pulse and irregular mechanical actions in investigating the deformation and rheological properties of different disperse systems [9–12].

CAPILLARY FORCES IN DISPERSE SYSTEMS

The above conditions are valid only for the case of relatively weak hydrophilicity, when contact angle θ is close to 90°. At high hydrophilicity of dispersion, i.e., when a clearly pronounced meniscus is formed in the gap between particles ($\theta << 90°$), the capillary pressure (Laplace pressure P_L) emerges that depends on the surface tension of water or other disperse medium σ and the so-called Kelvin radius for concave meniscus $r_\kappa = (1/r + 1/r^*)^{-1}$ [5], where radii r and r^* are determined in Fig. 1:

$$P_L = \sigma(1/r + 1/r^*). \tag{5}$$

At low humidity we have $r << r^*$, and the second term can be neglected.

It should be noted that the small radius of meniscus curvature contributes to creation of very high values of pressure. Hence, for example, the pressure of 10 N/cm^2 is achieved at $r = 0.72$ μm and $\sigma = 72 \times 10^{-3}$ N/m that is equivalent to the pressure of load having weight of 1 kg per the area of 1 cm^2.

Given the small humidity of dispersion on assumption that $h << h^*$ and with due regard for the area of wetted part of particle surface $\pi a h^*$, the force tending to bring together two spherical particles (F_c) can be presented as follows:

$$F_c = -\pi a h^* \sigma/2r. \tag{6}$$

The thickness of interlayer h^* at $r << r^*$ can be related to meniscus radius r and contact angle α by the following expression: $h^*/2 \approx r\cos\alpha$ that enables us to reduce formula (6) to the form:

$$F_c = -\pi a h^* \cos\alpha. \tag{7}$$

Thus, the emerging capillary forces practically do not depend on the amount of condensate. Having performed the appropriate calculations, it could be easily seen that, for example, for particles with radius a = 50 μm in aqueous medium at surface tension $\sigma = 72 \times 10^{-3}$ N/m and hydrophilicity ensuring contact angle $\alpha = 80°$, the emerging force of capillary attraction should be $F_L = -2 \times 10^{-6}$ N that is ~130000 times more than the force of repulsion in the region of barrier maximum F_{max} as shown in Fig. 2a. Such large difference is related not only to the value of capillary attraction force, but also to the use in calculations of sufficiently low surface potential $\psi = 5$ mV. At higher values of ψ, which are typical to many natural disperse systems, the ratio between the capillary attraction and the maximum of force barrier decreases. In particular, at $\psi = 25$, 50 and 100 mV, ratio F_c/F_{max} attains the values: 5200, 1300 and 325. At larger hydrophilicity of surface, when $\alpha = 60°$, ratio F_c/F_{max} increases by ~3 times for all values of ψ. On the contrary, if surfactants are present in dispersion that reduce the value of surface tension to certain value σ^* [13], the capillary attraction force and, correspondingly, ratio F_c/F_{max} reduces by a factor of σ^*/σ.

Another important cause that significantly reduces the role of capillary forces is the porosity and roughness of the surface of real disperse particles. At a small air humidity the condensed liquid, primarily, fills pores and hollows on the particle surface; as a result, the menisci are not formed and capillary attraction does not occur. However, if the air humidity is sufficient for condensation ensuring both the filling of internal cavities and roughnesses and also the accumulation of liquid forming menisci outside their limits, the capillary attraction can prove to be quite intensive. However, with further increase of the amount of moisture filling a substantial part of space between spherical particles, the attraction at the expense of capillary forces (6), (7) again decreases; as a result, beginning from a specific instant of time the interaction of particles will be described only by formulas (1) and (4). This phenomenon is related to the fact that the curvature of particle surface at the fixed value of contact angle α affects the meniscus radius r resulting in the situation where this radius also becomes dependent on angle θ, to which the film of liquid was spread that results in the reduction of the Laplace pressure.

