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# Computer simulation of the coagulation of suspended solids — The applicability of the Müller–Smoluchowski theory

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## ABSTRACT

The results of studies carried out using a computer programme simulating the coagulation of suspensions containing spherical sol particles and spherical coagulant particles are reported. The influence of the degree of dispersion of the system on the coagulation reaction kinetics was investigated. The obtained results of kinetic studies were tested in the light of classical Müller–Smoluchowski equations. The influence of the physical properties of the coagulant, such as size, density and mass, on the coagulation rate was tested. It was found that within the range described in this paper, the rate of the simulated coagulation process fulfils both the kinetic equation of a first-order reaction, and the kinetic equation of a second-order reaction. Within the tested range, a significant influence of the mass and size of the coagulant on the coagulation rate was ascertained. The kinetic Müller–Smoluchowski dependence is fulfilled in a broader range of the degree of dispersion, when the coagulant particle mass and the sol particle mass are equal. When the particle mass increases with an increase in the particle radius, the coagulation rate increases faster than it would result from the Müller's dependence.

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## Introduction

The process of aggregation or coagulation is a research subject for many scientists. These studies are of fundamental significance in many branches of science, such as colloid chemistry, biology, medicine, and even astronomy. They are also very important for environmental protection, because the treatment of water and sewage by biological or chemical methods is always accompanied by the process of aggregation and coagulation. Knowledge of the course of the coagulation process in a broad range of concentrations of the coagulant and the sol being coagulated is without doubt important, e.g. in the treatment of water for consumption and for industrial purposes, in the chemical treatment of municipal and industrial sewage, e.g. from the pulp and paper industry, and in generally understood nanotechnology intended for the

production of new materials or their components (Niu et al., 2011; Sahu and Chaudhari, 2013; Smoczynski et al., 2014).

Studies of aggregation, coagulation, flocculation, and sedimentation processes are carried out most often in natural systems, e.g. on waste water (Shak and Wu, 2014; Subramonian et al., 2014; Teh et al., 2014), but also on model systems, e.g. using silica suspension (Habasaki and Ishikawa, 2014; Shi et al., 2011; Skvarla, 2013). Also, computer simulations are used more and more frequently, enabling a visual observation of the aggregation process, stage by stage. These methods provide unlimited experimental opportunities for testing various factors affecting the aggregation and coagulation process, and its mechanism and kinetics (Ratnaweera et al., 2002; Smoczyński et al., 2009a, 2009b; Yu, 2014).

In the literature (Sonntag and Strenge, 1987) coagulation is defined as physical process, in which dispersed subunits and

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units combine, forming characteristic aggregates. Coagulation is a kinetic process, occurring with a higher or lower rate. The effectiveness of the whole coagulation process, as well as the properties of the final state of post-coagulation and condensation structures, depends to a high degree on the rate of aggregation (Ehrl et al., 2009; Tartaglia, 2009). Coagulation kinetics is described by the Smoluchowski (1917) theory. The theory defines the frequency of collisions for potential pairs of aggregating objects as products of concentrations of the combining components and rate constants, depending on the mechanism of the process and geometrical dimensions of the components of the aggregation stage. The Smoluchowski theory describes the simplest colloidal systems, in which spherical particles of the same size occur. However, in most cases we are dealing with more complex systems, in which particles with various sizes occur. Müller (1926) expanded the Smoluchowski theory on polydisperse systems, giving a dependence between the aggregation kinetics and the degree of dispersion of the system. More and more frequently, the Monte Carlo simulation method is used for the description of the aggregation kinetics (Costello and Euston, 2006; Zhang et al., 2012). In relation to the aggregation process, the state of the system in a given moment defines the distribution of the probability of the combination of two aggregates with specific masses and structures. According to this distribution, a stage of aggregation is selected, the consequences of which are then taken into account in an updated distribution of aggregation probability. This method both gives consideration to correlations between the numbers of the aggregates, and models fluctuations occurring in populations having limited sizes.

