

Modelling the Clusters Aggregation and Aggregative Stability of Suspensions

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The work considers the stability factor of disperse systems, which is determined by the rate of their aggregation. The novelty of submitted work is that the original heuristic model allowing for evaluating the elements of the aggregation matrix with moving from an infinite chain of aggregation equations to a closed finite system of equations has been proposed. Based on the model of the aggregation matrix and the symmetry of the aggregation process for each of the components, it was shown that it may be sufficient to consider the stabilization of the disperse composition of the suspension when aggregating globules of the same orders.

1. Introduction

The stability of dispersed systems is characterized by the invariance in time of the equilibrium distribution of the dispersed phase in the volume of the medium, which is determined by the interaction of intermolecular forces of attraction and electrostatic repulsive forces between particles (Sonntag, Strenge, 1987).

Dispersed systems are divided into lyophilic and lyophobic. The first ones are characterized by intense interaction of particles with the medium and thermodynamic stability (for example, soap dispersions, clays and aggregates of macromolecular compounds in water), and for the latter, the intensity of interaction between particles exceeds the interaction of particles with the medium, which makes the system thermodynamically unstable (for example, colloid solutions - sols of metal sulfides).

The ability of particles to resist gravity determines sedimentation stability, and the ability of particles to resist aggregation determines aggregative stability. These two types of stability are interrelated, and the violation of aggregative stability reduces the sedimentation stability of the system, contributing to the settling of particles. Currently, there is no practically significant approach to the analysis of aggregative stability (Larsson et al. 2012). This study is devoted to the analysis of the problem of aggregative stability based on the Smoluchowski kinetic equation and a new model of aggregation kernels (Brener, 2014). As a result, the control parameters that can be used in assessing the aggregative stability of suspensions have been identified.

Issues devoted to the influence a continuous medium hydrodynamics on the process of aggregation in disperse phase are not considered in this work. These issues are important for describing the process in specific apparatuses, and they are covered in some works (Yuan Yao and Capecelatro, 2021). The submitted model can presumably be used both in creating stable dispersions with particle sizes of about 40–50 nm in medicine and pharmacology and in developing methods for air purification from fine solid particles (PM_{2.5}) with sizes of about 2.5 μm.

2. Thermodynamic aspects of the problem

In suspensions (and emulsions), the processes of coagulation and coalescence can spontaneously occur, accompanied by a decrease in free surface energy (Kelbaliyev and Safarov, 2012). Lyophobic disperse systems are thermodynamically unstable due to the condensation and decreasing the surface energy in the interfacial

layers. During coagulation, a decrease in free surface energy is achieved as a result of partial mutual saturation of uncompensated molecular forces on the surface of particles at the points of their contact (Karpov et al., 2006). Lyophobic disperse systems are thermodynamically unstable due to the condensation of surface energy in the interfacial layers. During coagulation, a decrease in free surface energy is achieved as a result of partial mutual saturation of uncompensated molecular forces on the surface of particles at the points of their contact (Karpov et al., 2006).

A significantly greater decrease in the excess free energy takes place during coalescence (Huseynova, 2021). Thermodynamically unstable lyophobic disperse systems, however, can exist for quite a long time without coagulating, i.e. remain aggregative stable, which is due to the action of various stabilization factors (Gontijo et al., 2007). The smaller the polarity difference between the particles of the dispersed phase and the dispersion medium (Carrillo and Goudon, 2006), the more aggregative stable the suspension will be.

During sedimentation (settlement under the action of gravity), each particle in such suspensions settles separately, without forming aggregates with other particles. On the contrary, in a nonpolar dispersion medium, hydrophilic powders form aggregative unstable suspensions. In this case, the particles coagulate, and the settling of the dispersed phase in such suspensions occurs much faster. In sediments, the cohesive forces between particles are large compared to the mass of the particles that is especially true for nanoparticles (Singh et al., 2020).

The basic principle of suspension stabilization is reduced to enhancing the interaction of the molecules of the dispersion medium with the surface of the particles of the dispersed phase by directed modification of this surface. This can be achieved by adding to the dispersion medium certain surfactants adsorbed at the interface. In order to stabilize a suspension of a hydrophobic powder in water, it is necessary to introduce an additive that would cause hydrophilization of the surface of the particles. Usually, water-soluble surfactants are used for this purpose (Larsson et al., 2012).

In coagulation structures, the interaction of particles in contacts is limited by their "contact" - through the remaining equilibrium interlayers of the dispersion medium or directly. Such contacts and structures as a whole are characterized by mechanical reversibility - the ability to spontaneous recovery after mechanical destruction (thixotropy).

