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ORIGINAL CONTRIBUTION

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Model of aggregation of colloidal fine particles in the presence of supersized polymer

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Abstract A simple model of the process of stabilization and destabilization of fine colloidal suspensions induced by supersized linear polymers has been tested by the direct simulation method. In the model, a single polymer molecule may bind a number of colloidal particles and thus form an aggregate. It is assumed that a simultaneous attachment of a few fine particles to one macromolecule does not necessarily destabilize the suspension. The destabilization of the system (occurring if aggregate sedimentation dominates its diffusion ability) takes place only when the number of the attached particles per macromolecule exceeds the critical value which depends on the polymer coil dimension in the dispersion medium. The model permits interpretation of several experimental observations of the behavior of colloidal sols upon introduction of very high molecular-weight polymers. The simulation results have been compared with the experimental data on the effect of polyacrylamide on the stability of AgI sol.

Key words Polymer flocculation and stabilization – high polymers – polyacrylamide – AgI-sol

Introduction

Polymers of very high molecular weight are, in general, the best flocculants and stabilizers. The influence of chain length of the linear nonionic polymers in a good solvent on the colloidal system stability can be concluded from several theoretical models concerning bridging flocculation and steric stabilization mechanisms [1–9]. However, the higher the molecular weight of the polymer the more difficult the problem becomes in terms of the cited theories. For example, it is difficult to assume that the thickness of the supersized polymer layer is negligibly small when compared to the particle diameter (La Mer theory [3–6]). A polymer flocculation model of Pelssers et al. [7, 8] gives no explanation of the quantitative aspects of the flocculation induced by large polymer molecules. Also, a computer simulation of bridging flocculation is restricted to polymers of a rather small polymer segment number [9].

Taking into account the systems containing fine particles with a diameter of an order of 10 nm and very large polymer molecules consisting of approximately 10^5 segment units (in this case a polymer coil volume in a good solvent is several-hundred times larger than the particle volume), one has to re-evaluate the aggregation process by considering the attachment of particles to a molecule rather than the adsorption of molecule onto particles [4, 10]. It was observed experimentally that when the sizes of polymer coils considerably exceeded those of particles, many particles were attached to a single macromolecule [10–15].

For dilute macromolecular solutions, a simple model of aggregation of fine particles by high polymers has been

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developed [16]. The model was based on the assumption that the number of colloidal particles attached to a single polymer molecule is a random quantity and that a certain minimum number of particles must be attached to a macromolecule to cause its removal from the system. The model well simulates the qualitative features of the effect of polymer concentration on flocculation efficiency. However, the static character of the model does not take into account the diffusion effects and the stage nature of aggregation process.

The final result of the process induced in colloidal systems by very high-molecular-weight polymers is a result of many elementary processes, some of which are difficult to distinguish in experiment. Therefore, aiming at the step-by-step monitoring of processes occurring in the system composed of fine particles and supersized macromolecules, we have performed a computer simulation of particle diffusion and aggregation in a cubic lattice following the direct simulation method [17, 18]. The simulation method permits to take into account kinetic factors of aggregation which are of importance in understanding the mechanism of polymeric flocculation and stabilization [8, 19].

Description of the model

In further considerations, colloidal particles will be referred to as C-particles, polymer coils as P-particles, whereas aggregates consisting of a P-particle and of *m* C-particles as *m*C-P multiplets.

The general assumption for the simulation experiment is that the linear polymer molecules under consideration have an extremely high molecular weight and are in a good solvent. The above assumption implies the following: 1) P-particles are larger than C-particles. 2) There is a specified maximum number V of C-particles that can be attached to a single P-particle. 3) There is a minimum number of C-particles that must be attached to a polymer molecule to cause the removal of aggregate from the system. 4) P-particles are characterized by a much lower value of diffusion coefficient than C-particles. 5) Temporarily, after sol and polymer solution are brought together, there are domains of C- and P-particles in the system (non-ideal mixing due to a high viscosity of polymer solution).