The coagulation kinetics and the mechanism of this process require continuous research, both of fundamental (Grant et al., 2001; Pushkin and Aref, 2002; Yang et al., 2013) and utilitarian characters. The latter include, among others, the coagulation ability of new inorganic preparations or organic flocculants, as well as the rate and efficiency of their activity in the conditions of a sewage treatment plant (Bolto and Gregory, 2007; Jangkorn et al., 2011; Yan et al., 2008). The rate and effectiveness of the coagulation process are affected by many factors, for instance temperature, stirring, shaking, irradiation with electromagnetic rays, etc., but the main factors undoubtedly include the selection of a proper coagulant.

In the paper, the results of studies on the coagulation–flocculation–sedimentation of a computer-simulated system containing spherical suspension particles and spherical coagulant particles are presented. Corresponding reaction rate constants have been determined, the issue of whether the Smoluchowski–Müller dependence is satisfied has been studied, and the influence of the physical properties of the coagulant (such as size, mass, density) on the rate of the coagulation process has been determined.

## 1. Materials and methods

### 1.1. The simulation model

The ZB2 simulation model (Smoczyński et al., 2013) used is a stochastic-dynamic model. Its operation is based on random variables, and the state of the system varies thanks to the flow

of the simulation time. The core of the programme is constituted by a module solving an equation of the motion of a defined number of material particles in a closed vessel. The programme simulates the aggregation–coagulation–sedimentation process of spherical sol particles by the spherical particles of a coagulant. It is a process of fast, perikinetical aggregation, in which every collision of a coagulant particle and a sol particle leads to an inseparable combination. The simulated coagulation system assumes that the particles have no electrical charge. They move in every direction by Brownian motion. The number of the particle collisions is defined only by translational Brownian motion. Two spherical particles, that of the sol and that of the coagulant, undergo an aggregation when they approach one another to a distance smaller than the attraction zone radius, thus the aggregation occurs practically on their direct contact. The coagulation threshold, denoted with ( $E$ ), indicates the number of sol particles initiating settling. It is defined so that there is a defined, given number of sol particles per coagulant particle. Particles of the same type do not combine. The settling rate increases with an increase in the number of sol particles in a cluster. Every particle has a randomly attributed initial velocity ( $V$ ), and if the particle velocity  $V = 50$ , all particles have a velocity attributed in the range of 1–50. The initial values of particle locations are generated randomly according to a uniform distribution in the vessel volume. Both the direction of movement of the particles, and their initial locations are randomised by RANDOM instruction. The rebound angle of the particle from the wall is always equal to its incidence angle. The settling coefficient ( $F$ ) takes into account the fact that in the motion of the flock, its velocity decreases by 30% after rebounding from the vessel's bottom. In order to simulate friction between the particle and the liquid, the flock velocity towards a surface is reduced by 0.1% per unit of travelled distance. Changes in the particle radius ( $r$ ) are not visible onscreen, but they are visualised as an increase in the distance between the particles in the formed flock. The ratio of the coagulant particle mass to the sol particle mass ( $m_c/m_s$ ), depending on the size of coagulant and sol particles, is calculated as follows:  $m = d \cdot V$ , the coagulant and sol particles have a spherical shape, so  $V = 4/3\pi r^3$ , thus (Smoczyński et al., 2013):

$$\frac{m_c}{m_s} = \frac{d_c}{d_s} \frac{4/3\pi r_c^3}{4/3\pi r_s^3} \quad (1)$$

where,  $d_c$  is coagulant density,  $d_s$  is sol density,  $r_c$  is coagulant radius, and  $r_s$  is sol particle radius

### 1.2. Variable parameters of the simulation programme

In the paper the sol is a simulated solution of a mineral suspension coagulated by simulated inorganic coagulants with a variable size, mass, and density. Every time, the quantitative ratios of these two types of particles fulfilled the condition of the computer-simulated coagulation threshold, which remained close to actual conditions, e.g. in a sewage treatment plant.