In phase contacts, the adhesion of particles is carried out due to close-acting cohesive forces implemented on an area that significantly exceeds the area of the unit cell, i.e. linkage is due to a lot of bonds. Unlike coagulation structures, which have the property of thixotropy, structures with phase contacts are destroyed irreversibly. Solid spatial networks - loose dispersed coagulation structures - can be formed at very low volume concentrations of particles of the dispersed phase (0.1-0.01%) (Bohling, 2015). This takes place at a sufficiently high dispersion, when the number of particles (free kinetic units) per unit volume of the system is sufficiently large (Smith, 2006).

As a result of favorable Brownian collisions, the nanoparticles, having joined their ends, are able to form a disordered structural grid in a form of a rather rigid frame (Velegol and Thvar, 2001). Since the fraction of the particle surface occupied by coagulation centers, is small for such particles, loose dispersed structures are formed upon their adhesion, and can reinforcing the entire volume of the system (Sunkel, 1998). The magnitude of the strength of coagulation contacts can be estimated based on the concept of the nature of the forces that determine the adhesion of particles (Ginzburg, 2022). In the simplest case of a monodisperse structure with spherical particles, the structural parameter that depends on the porosity has the meaning of the average number of particles in the chain between nodes (Ginzburg, 2010).

The model presented below is based on the assumption that the stability of disperse systems is determined by the rate of their coagulation. This rate depends on the sign and magnitude of the total interaction energy, which, in accordance with the Deryagin-Verwey-Overbeck (DVO) theory (Sonntag and Strenge, 1987), is determined by the superposition of the ion-electrostatic force of repulsion and the van der Waals-London attraction force (Contijo et al., 2007).

3. Binary model of aggregative stability

At present, the theory is considered the most reliable, according to which the dipole-dipole interaction of adsorbed molecules of water or other liquid, which forms the basis of the suspension, is the main controlling factor of flocculation (Larsson et al., 2012). It follows that the ratio between the components of the total interaction energy of particles is determined by two geometric parameters: the effective radius of the particle, which depends on the order of the measure, and the distance between the particles (Korlepara et al., 2019).

Figure 1 shows the results of calculations for the dependence of the dipole-dipole interaction energy on the distance between globules, and the same figure shows experimental data (Silbey et al., 2005). According to (Sonntag and Strenge, 1987), the arrangement of two particles with oriented adsorption layers corresponds to the energy minimum if they come into contact.

The accepted assumption means this minimum is realized when the distance between particles is comparable to the dipole arm (Lima et al., 2011). Otherwise, particle repulsion will predominate and coagulation will not occur (Singh et al. 2020). To use this assumption, an estimate of the dependence of the average distance between the surfaces of particles when they come into contact on the order i -mers should be given.

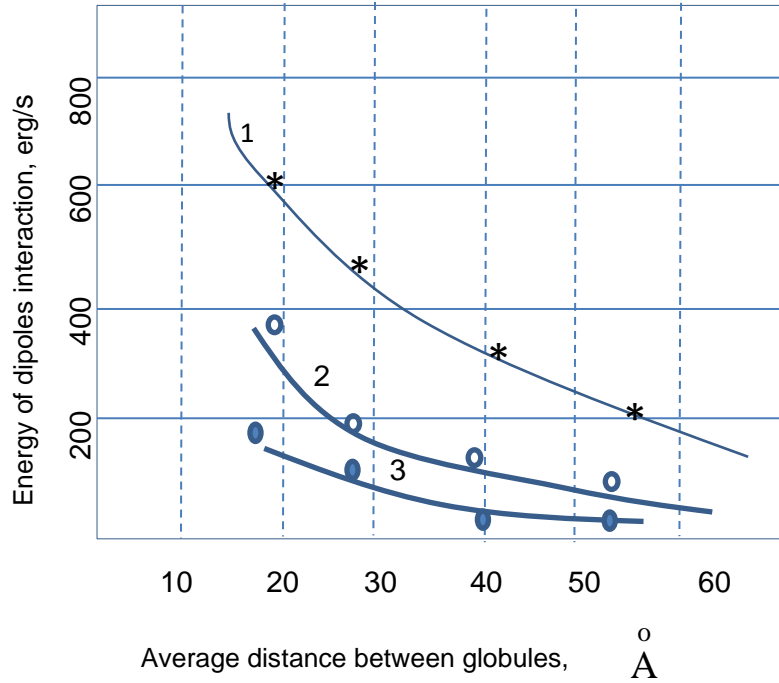


Figure 1: Dependence of the dipole-dipole interaction energy on the distance between globules. The level of dipoles orientation is: 1- 100%; 2- 55%; 3- 35%