Given the assumptions mentioned above, the simulation has been performed in a three-dimensional lattice composed of 4096 cells. Periodic boundary conditions have been adopted. Initially, the system is divided into two parts, one containing only C- and the other only P-particles. The starting particle positions are independently generated for each experiment. The initial distributions of C and P-particles are uniform. It is assumed that C occupies a single site, whereas P takes up V sites. Thus, V stands for the P to C volume ratio. It is assumed that only C-particles can migrate. Their diffusion and aggregation is simulated using a modified direct simulation method (DSM) [17, 18] by step-by-step random walk in the lattice: at each computation step a C-particle is picked up at random and then it is shifted to one of the neighboring sites with equal probability. If C encounters another C outside a P-particle, the C-C aggregation takes place with the probability of p_{coag} (the coagulation rate). As a result of the aggregation a new *n*C-particle occupying only one cell, but with a multiplicity n equal to the summed multiplicities of colliding particles, is formed. This process (simulating the coagulation in real colloidal systems) is assumed to be irreversible.

If the C trajectory collides with sites occupied by a motionless P-particle, then C may enter the P space and form the *m*C-P multiplet. The probability of C penetration into P (that is the rate of C-P aggregation process) is determined by two factors. The one results directly from the fact that the destination site may be occupied by another C (the accessibility of a new position is tested by the procedure which shifts particles in the lattice), whereas the other is arbitrarily given as an incorporation probability, p_{inc}. The incorporation of C into P is also assumed to be irreversible. Moreover, in the model C particles cannot aggregate inside P. The generated particle shifts which do not satisfy the limitations mentioned above are rejected.

The *n*C and *m*C-P multiplets satisfying predetermined separation criteria are assumed to be separated from the bulk. These criteria are related to the minimum number of C-particle which an aggregate should contain to be able to leave the system. It is assumed that *n*C multiplets of $n \geq K_c$ and *m*C-P multiplets of $m \geq K_i$ disappear. In most experiments the criterion K_i is arbitrarily taken as equal to $V/2$. In the coagulation process, the particle multiplicity equal to 2 is accepted as a criterion K_c of sedimentation. Therefore, the following aggregation processes are taken into consideration:

$$\mathrm{C} + \mathrm{C} \to 0 \tag{1}$$

$$\mathrm{C} + m\mathrm{C\text{-}P} \to \begin{cases} (m+1)\mathrm{C\text{-}P} & [m+1 < K_i] \\ 0 & [m+1 \geq K_i] \end{cases} . \tag{2}$$

The initial number of C-particles (n_c^0) in each experiment is the same and equal to 150. The initial number of P-particles (n_p^0) varies within 0–75. The range of n_p^0 fulfills the conditions of dilute polymer solution [20–22], i.e., the polymer concentration range in which macromolecule coils do not overlap. The C- and P-volume fractions applied in simulations are equal to 0.037 and 0–0.15 (at $V = 8$), respectively.

The maximum relative time of modeling corresponds to 300 000 particle shifts. In most experiments, when values of P_{coag}, P_{inc} and n_p^0 are not very low, the shorter simulation time is needed since the entire consumption of free C-particles takes place before the end of experiment. After the experiment is over, the number of C-particles left in the system, n_c^T, is determined. In the reference experiment, the number of C-particles left in the system upon performing the simulation in the absence of P-particles, n_c^{ref}, is obtained. Then, the destabilization efficiency, D, defined by:

$$D = 1 - \frac{n_c^T}{n_c^{\mathrm{ref}}} \tag{3}$$

is calculated. It may take values within the range (0, 1) if the addition of polymer leads to destabilization of the colloid, or negative values if the polymer imparts the stabilizing effect.

All the D values cited in the following are the mean values of 10 experiments.

The suitability of the applied procedure for modeling of aggregation process in real systems was checked by comparing coagulation kinetics (Eq. (1)) with the Smoluchowski theory [23, 24]. The consistence between the simulation and the theoretical results, assessed by statistical methods [25], is satisfactory.

Results and discussion

Figure 1 presents an exemplary evolution of the model upon simulation of diffusion and aggregation. The sets of data in Figs. 1a and 1b are obtained for two different initial P contents in the lattice, 75 and 20, respectively. All other parameters affecting the process are the same in both experiments.

In the initial stage of the process, independently of n_p^0, a rapid disappearance of free C-particles is observed as a result of both the coagulation (increase in n_c^C) and C incorporation into P-particles (increase in n_c^A).