In the simulation studies, the following input data were assumed:  $N_c$ : number of coagulant particles; in the studies  $N_c = 100 = \text{const}$ ;  $N_s$ : number of sol particles; in the studies  $N_s = 1000 = \text{const}$ ;

$V_c$ : initial velocity of coagulant particle;  $V_c = 50 = \text{const}$ ;  $V_s$ : initial velocity of sol particle;  $V_s = 50 = \text{const}$ ;  $E$ : coagulation threshold;  $E = 10 = \text{const}$ ;  $F$ : settling coefficient;  $F = 0.2 = \text{const}$ ;  $r_c$ : coagulant radius;  $r_c = 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9$ ;  $r_s$ : sol particle radius;  $r_s = 0.5 = \text{const}$ ;

$m_c/m_s$ : ratio of the coagulant particle mass to the sol particle mass;  $m_c/m_s = 1, 8, 64, 216, 512, 1000, 1728, 2744, 4096, 5832$ .

All the units are the simulated values throughout this work. Therefore (for instance), a time unit is the simulated second. The programme is equipped with an S = stop function, i.e. with a “timer” measuring the simulated process duration, and with a counter for the number of “coagulated” particles in the sediment. All time (t) measurements were carried out seven times, and after the elimination of one maximum value and one minimum value, an arithmetic average was calculated from the remaining five. The values of standard deviation have been plotted conventionally on the corresponding diagrams.

## 2. Results and discussion

### 2.1. Reaction order of the simulated coagulation process

The order of the simulated coagulation process was determined graphically by a conversion (linearization) of kinetic equations of first-order and second-order reactions, respectively.

$$\frac{dN_s}{dt} = -k \cdot N_s^2 \tag{2}$$

$$t = \frac{1}{k_{II}} \cdot \left( \frac{1}{N_s} - \frac{1}{N_{s0}} \right) \tag{3}$$

Where,  $N_{s0}$  is a primary number of the sol particles,  $k_I$  and  $k_{II}$  are rate constant of the first and second order reactions respectively.

Fig. 1 shows example results of the simulation studies carried out. The diagrams present linear dependencies  $t = f(1 / N_s)$  (Fig. 1a, b) and  $t = f(\ln 1 / N_s)$  (Fig. 1c, d), respectively, for coagulation systems, in which the diameter of the coagulant is equal to  $r_c = 6$ , the diameter of the sol  $r_s = 1$ , and the ratio of the coagulant particle mass to the sol particle mass amounts to  $m_c/m_s = 1$  (Fig. 1a, c) and  $d_c/d_s = 1$  or  $m_c/m_s = 216$  (Fig. 1b, d), respectively. The coefficients of determination  $R^2$  of the four linear regressions shown here were in the high-value range from 0.95 to 0.99. However, for comparable pairs of general dependencies  $t = f(\ln 1 / N_s)$  and  $t = f(1 / N_s)$ , respectively, they did not prove unequivocally a more favourable kinetic equation describing the coagulation rate of the simulated sol.

In Table 1, all  $R^2$  values determined for mathematical models of  $t = f(\ln 1 / N_s)$  and  $t = f(1 / N_s)$  are gathered. The studies were carried out in simulation systems, in which the ratio of the coagulant particle mass to the sol particle mass  $m_c/m_s = 1$  does not change with the increase in the ratio of the coagulant particles’ radii to the sol particles’ radii ( $r_c/r_s$ ), so an increase of the coagulant size is accompanied by a decrease in its density. Also, the studies were carried out for coagulation systems, in which an increase in the coagulant radius is accompanied by an increase in its mass, and the density of the coagulant particles equals the density of the sol particles ( $d_c = d_s$ ). The mean value of  $R^2$  obtained for  $t = f(\ln 1 / N_s)$  was equal to 0.97 and it proved to be slightly higher than  $R^2$  for  $t = f(1 / N_s)$ , amounting to 0.95 on average. As the average value of the coefficients of determination is so minimally differentiated, none of the mathematical models was turned