In order to prove these qualitative findings, we shall develop a model of capillary attraction for the case of increased humidity of dispersion when formula (6) cannot be applied. In this case we shall take into account that the film in the gap between particles in Fig. 1 is limited on the top and on the bottom by spherical surfaces and on the side by a meniscus, which is a part of the torus surface in the three-dimensional space. Based on the analysis of geometrical characteristics of these surfaces at $h = 0$ (see Fig. 1) we can find that meniscus radius r and the typical size of film across gap r^* are related with particle radius a_0, contact angle α and certain angle θ on the sphere surface, where the film of condensed moisture terminates, by the following relationships:

$$r(\theta,\alpha) = a\frac{1-\cos\theta}{\cos(\theta+\alpha)}; \tag{8}$$

$$r^*(\theta, \alpha) = a\sin\theta - r(1 - \sin(\theta + \alpha)), \tag{9}$$

while the distance between the end points of liquid interlayer at angle θ by the following relationship:

$$h^*(\theta, \alpha) = 2r(\sin\theta, \alpha)\cos(\theta + \alpha). \tag{10}$$

With due regard for these expressions, the volume of film can be presented by expression:

$$V(\theta,\alpha) = a^3\left\{\pi(1-\cos\theta)\left(\sin^2\theta - \frac{1}{3}(1-\cos\theta)^2\right) - \left(\frac{1-\cos\theta}{\cos(\theta+\alpha)}\right)^2\right.$$
$$\left.\cdot\left[\frac{\pi - 2(\theta+\alpha) - \sin\left(2(\theta+\alpha)\right)}{2}\right]\cdot\left[\sin\theta - \frac{1-\cos\theta}{\cos(\theta+\alpha)}\left(1-\sin(\theta+\alpha)\right)\right]\right\}, \tag{11}$$

while the volume fraction of moisture on condition of the cubic packing of particles:

$$\phi(\theta,\alpha) \approx \frac{3V(\theta,\alpha)}{8a^3}. \tag{12}$$

Now, since, unlike the small amount of moisture, curvature radii r and r^* can be compared in terms of their magnitudes, the formula for capillary attraction F_c with due regard for expression (5) assumes the following view:

$$F_c(\theta,\alpha) = -\pi a\sigma h^*(\theta,\alpha)\left(\frac{1}{r(\theta,\alpha)} + \frac{1}{r^*(\theta,\alpha)}\right). \tag{13}$$

The results of calculating the relationship of F_c as a function of the volume fraction of moisture $\phi(\theta)$ with due regard for expressions (8–13) are presented in Fig. 3.