When n_p^0 is large (Fig. 1a) then a considerable number of stable mC-P multiplets of $m < K_i$ is left in the system in the end of aggregation process. Curves $n_c^T = f(t)$ and $n_c^A = f(t)$ tend to overlap with a common ordinate. This implies that the system has reached a steady state and no further disappearance of C-particles will take place. In other words, the polymer stabilization of a colloidal system is observed. In our previous paper [26], we reported that the system containing aggregates of very-high-molecular weight polyacrylamide and fine AgI particles may be stable, provided that the polymer coil is large and the number of colloidal particles per polymer molecule is not too high. Non-associating multiplets made of one macromolecule and a few particles are also reported by Spalla and Cabane [11].

If n_p^0 is low (Fig. 1b), the destabilization of colloid is observed except in the initial stage of aggregation process (increase in n_c^A). At the beginning of the process mC-P multiplets are too small ($m < K_i$) to be eliminated from the system. The initial increase of n_c^A corresponds to the experimentally observed "dead time" of polymer-induced destabilization [7, 8]. After the initial increase, the n_c^A number decreases gradually, whereas curves representing $n_c^C = f(t)$ and $n_c^I = f(t)$ dependencies rise as long as the number of free C-particle in the system drops to zero. This stage of the aggregation process corresponds to an intensive destabilization induced by polymer. At the end of the process, the n_c^T number does not drop to zero but reaches a stable small value, which means that a certain amount of stable mC-P aggregates is left in the system. This result can be interpreted as an experimentally observed residual turbidity of the colloidal system in which the polymer induced destabilization took place [7, 8].

The dependencies of D on x, where $x = n_p^0/n_c^0$, at different V values are shown in Fig. 2a. For all the obtained

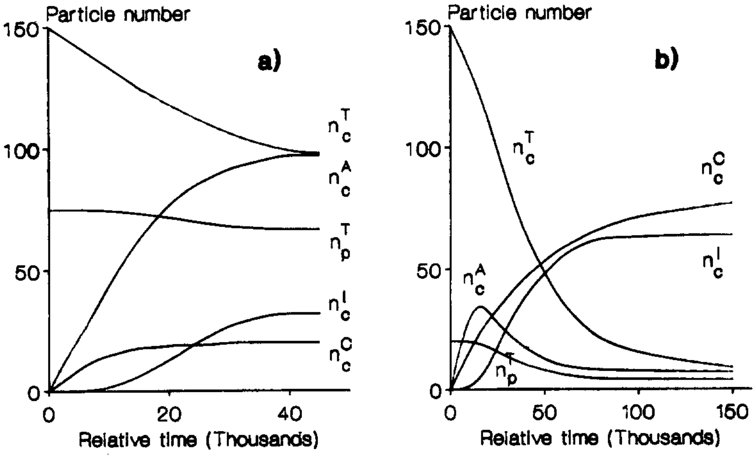


Fig. 1 Evolution of the modeled system with the simulation time (n_c^T -total number of C-particles in the system, n_c^A- number of C-particles in mC-P aggregates, n_p^T- total number of P-particles in the system, n_c^I- number of C-particles removed from the system as mC-P aggregates, n_c^C- number of C-particles removed from the system due to coagulation process). (Simulation conditions: $p_{\mathrm{coag}} = 0.02$, $p_{\mathrm{inc}} = 0.2$, $V = 8$, $K_i = 4$, $K_c = 2$, $n_c^0 = 150$, *a*) $n_p^0 = 75$, b) $n_p^0 = 20$)

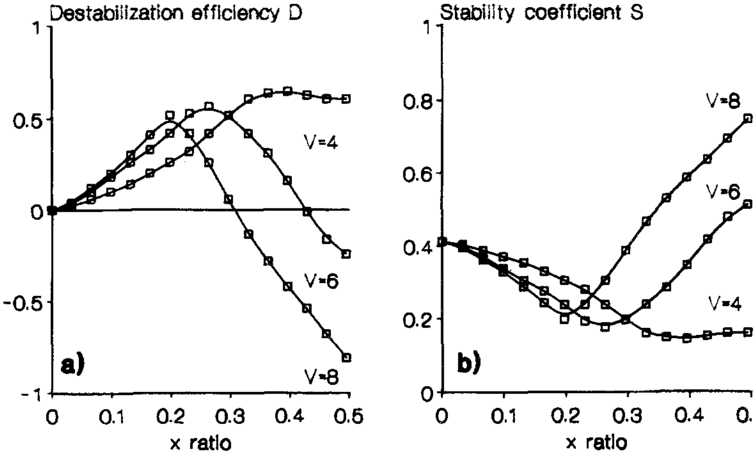


Fig. 2 Dependence of destabilization efficiency, D, and stability coefficient, S, on the ratio of the initial number of polymer to colloid particles, x ($p_{\text{inc}} = 0.1$, $p_{\text{coag}} = 0.01$)