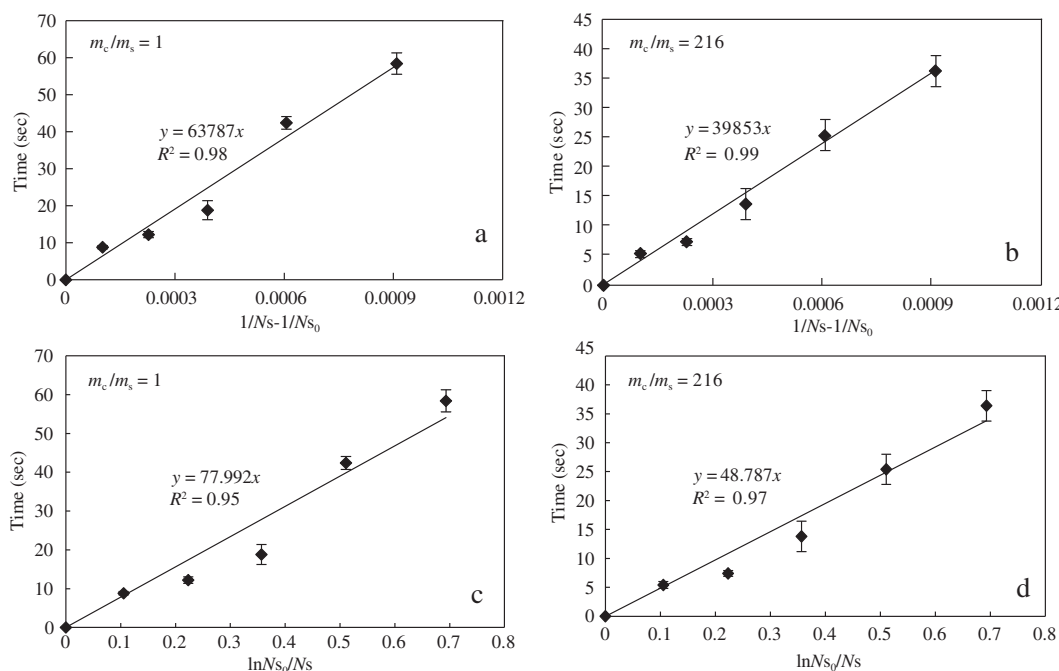


Fig. 1 – Relationships  $t = f(1 / N_s)$  (a, b) and  $t = f(\ln 1 / N_s)$  (c, d), for  $m_c/m_s = 1$ , and  $m_c/m_s = 216$ .

down in further considerations while describing and interpreting the investigated simulated process.

## 2.2. The Müller–Smoluchowski theory

The theory of rapid coagulation kinetics was developed by Smoluchowski (1917). However, it pertained to monodisperse systems, in which spherical particles with uniform size occurred. According to Smoluchowski, the basic cause of coagulation consists in Brownian motion, facilitating collisions between the particles. It may be considered a process of continuous undiminished diffusion of the disperse phase deeper into the continuous phase. Therefore, the diffusion coefficient is a measure of the intensity of Brownian motion. Every particle is surrounded by an attraction sphere with a defined radius  $A$ . In order for two particles to collide, they must approach one another to a distance smaller than the attraction zone radius. However, such a close approach is possible only when the particles have either completely lost their electrical charges, with their electrokinetic potentials equal to zero, or discharged to values below their critical potentials. Brownian motion will be free until a particle enters the sphere of attraction of another particle. Then, both particles will merge, forming a whole travelling by Brownian motion again, with a rate decreased accordingly with the increased mass of the new particle. Based on mathematical analysis Smoluchowski substantiated that the probability of the collision of two particles with the same radius is defined by the coefficient  $k$ , namely:

$$k = 4\pi AD \quad (4)$$

where,  $A$  is the radius of the attraction sphere, and  $D$  is the diffusion coefficient (diffusivity).