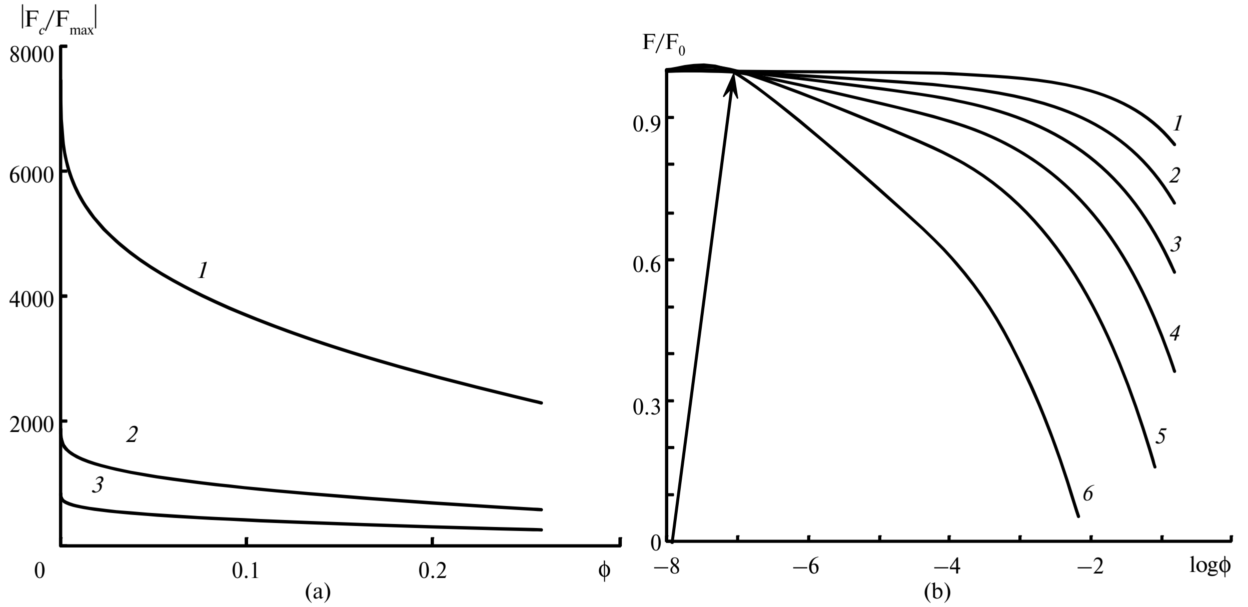


Fig. 3. The relationship of ratio F_c/F_{max} as a function of ϕ at $\alpha = 60°$, $C_0 = 0.001$ mol/dm^3, $\psi = 25$, (*1*), 50 (*2*) and 75 (*3*) mV (a), and ratio $F_c(\theta)/F_{c0}$ $(\theta \to 0)$ as a function of ϕ at $\alpha = 30°$ (*1*), 40 (*2*), 50 (*3*), 60 (*4*), 70 (*5*), and 80° (*6*) (b). $a = 200$ µs.

For convenience of comparing F_c values at different wetting angles α and also for comparing them with the maximum of DLVO forces (F_{max}), the calculation results are presented in the form of normalized quantities $|F_c(\theta)/F_{max}|$ (see Fig. 3a) and $F_c(\theta)/F_{c0}$ $(\theta \to 0)$ (see Fig. 3b).

As can be seen from Figs. 3a, 3b, with the rise of humidity the capillary attraction rapidly decreases; as a result, when the dispersion is completely filled with water (for cubic packing of identical particles this corresponds to humidity $\phi_{max} = 0.526$), only electrostatic repulsion forces and the Van der Waals attraction forces remain, i.e., the stability of such systems is described by the standard DLVO theory [2]. It is natural that the role of capillary pressure is more pronounced for less charged particles when the surface potential and, correspondingly, the energy barrier between particles at the expense of the DLVO forces are lower (see Fig. 3a).

The performed calculations show that the strong capillary attraction occurs at very low values of ϕ (stepwise emergence of attraction forces is noted by arrow in Fig. 3b), and then slowly decreases in a very large interval of humidity. The larger is hydrophilicity, i.e., the smaller is the wetting angle, the slower is the reduction of attraction force that is stipulated by a weaker relationships of $r(\theta,\alpha)$ and $r^*(\theta,\alpha)$ (see formulas (8) and (9)) as a function of the total angle $(\theta + \alpha)$ determining the characteristics of liquid interlayer. It should be emphasized that the applicability of above formulas is limited by angle $\theta = 45°$ when the interlayers of liquid from adjacent gaps fuse that explains why the curves in Fig. 3 terminate at $\phi < \phi_{\max.}$ The notion of wetting angle loses the meaning with further increase of humidity, because spherical bubbles (hollow spaces) are formed between particles, i.e., the relative role of capillary attraction forces in interaction with particles decreases still faster than it follows from the slope of curves in Fig. 3. It should also be noted that the liquid filling the space between particles in coarse dispersion systems can trickle down into dispersions located below thereby modifying the pattern of particle interaction by height.

Thus, the relationship of capillary forces as a function of humidity has an extremal character that can be important in the analysis of properties of concrete artificial or natural disperse systems.

CONCLUSIONS

The theoretical analysis made it possible to determine the applicability conditions of the DLVO theory formulas that form the basis for establishment of the governing laws of changes of interaction between particles occurring during the transition from the dry to wet dispersion. The theory of capillary attraction between spherical particles at variable humidity of dispersion has been developed. It is shown that the formation of thin restricted layers of liquid in gaps between hydrophilic particles leads to occurrence of conditions for attraction of particles stipulated by the capillary forces significantly exceeding the forces of electrostatic repulsion and Van der Waals attraction. As the humidity of dispersion increases, the capillary attraction weakens, and at the complete wetting of dispersion the interaction of particles again is described only by the DLVO forces [2, 5].

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