curves, with an increasing x value first D increases until a certain maximum value, further referred to as $D^{\max}$, then the destabilization efficiency decreases, and finally the stabilizing effect is observed. The changes in the system stability with x can be explained as follows. For low values of x, the coagulation proceeds along with the formation of mC-P multiplets. Since the relative C to P concentration is high, the multiplets reach the criterion $m \geq K_i$ easily. When x rises, C may get distributed over a greater number of P. Thereby, the probability of reaching $m \geq K_i$ and, hence, of sedimentation of mC-P species, decreases. Moreover, due to an increase in P concentration, the probability of C-C collisions decreases, whereas the probability of C-P collisions, resulting in a formation of unsaturated mC-P multiplets, rises. These results agree with the experimental fact that there is an optimum amount of polymer per particle for the efficient system destabilization [7, 8, 27].

A comparison between $D = f(x)$ curves obtained for different V values shows that a decrease in the size of P-particle is accompanied by an increase in $D^{\max}$ and by a shift of $x^{\max}$, i.e., x values corresponding to $D^{\max}$, towards higher values. In order to analyze the effect of P size on stabilizing/destabilizing properties of polymer, one has to realize that a decrease in V reduces the C-P collision probability and at the same time enhances the probability of attainment of $m \geq K_i$ (since $K_i = V/2$). The former effect brings about a decrease, whereas the latter causes a rise in D. Since the reduction of V involves increase in $D^{\max}$ (Fig. 2), one can conclude that under the examined conditions the change in P size affects mainly the probability of reaching critical K_i value.

Figure 2b presents the dependence between x and the total stability coefficient, defined as the ratio of the final number of C-particles in the system to their initial number, $S = n_c^T/n_c^0$. It clearly illustrates a competition between the coagulation and the mC-P multiplet formation processes. For small x (low P content) the C-P aggregation co-operates with the coagulation in the removal of C-particles from the system, whereas when x is high, stable, that is non-sedimenting aggregates are formed and the coagulation is prevented. The larger the P-particles, the more effective destabilization or stabilization (larger number of stabilized colloidal particles, lower polymer concentration required for stabilization) they can produce. These facts also agree with experimental observations [27].

In real systems, factors inducing changes in the size of polymer coils cause, at the same time, changes in some other parameters determining the system stability. For instance, changes in the ionic strength of the dispersion medium affecting the conformation of polymer molecule, can also influence the energy of interparticle electrical repulsion, the equilibrium of polymer segment adsorption onto particle surface, and hence they may cause the formation of multiplets of a different type. Therefore, to separate the effect of C-P and C-C collision efficiency on the system stability from the effect of polymer coil volume, simulations were carried out for p_{inc} and p_{coag} values changed independently.

Figure 3 represents the $D = f(x)$ dependencies obtained for different p_{inc} values. With increasing C-P collision efficiency, the values of $D^{\max}$ and $x^{\max}$ also increase, whereas the stabilizing effect of polymer weakens. Because of the assumption of initial separation of C- and P-particles and due to the increase in C-P collision efficiency, C-particles are less uniformly distributed among P-particles. The C-P aggregation occurs mainly in the region close to the initial separation boundary and the probability of reaching the critical K_i value increases. On the other hand, when p_{inc} is low, free C can penetrate deeper into the P region. As a result, the distribution of C among P becomes more uniform and the probability of reaching $m \geq K_i$ decreases which implies the enhancement of colloid stability (Please note that a decrease in P concentration or in P size also leads to a deeper penetration of C into the P region,

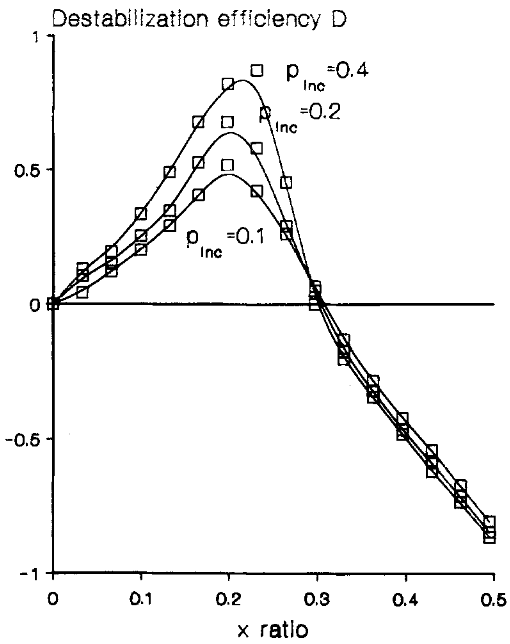


Fig. 3 Dependence of destabilization efficiency, D, on the x ratio at different $p_{\rm inc}$ values ($V = 8$, $p_{\rm coag} = 0.01$)