Müller expanded the Smoluchowski theory to the polydisperse systems containing particles of various sizes. It was found experimentally that the radius of the attraction sphere is approximately equal to the particle diameter. The simplest polydisperse sol consists of two types of particles with radii  $r_1$  and  $r_2$ . Therefore, the radius of the attraction sphere  $A$  is equal to (Smoluchowski, 1917):

$$A = r_1 + r_2. \quad (5)$$

On the other hand, the probability of the collision of a larger particle with a smaller one equals (Müller, 1926):

$$k_1 = 2\pi A(D_1 + D_2) \quad (6)$$

where,  $D_1$  and  $D_2$  are the diffusion coefficients for a sol with particle radii  $r_1$  and  $r_2$ . While substituting the value of the diffusion coefficient from the Einstein equation:

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \quad (7)$$

to Eq. (6), we obtain:

$$k = 2\pi A \left( \frac{RT}{N} \cdot \frac{1}{6\pi\eta r_1} + \frac{RT}{N} \cdot \frac{1}{6\pi\eta r_2} \right) = \frac{RTA}{3N\eta} \left( \frac{r_1 + r_2}{r_1 \cdot r_2} \right). \quad (8)$$

Substituting the value of  $A$  from Eq. (5), we obtain:

$$k_1 = \frac{RT}{3N\eta} \cdot \frac{(r_1 + r_2)^2}{r_1 \cdot r_2}. \quad (9)$$

In Eq. (9), particle radii occur, so as a consequence the coagulation rate in polydisperse systems depends on the degree of dispersion. In the case of a monodisperse sol, where  $r_1 = r_2$ , Eq. (9) assumes the following form:

$$k = \frac{4RT}{3N\eta}. \quad (10)$$

Particle radius does not occur in this equation. Thus, the coagulation rate of monodisperse sols does not depend on the degree of dispersion of the system. Eqs. (9) and (10) lead to the following dependence between the coefficients:

$$k_1 = k \cdot \frac{(r_1 + r_2)^2}{4r_1 \cdot r_2}. \quad (11)$$

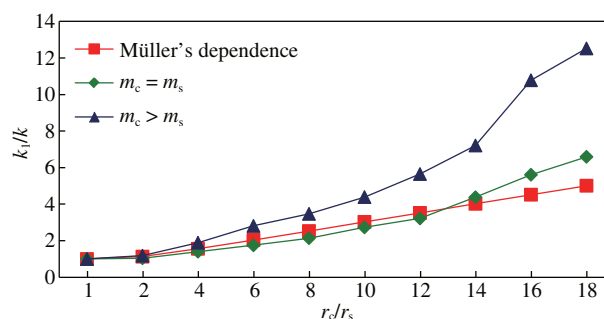
The coagulation rate in polydisperse systems is higher than that in monodisperse systems  $k_1 > k$ .

## 2.3. Kinetics of the simulated coagulation in the light of Müller dependence

The above Müller's dependence was tested in the simulation studies. The straight line  $a$  in Fig. 2 illustrates the Müller's dependence (Eq. (11)), or the increase in the coagulation rate of a polydisperse sol in relation to the coagulation rate of a

**Table 1 – Values of  $R^2$  for the studied dependencies  $t = f(\ln 1 / N_s)$  and  $t = f(1 / N_s)$ .**

| $r_0/r_s$         | $R^2$ for $\ln N_{s0}/N_s$ |                   | $R^2$ for $1/N_s - 1/N_{s0}$ |               |
|-------------------|----------------------------|-------------------|------------------------------|---------------|
|                   | $m_c/m_s = 1$              | $m_c/m_s > 1$     | $m_c/m_s = 1$                | $m_c/m_s > 1$ |
| 1                 | 0.94                       | 0.94              | 0.99                         | 0.97          |
| 2                 | 0.95                       | 0.96              | 0.99                         | 0.98          |
| 4                 | 0.97                       | 0.99              | 0.97                         | 1             |
| 6                 | 0.98                       | 0.99              | 0.95                         | 0.97          |
| 8                 | 0.98                       | 0.98              | 0.94                         | 0.95          |
| 10                | 0.98                       | 0.96              | 0.90                         | 0.91          |
| 12                | 0.94                       | 0.97              | 0.87                         | 0.93          |
| 14                | 0.97                       | 0.98              | 0.93                         | 0.95          |
| 16                | 0.96                       | 0.96              | 0.93                         | 0.97          |
| 18                | 0.94                       | 0.93              | 0.96                         | 0.96          |
| Mean $R^2 = 0.97$ |                            | Mean $R^2 = 0.95$ |                              |               |