Taking the characteristic radius of the monomers to be the same, the characteristic radius of i -mer when monomers are combined can be found from the following condition

$$a_i^3 \approx i a^3. \quad (1)$$

Then the average distance between the particles (see Figure 2 A)) is found from the estimate:

$$H = \frac{V_{ABECDF}}{\pi a_i^2} = \frac{\pi a_i^2 (h + 2a_i) - \frac{4}{3} \pi a_i^3}{\pi a_i^2} = h + \frac{2}{3} a_i \sqrt[3]{i}. \quad (2)$$

Figure 2 B) shows the graphs of the dependence of the average distance between the particles at the time of their contact, depending on the order of the particle and its radius. Comparison of figures 1 and 2B) demonstrates the decrease in the energy of dipole-dipole interaction between particles when increasing their size. This phenomenon serves as an additional argument in favor of the appropriateness of the approach proposed below to modeling the elements of the aggregation matrix (Wattis, 2006).

The base supposition here is that from the symmetry considerations of the aggregation process for each of the components, it is sufficient to consider the stabilization of the disperse composition of the suspension when aggregating globules are of the same orders (Carrillo and Goudon, 2006). Since the intensity of the process decreases with the growth of the particle order in accordance with the submitted model and conclusions of the DVO-theory (Ninham, 1999), the consideration can be limited by two terms on the right side of the Smoluchowski equation (Halsey, 2000) to aggregate 2i-meres:

$$\frac{dC_{2i}}{dt} = \frac{1}{2} \Phi_{i,i} C_i^2 - \Phi_{i,2i} C_i C_{2i} = 0. \quad (4)$$

For the rate of growth of fine and nano i-meres, the main ones can be an increase in the effective capture cross section with an increase in the characteristic radius of particles, as well as a decrease in the mobility of particles with an increase in their size and mass (Herega, 2018).

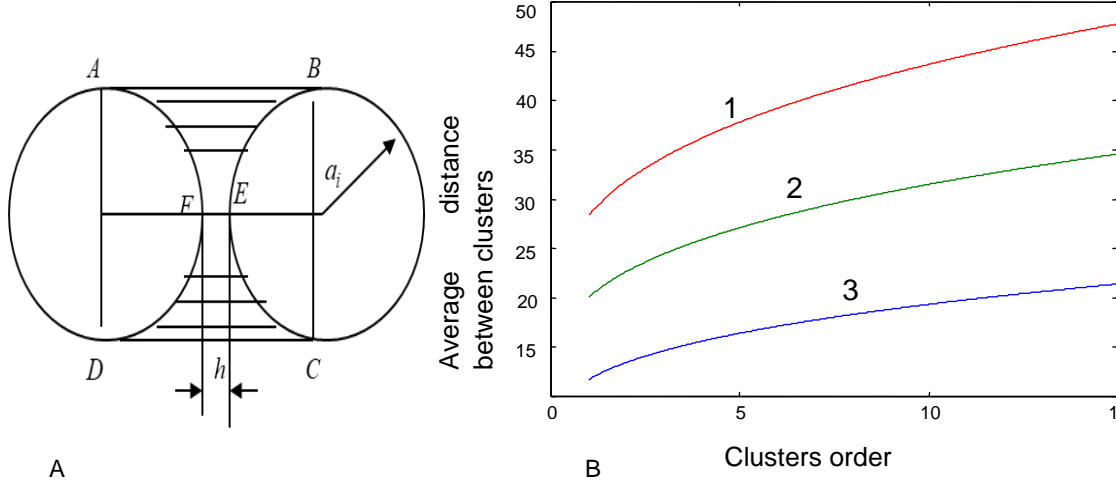


Figure 2: The dependence of the average distance between the particles in contact on the order of particles. The particle characteristic order (in angstroms): 1- 20; 2- 15; 3- 10

Various models are used to solve the problem of the form of the aggregation matrix (Wattis, 2006). The following model for the elements of the aggregation matrix in the form of special function of the clusters orders has been proposed in this work on the base of the above considerations.

$$\Phi_{i,j} \approx \frac{k}{(i+j)^\beta} + c \left(\frac{i-j}{i+j} \right)^2. \quad (3)$$

Detailed analysis shows that for the stationary process, the ratio of concentrations of 2i- meres and i-meres reads:

$$\tilde{W} = \frac{C_{2i}}{C_i} = \frac{\Phi_{i,i}}{2\Phi_{i,2i}} = \frac{(3/2)^\beta}{1+(zi)^\beta}, \quad (5)$$

where

$$z = 3 \left(\frac{c}{9k} \right)^{1/\beta_2}. \quad (6)$$

The term \tilde{W} can be called as “the factor of instability of the aggregation”. Such notation is accepted for there would be no confusion with the term- “stability factor”, which is usually accepted to assess the stabilizing influence of electrolytes (Endres et al., 2021).