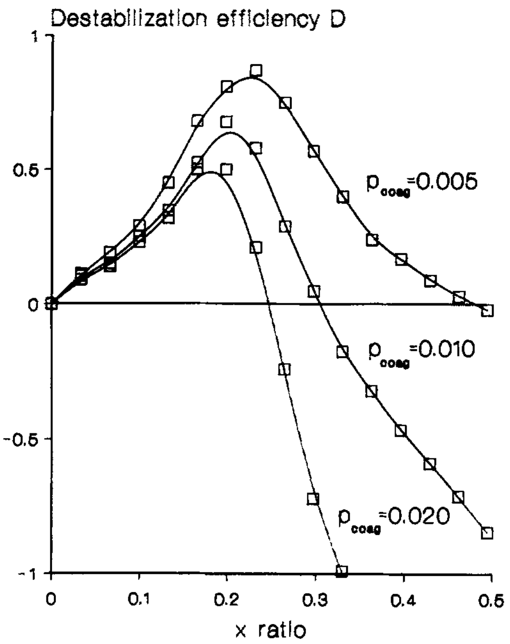


Fig. 4 Dependence of destabilization efficiency, D, on the x ratio at various $p_{\rm coag}$ ($V = 8$, $p_{\rm inc} = 0.2$)

resulting in a more unifrom distribution of C among the multiplets.)

As is shown in Fig. 4, an increase in $p_{\rm coag}$ involves a decrease in $D^{\rm max}$ and an enhancement of the stabilizing action of the polymer, which is evidenced by the lowering of $D = f(x)$ curve, in particular, in the region of high x values. Moreover, the increase in $p_{\rm coag}$ shifts the abscissa at which D takes zero (i.e., a relative polymer concentration at which its stabilizing action just begins) towards lower values. Thus, the protecting action of the polymer is more evidenced in systems of higher $p_{\rm coag}$. This is so because faster coagulation brings about a more distinct difference between the rates of the C-particle disappearance in the presence and in the absence of the polymer. Moreover, since the intensive coagulation strongly reduces the C content in the system and hence diminishes the probability of reaching $m \geq K_i$, a decrease in D with increasing $p_{\rm coag}$ is obtained.

The model parameters affecting the colloid system stability can be related to some physical parameters. And so, the V parameter can be referred to the mean ratio between polymer coil and particle volume. K_c and K_i parameters determine the aggregate annihilation, which is the model simplification of the sedimentation process. These parameters may be estimated from measurements of the aggregate size (using for example, particle sizer). The $p_{\rm coag}$ and $p_{\rm inc}$ collision efficiency parameters can be concluded from experiments on the coagulation and polymer adsorption kinetics, respectively. However, it should be stressed that values of V, K_c and K_i should be regarded as illustrative intra-model parameters rather than well-defined quantities characterizing complex experimental systems.

Theory vs experiment

Regarding the above, we have checked the ideas presented in this paper by a direct comparison of the model and experimental results. We have used experimental data obtained from investigations of the system composed of AgI-sol and a very high-molecular-weight polyacrylamide (PAAm). The molecular weight of PAAm was about $5*16^6$. Mean AgI particle diameter was equal to 50 nm. A detailed description of the materials and methods used in the experiment is given in ref. [27]. For the convenience of the reader, however, a short description of the method used in determining the effect of PAAm concentration on AgI sol stability is given here. To a certain volume of aqueous solution containing PAAm and the electrolyte, a certain volume of AgI hydrosol was introduced. After the 24 h incubation the destabilization efficiency was measured. To this end samples were centrifuged and the scattered light intensity, R, and the absorbance, A, of the supernatant, by then suitably diluted, were measured. Then, the destabilization efficiency, $D_{\rm exp}$, (accepted as a mean of $D^R_{\rm exp}$ and

D^A_{exp} values defined by Eq. (4)) was calculated.