**Fig. 2 – Increase in the coagulation rate of a polydisperse sol in relation to the coagulation rate of a monodisperse sol ( $k_1/k$ ) depending on the degree of polydispersion of the system.**

monodisperse sol, in which the ratio of the coagulant particles radii ( $r_c$ ) to the sol particles radii ( $r_s$ ) varies correspondingly from 2 to 18. According to the Müller theory, the difference between the course of monodisperse and polydisperse coagulations is evident when the ratio of the particle radii is high, for instance  $r_1/r_2 = 10$ . Then, as one can see in Fig. 2, line a,  $k_1 = 3k$ .

Fig. 2, line b is obtained in the result of computer simulation, and it represents the above dependence, or the dependence of the influence of the dispersion degree of the system on the coagulation rate, in which a constant ratio of the coagulant particle mass to the sol particle mass  $m_c/m_s = 1$  is assumed, thus an increase in the coagulant size is accompanied by a decrease in its density ( $d_k < d_s$ ). As one may see in the figure, an increase in the ratio of the coagulant particle radius to the sol particle radius leads to a similar increase in the coagulation rate of a polydisperse sol in relation to the coagulation rate of a monodisperse sol, as in the case of theoretical Müller's dependencies, but only to some point. When the ratio of the coagulant particle radius to the sol particle radius is higher than 14, a higher increase in the reaction rate occurs than results from Müller's calculations.

Fig. 2, line c illustrates the discussed dependence with the assumption of an increasing ratio of the coagulant particle mass to the sol particle mass ( $m_c/m_s$ ), together with an increasing ratio of the coagulant particle radius to the sol particle radius ( $r_c/r_s$ ), the coagulant density and the sol density remain the same ( $d_k = d_s$ ). In this case, the curve is conformant with the Müller's curve, when the ratio of the coagulant and the sol radii does not exceed 4 ( $r_c/r_s \leq 4$ ). Above this value, significantly higher values of  $k_1/k$  were obtained than those resulting from Müller's theoretical calculations. Thus, for  $r_c/r_s = 18$ , a 12-fold increase in the coagulation rate of a polydisperse sol in relation to that of a monodisperse sol occurred, while in the Müller's dependence,  $r_1/r_2 = 18$  leads to a quintuple increase in the reaction rate. The simulations carried out indicate that the Müller's dependence is fulfilled only to some point, to a specific  $r_1/r_2$  ratio and with the assumption of the same particle mass of the polydisperse sol. When the mass and the radius increase, and while maintaining the same densities of the coagulant and the sol, the reaction rate increases faster than it would result from the Müller's dependence.

#### 2.4. Influence of the physical properties of the coagulant on the coagulation rate

In Fig. 3, reaction rate constants are compared, obtained in the result of a computer simulation of the coagulation process. In this simulation, sol parameters were constant, while the coagulant type was changed by changes in its radius, mass, and density. Thus, series a represents the influence of the sizes and masses of the coagulants on the rate constants of the sol coagulation reactions, with an assumption that the densities of the coagulants and the sol are the same ( $d_k = d_s$ ), and therefore an increase in the coagulant size is accompanied by an increase in its mass in relation to the sol particle mass, from  $m_c/m_s = 8$  at  $r_c = 0.5$  up to  $m_c/m_s = 5832$  at  $r_c = 9$ . On the other hand, in series b, the ratio of the coagulant particle mass to the sol particle mass remains constant,  $m_c/m_s = 1$ ,