This makes it possible to relate two parameters that control the suspension stability to two parameters that control the energy of intermolecular interaction in the van der Waals–Hamaker theory (Somers, 2018):

$$V_m = -\frac{A^*}{12\pi h^2}, \quad (7)$$

However, this issue is still waiting for a special study.

Figure 3 depicts some results of calculating the instability factor depending on the order of the particles.

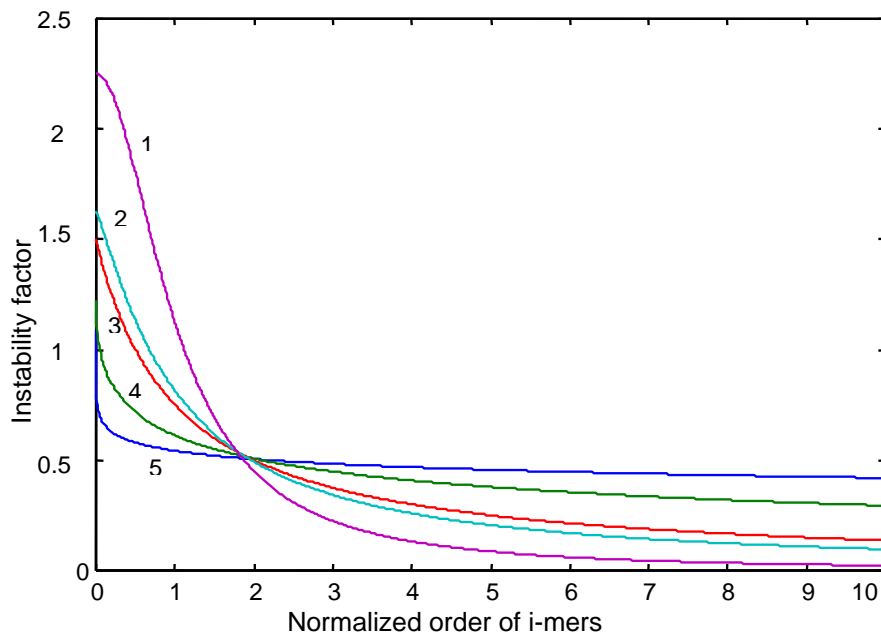


Figure 3: Dependence of the instability factor from the reduced order of globules. Control parameter β according to model (3): 1- 0.2; 2- 0.5; 3- 1.0; 4- 1.2; 5- 2.0

It can be seen from the graphs that the entire behavior of the curves relative to each other has a singularity in the certain region. Thus, the aggregation model introduced in Section 3 acquires a physical justification, and it becomes possible to calculate the control parameters of this model from the known physical characteristics of the media. Using the described approach, stability estimates may be useful for evaluation stability of a number of suspensions used in pharmacy, and recommendations for their stabilization can be given (Huseynova, 2021).

4. Conclusions

As a result of the analysis of physical regularities and models of the kinetics of the aggregation process, a simplified model of aggregation kernels in the Smoluchowski equation as functions of the orders of interacting particle clusters has been proposed.

The base supposition is that from the symmetry considerations of the aggregation process for each of the components, it is sufficient to consider the stabilization of the suspension disperse composition when aggregating globules are of the same orders. A new factor of aggregative instability has been introduced, several control parameters of the model have been identified, and a numerical study has been also has been made. The issues of adapting the model to the evaluating stability of specific nano-disperse systems are still waiting for a special study.

Nomenclature

a - characteristic size of the monomer, m

a_i - characteristic size of the i-mer, m

A^* - the van der Waals-Hamaker constant, $1/m^6$

c - control parameter of the binary model for aggregation matrix

C_i - concentration i-order clusters

h - minimal distance between particles, m

H - average distance between particles, m

i, j - clusters orders

k - control parameter of the binary model for the aggregation matrix

t - time, s

\tilde{W} - the factor of aggregation instability

z - control parameter of the binary model for the aggregation matrix

β - control parameter of the binary model for the aggregation matrix

$\Phi_{i,j}$ - aggregation matrix

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