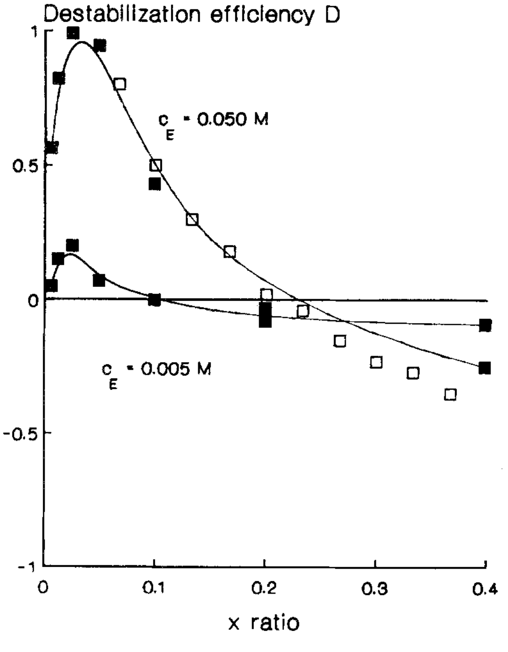
$$D^R_{exp} = 1 - \frac{R}{R_{ref}} \quad \text{and} \quad D^A_{exp} = 1 - \frac{A}{A_{ref}} \tag{4}$$

The *ref* index denotes values obtained for reference systems (i.e., not-containing polymer).

We would like to point out here that rapid changes of R and A in destabilized samples were observed only during the first few minutes after sol and polymer had been brought together. Thus, at the moment of measurement, the D_{exp} coefficient kept a stable value which seems to evidence that it is determined mainly by the initial stage of the aggregation process, not by slow, later stages leading to the final structure of the sediment.

Figure 5 shows $D_{exp} = f(x)$ obtained for the PAAm-AgI system at two different electrolyte concentrations. The parameters of the investigated system, which are interesting from the point of view of the model, are compiled in Table 1. The volume of polymer coil was taken as the equivalent sphere volume of a macromolecule [28] calculated from viscosimetric data [29]. It is noteworthy that the volume of PAAm molecules does not change significantly after they are brought into contact with AgI particles [26]. Also, Spalla and Cabane [11] have found that the attachment of few fine particles to one large macromolecule does not influence the polymer coil diameter provided that the adsorption is not too strong. A volume of the sphere whose radius corresponds to the mean particle radius determined electronmicroscopically [27] and enlarged by the distance of the effective interparticle repulsion [30, 31] was accepted as the colloid particle volume. It was shown that distances between fine silica particles bound to high-molecular weight polymer are governed by electrostatic repulsion [12]. The collision efficiency in coagulation process was calculated from coagulation kinetics data [27].

Fig. 5 Comparison between experimental and simulated destabilization efficiency, *D*, as a function of *x* (■- experimental results for AgI-PAAm system at two different KNO_3 concentrations [27], □-results of computer simulation)



The model presented in this paper takes into account only formations of C-C dimers and aggregates between one polymer molecule and several colloidal particles, i.e., *m*C-P multiplets. In real systems, however, the secondary processes like the polymer bridge formation between *m*C-P multiplets and also the binding of free polymer molecules or colloidal particles to the multiplets take place [11]. Also, in real systems, the coagulation process does not stop at the dimer formation stage. Thus, one may wonder whether a comparison between the results of experiment quoted above and predictions of the model can be made. Below, we consider the effect of possible secondary interactions between the various model individuals on the value of *D* coefficient, that is, the parameter by means of which the validity of the model is probed.