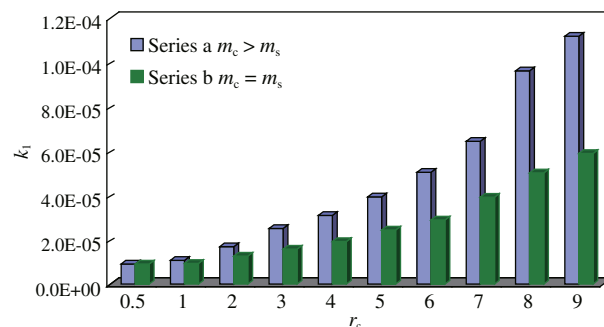
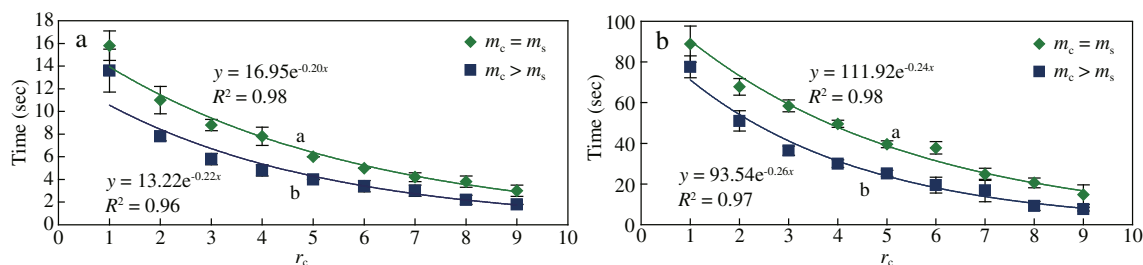


Fig. 3 – Influence of the coagulants' size on the rate constants of coagulation reactions.

or when the coagulant particle size increases, its density decreases ( $d_k < d_s$ ). Comparing both series, we may see that every time, the increase in the radius is accompanied by an increase in the reaction rate ( $k$ ), and this increase is larger when the mass also increases with the increase in the radius (series a). The maximum obtained value of the rate constant  $k = 1.12 \times 10^{-4}$  achieved for the simulated conditions ( $r_c = 9$ ,  $m_c/m_s = 5832$ ,  $d_k = d_s$ ) is nearly two times higher than  $k = 0.59 \cdot 10^{-4}$  obtained while using a coagulant with the same radius but with  $m_c/m_s = 1$ ,  $d_k < d_s$ . The phenomenon seems to be caused by the sedimentation process, in which the particle mass is of great importance. Then, an increase in the number of collisions occurs, connected with various sedimentation rates of particles with different masses and sizes, resulting in an acceleration of coagulation.

An important stage of the coagulation process consists in the so-called latent coagulation — an initial step, frequently conditioning the whole coagulation process, as well as specific coagulation time, in which the total number of colloidal particles in the system will decrease twice in relation to the initial value. Fig. 4 is an illustration of the influence of the simulated size with no changes in mass, so the coagulant density decreases with its increasing size (curves I a), and the simulated size and increasing coagulant particle mass, the coagulant density is equal to that of the sol (curves II b) on the time needed for destabilisation of 10% of the system, or sedimentation of 110 particles of the studied dispersoid (Fig. 4A), and removal of 550 particles or destabilisation of 50% of the system (Fig. 4B). A maximum match of the obtained results  $R^2 > 0.95$  was achieved for an exponential dependence. The corresponding equation and  $R^2$  are shown on the graph. It turns out that constant "b" of the corresponding  $y = ae^{bx}$  equations is in a relatively narrow range from  $-0.20$  to  $-0.26$ , possibly indicating that it is a constant slightly depending on the degree of system instability, and the coagulant size and mass in the studied dispersoid. Thus, constant "a" is mainly responsible for the diversification of the curves' courses. Every time, an increase in the coagulant particle size is accompanied by a decrease in the destabilisation time, both in the initial coagulation stage, and in its later period. The time decreases additionally when the coagulant mass increases with an increase in the coagulant particle size, and a more evident influence of size and mass is observed for 50% destabilisation, where the corresponding constants  $a = 111.92$



