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

Regina Wardzynska, Beata Załęska-Chróst*

Department of Chemistry, University of Warmia and Mazury in Olsztyn, Plac Lodzki 4, 10-957 Olsztyn, Poland

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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 that it would result from the Müller's dependence.

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

* *Corresponding author*. E-mail: hannawar@uwm.edu.pl (Regina Wardzynska).

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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, perikinetic 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):

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

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 $N_s = 1000 = \text{const}$;