1) The bridge formation between *m*C-P multiplets of $m < K_i$ should be prevented by the same mechanism which is responsible for the steric stabilization of colloids [19], and hence its effect on *D* value can be neglected.
2) The mutual binding between sedimenting *m*C-P or *n*C multiplets, that is, of $m \geq K_i$ or $n \geq K_c$, results in the formation of secondary aggregates of larger size and greater weight. These aggregates undergo sedimentation as well. Hence, the *D* coefficient should remain unaffected.
3) The binding between sedimenting multiplets ($m \geq K_i$ or $n \geq K_c$) and free colloidal particles, free polymer molecules or "unsaturated" multiplets ($m < K_i$) may influence the *D* value. Processes in which the free polymer molecules or "unsaturated" multiplets take part are much slower than the initial C incorporation into P-particles and "unsaturated" multiplets because of the difference in the diffusion rate of the large P-particles or multiplets and fine C-particles. Taking into account the fact that these processes can occur only during the settlement of sedimenting multiplets (the time-restricted processes), we can expect at most their small contribution to *D* value. The resultant effect of aggregation between free colloidal particles and sedimenting multiplets should also not be significant because this process is also time restricted and, moreover, it follows the incorporation of C into P-particles and "unsaturated" *m*C-P multiplets and, hence, it does not start before the initial number of free colloidal particles is reduced. In the *x* range applied for the comparison of the

model and experimental results ($0.05 < x < 0.4$), this number decreases by about 10 times (as shown in Fig. 1b).

The considerations presented above indicate that this is the initial stage of polymer-particle aggregation process which exerts a decisive influence on the destabilization efficiency. Thus, we found it reasonable to test the model proposed by comparing D and D_{exp}.

For the sake of comparison between the experimental and model results, the simulation time was chosen to ensure that the coagulation degrees in the reference probes are the same as the ones in the corresponding real samples. At the end of the simulation, the modeled system reaches (similar to the real system) the steady state ($n_c^T = n_c^A$) in the x range applied for comparison.

Figure 5 represents the $D = f(x)$ dependence obtained from the simulation experiment. The computer simulation was performed with the same parameters (collected in Table 1) as the ones estimated for the AgI-PAAm system at KNO_3 concentration equal to 0.050 M. Other parameters like K_c and K_i were found by fitting the model results to the experimental data in the x range of 0.05 to 0.4. Since one can assume that the PAAm adsorption potential barrier is very low at higher electrolyte concentration [32], the C-P collision efficiency was taken as equal to 1. Both the experimental and the simulation points are in a relatively good agreement and appear to support the validity of the main model assumptions, though we have to stress that the AgI sol studied was a polydisperse system [16] and that the comparison has been drawn on the border line between the available experimental results and limits of computer simulation conditions which are required to get statistically significant results.

Table 1 Parameters of aggregation processes adopted for comparison between the experimental results of AgI-sol destabilization efficiency induced by very-high-molecular-weight PAAm [25, 26, 29, 32] and the results of computer simulation

Parameter	Experiment		Simulation
	$C_E = 0.005$ M	$C_E = 0.050$ M	
V	17	8	8
t	24 h	24 h	37 500 units of relative time (fitted to the value corresponding to the same coagulation degree (0.84) in experimental and model reference systems)
p_{coag}	0.06	0.2	0.2
p_{inc}	low	high	1
K_c	?	?	2(fitted)
K_i	?	?	3(fitted)

C^E denotes the KNO_3 concentration in dispersion medium.

We would also like to point out that the model presented in this work solves the weakness of the earlier model [16] which was the incorrect prediction of the trend in changes of D^{max} and x^{max} upon changing the size of polymer coil.

Conclusions

A simple model of the diffusion-controlled fine particle aggregation induced by the introduction of very high molecular weight polymer has been studied by the computer simulation method. The model is based on following assumptions: 1) a single polymer may bind a number of colloidal particles, 2) there is a minimum number of particles, K_i, that must be attached to a polymer molecule to cause the removal of aggregate from the system, 3) K_i value depends on a relative particle to polymer coil volume. The model predicts some general, experimentally observed features of the stabilizing and destabilizing action of polymers towards colloidal suspensions. And so the model predicts that 1) there is an optimum polymer dosage needed for the efficient flocculation to occur, 2) the increase in the coil size of polymer improves both its stabilizing and destabilizing properties, 3) the polymer destabilization starts after a certain period of time from the process initiation ("dead time" of polymer induced destabilization), 4) a residual turbidity is observed in the end of polymer destabilization process. Moreover, the model indicates how kinetic parameters, i.e., coefficients of collision efficiency p_{coag} and p_{inc}, can affect the stability of systems composed of fine particles and high polymers.

A comparison of the simulation results with the data obtained from the study of PAAm influence on AgI sol stability shows that there is a relatively good agreement between the model and the real system behavior. Thus, one may infer the correctness of the basic idea of the model, i.e., that the stability of the system containing fine colloidal particles and high polymer molecules is determined mainly by the properties of polymer-particle multiplets which are formed in such a system.

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