**Fig. 4 – Time necessary for sedimentation. (line a) 10%, (line b) 50% particles of the system, depending on the size and mass of the coagulant.**

and  $a = 93.54$  are approximately 7 times higher than  $a = 16.95$  and  $a = 13.22$  in equations for 10% destabilisation. This may indicate that the coagulant particle size and its mass affect the latent coagulation rate only to a slight degree, remaining consistent with the theory of Smoluchowski, who, in the case of rapid coagulation, assumed that the rate constant does not depend on the size of aggregates. The assumption is fulfilled in the initial coagulation stage.

Coagulation process kinetics, both of monodisperse and polydisperse sols, remains not completely investigated or explained. This results from limitations in the area of laboratory experiments, particularly in the area of the full control of the course of the studied process. Smoluchowski, Müller, or Tuorila cannot “enforce” defined conditions in their studies, e.g. a constant and known ratio of the coagulant particle mass and the sol particle mass in the aggregates — flocs — being formed. Therefore, their thesis, for instance, that a difference between the monodisperse and the polydisperse coagulation evidently occurs when the ratio of the particle radii is too high,  $r_1/r_2 \sim 10$  may be insufficient. The simulation studies carried out indicate that when an increase in the radius is accompanied by an increase in the mass, the coagulation rate increases significantly. The coagulant, by a neutralisation of the electrokinetic charge of sewage colloids, causes their destabilisation, but it simultaneously acts as a colloid sorption centre on its developed surface. The larger the surface and the coagulant size, the higher the sorption capacity. At the same time, according to the Smoluchowski theory, the probability that a particle will meet another particle on its way increases with an increase in the translation (per unit time) in Brownian motion. The translation must be practically directly dependent on the diameter attributed to the particle in the simulation programme. Although the increase in the particle size leads to a smaller translation, after the rapid coagulation and agglomeration–flocculation stage, a sedimentation process occurs where the aggregate mass is of great importance. Large clusters with high masses sediment gravitationally (orthokinetically) faster than small ones, catching up with each other and colliding, which may also lead to orthokinetic coagulation. The carried out studies confirm the great importance of orthokinetic coagulation in the process of purification of liquids from fine suspensions and emulsions. The choice of a coagulant with a large size and high mass may significantly accelerate the coagulation–flocculation–sedimentation process during water or wastewater treatment. Obviously, a computer simulation

cannot replace laboratory investigations, but it may supplement them or define new directions for laboratory studies. The results of computer simulations serve the purpose of the development of a database of a fundamental character, and considering some suggestions and application conclusions, they may constitute an interesting alternative for applied research.

### 3. Summary and conclusion

The studies on the kinetics of the destabilisation of the simulated sol proved that  $1/N(t)$  dependences have a linear character supported by a very high value of the coefficient of determination  $R^2$ . Within the range described in this paper, the rate of the simulated coagulation process fulfils both the first-order kinetic equation and the second-order kinetic equation. The rate of the simulated coagulation process depends on the degree of dispersion, and increases together with an increase in the ratio of the large particle radii — those of the coagulant — to the small particle radii — those of the sol ( $r_c/r_s$ ). The kinetic Müller–Smoluchowski dependence is fulfilled in a broader range of the degree of dispersion ( $r_1/r_2$ ), when the coagulant particle mass and the sol particle mass are equal. When the particle mass increases with an increase in the particle radius, the coagulation rate increases significantly. The Müller–Smoluchowski is fulfilled only for particles not exceeding a fourfold difference of sizes and 64-fold difference of masses. Above these values, the coagulation rate increases more than it would result from the Müller’s dependence. The coagulant particle size and mass affect the initial (latent) coagulation rate slightly. However, an evident influence of the coagulant size and mass on the coagulation rate is observed for the specific coagulation time, in which the total number of colloidal particles in the system will decrease twice in relation to the initial value. An increase in the coagulant mass affects sedimentation, which significantly accelerates coagulation.

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